GEOCHEMICAL INVESTIGATION OF UNION COLLIERY UNDERGROUND MINE WORKINGS, MPUMALANGA, SOUTH AFRICA

ALBERTA J. STEYN

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Supervisor: Dr. Robert N. Hansen

Co-supervisor: Mr. Eelco Lukas

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DECLARATION

I, Alberta J. STEYN, 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.

I furthermore cede copyright of the dissertation and its contents in favour of the University of the Free State.

Alberta J. STEYN

31 January 2019

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS AND ABBREVIATIONS

ABA	Acid-base Accounting
AEV	Acute Effect Value
AGSA	Auditor-General of South Africa
AMD	Acid Mine Drainage
AP	Acid Potential
BFAP	The Bureau for Food and Agricultural Policy
COV	Coefficient of Variance
D/S	Downstream
DEAT	Department of Environmental Affairs and Tourism
DL	Detection Limit
DME	Department of Minerals and Energy
DME	Department of Minerals and Energy
DO	Dissolved Oxygen
DoH	Department of Health
DWA	Department of Water Affairs (formerly DWAF)
DWAF	Department of Water Affairs and Forestry
EC	Electrical Conductivity
fO$_2$	Oxygen fugacity
GWB	The Geochemists Workbench
HFO	Hydrous Ferric Oxide
IGS	Institute for Groundwater Studies
INAP	The International Network for Acid Prevention
km	Kilometre
LOI	Loss on Ignition
mamsl	Metres above mean sea level
mbgl	Metres below ground level
mg/L	Milligrams per litre
MIW	Mining-influenced Waters

ML   Metal Leaching

M m^3 Mega cubic meters (1 M m^3=1 000 000 m^3)

MPRDA   Mineral and Petroleum Resource Development Act

NAG   Net Acid-generating

NGO   Non-governmental Organisation

NNP   Net Neutralisation Potential

NP   Neutralisation Potential

NPR   Neutralisation Potential Ratio

NWA   National Water Act

SABS   South African Bereau of Standards

SANAS   South African National Accreditation System

SANS   South African National Standards

SS   Suspendid Solids

TDS   Total Dissolved Solids

TWQR   Target Water Quality Range

U/S   Upstream

UFS   University of the Free State

WRC   Water Research Commission

WWF-SA   World Wildlife Fund South Africa

XRD   X-ray Diffraction

XRF   X-ray Fluorescence

CHAPTER 1:
INTRODUCTION

1.1   STUDY OVERVIEW

Active underground coal mining activities at the decommissioned Union Colliery ceased in the mid-1980's. On completion of mining activities, the owning company, South 32 Coal South Africa Limited, is required by South African legislation to undertake a process that must conclude in the granting of a mine closure certificate. In this process the mine must satisfy various requirements that relates to the identification of long-term residual and latent environmental risks and liabilities. Specific focus is placed on the prediction of long-term volumes and quantities as well as qualities of various discharges and the associated impacts on adjacent water bodies. Where such impacts are unacceptable to the government and downstream water users, management strategies that can be practically applied to mitigate these impacts must be identified.

With the aforementioned in mind, this document is a written dissertation for research performed to evaluate and predict temporal variability in mine waste drainage quality resulted from decommissioned underground coal mine workings. Evaluation and prediction of mine waste drainage quality is aimed to identify and quantify current and anticipated risks to groundwater and surface water resources. Literature and research reviews were undertaken to evaluate previous work, both national and international, on predictive modelling of underground coal mine drainage. Case studies similar to the project undertaken for this study together with general geochemical literature research applicable to the research area was also reviewed.

The process undertaken represents that of a multidisciplinary, integrated modelling approach including waste characterisation, development of conceptual models, input data collection (including characterisation results), model selection, continuous calibration, sensitivity analysis, and evaluation of results. The information presented in this dissertation recognises and acknowledges the challenges and uncertainties associated with predicting water quality at mine sites and may assist geohydrologists with minimal geochemical capability involved in similar mine waste characterisation and modelling projects.

1.2   BACKGROUND AND RATIONALE

There is a growing concern in South Africa among the mining industry, government and researchers that if left unchecked, acid generation and associated metal(loid) release from past and present sulphide-related mining operations poses significant risks to surface and groundwater contamination. Mining in

South Africa generates large volumes of mine wastewater that have the potential to adversely affect an already scarce water resource if not properly managed (Annandale *et al*., 2007). Camden-Smith *et al*. (2015) demonstrated that mining accounts for the largest part of water pollution in South Africa which is mainly due to decommissioned and abandoned mine sites that have, over the years, continued to seep and discharge into surface and groundwater sources unabated.

Most collieries in South Africa are located in the Mpumalanga Province, and are especially concentrated around the towns of Emalahleni (formerly Witbank), Middelburg, Ermelo and Secunda (McCarthy & Humphries, 2013). Coal mining in the Mpumalanga Province dates from the late 1800s (Vermeulen & Usher, 2006a). According to Coetzee *et al.* (2010), South Africa's mining history has generated vast economic benefit and still plays a pertinent role in ensuring the country's position in the global market. The importance of coal in South Africa's economy cannot be understated as coal fired stations account for approximately 93% of the country's electricity generation (McCarthy & Humphries, 2013). However, mining activities require the lowering of groundwater levels to gain access to the subsurface mineral resources and thus invariably disturbs the hydrogeological environment (Pauwels *et al*., 2010; Haunch, 2013). Large-scale closure of mining operations and the subsequent cessation of abstraction of underground water from the mine voids, which contributes to piezometric recovery from the previously developed cone of depression, have given rise to significant national concerns as it often results in decant of contaminated water (Pauwels *et al*., 2010). Decommissioned and abandoned mines, which are usually associated with the discharge of contaminated water, are globally recognised as a significant source of contamination (Pulles *et al*., 1995; Bennett, 2016; Goerke-Mallet *et al*., 2016).

According to a report submitted by the Auditor-General of South Africa (AGSA) in collaboration with the Department of Minerals and Energy (DME) (2009) there were 5 906 officially listed abandoned mines in South Africa as of the end of May 2008. The majority of the 5 906 abandoned mines closed prior to 2002 when the amended Minerals and Petroleum Resource Development Act came into effect. Furthermore, the report demonstrated that despite the significance and extent of the environmental impact of unrehabilitated abandoned and defunct mines, measures were not in place to ensure that these mines were rehabilitated effectively and timeously. Younger and Robins (2002) explained that although there has been risk to water resources from mining for decades, the scale of modern mining methods and the gradual change in environmental consciousness have worked together to exacerbate risks to the point of unacceptability.

The actions of mining processes can result in the oxidation of reduced sulphide minerals in the mining waste, including the extraction areas (open pit or underground) as well as surface waste disposal facilities (Maest *et al*., 2005) releasing metal(loid)s and other contaminants into the groundwater and surface water resources (Price, 2009; Haunch, 2013) Waste generated by mining activities may remain in an area long after active mining and processing activities have ceased and may therefore generate poor water quality drainage for centuries post-closure (Haunch, 2013; Bennett, 2016). According to Jarvis and Younger (1997) discharge of these contaminated waters into surrounding water bodies has

deleterious impacts on ecology, water quality and sometimes human health if eco-toxic metal(loid)s are mobilised (Duker *et al*., 2005; Haunch, 2013).

The options available to today's planners and engineers are unquestionably limited by the actions of previous generations of miners whose actions pre-dated the emergence of the concept of sustainable and environmentally conscious development (Younger & Robins, 2002). Considering the extent and dynamics of the South African mining industry, it is clear that mine water management related challenges cannot simply be administered by either government or the mining sector alone (Coetzee *et al*., 2010).

Water quality in South African coal mines is a critical consideration for the long-term management of mining impacts (Usher, 2003). An understanding of the key drivers on water quality in South African collieries is crucial to deal with aforementioned issues (Camden-Smith *et al*., 2015). Given the complexity of natural systems, a multidisciplinary research approach is required to effectively identify and quantify risks to the receiving environment from mine wastes after closure and to subsequently manage water quality issues (Hattingh *et al*., 2002; Usher *et al*., 2003; Zhao *et al*., 2010). However, a multidisciplinary integrated approach to answer research questions is rarely performed. According to Hattingh *et al.* (2002) integrated efforts involving detailed situation analysis, hydrology, geohydrology, mineralogy, predictive geochemical modelling and systems environmental management should be directed to characterise the study area as accurately as possible. Results supplied by the characterisation of the study area and the subsequent modelling must at the end of the day be directed in such a way that it leads to environmental mine waste management programs that are practical and verifiable in the field (Maest *et al*., 2005). Successful and cost-effective mitigation measures largely depend on accurate predictions of future drainage quality (Price, 2009) which can only be evaluated with constant revisit and calibration of the geochemical models as new data is made available.

The long-term nature of mining-impacts requires predictive tools and monitoring of any changes in the geochemistry of the mine waste material over time (Lapakko, 2002). Thompson (1980) and Meast *et al.* (2005) highlighted that the quantity and characteristics of mine wastes are among the most important determinants of water quality and type of drainage water at a mine site. Various techniques for the geochemical characterisation of mine wastes exist and includes conventional geochemical and mineralogical analyses, static tests, short term dissolution tests, kinetic tests (Usher *et al.,* 2003) as well as numerical kinetic modelling (Usher, 2003; Maest *et al*., 2005; Zhao *et al.*, 2010). Each technique is associated with advantages and limitations and yields sources of uncertainty.

Geochemical modelling has proven to be an invaluable tool for predicting future drainage chemistry and serve a complimenting role to conventional analytical techniques which is based on field data and laboratory experiments. It enables the interpretation of complex systems as well as the prediction and anticipation of how geochemical systems evolve over time (Bethke, 2008). According to Camden-Smith *et al.* (2015) geochemical modelling is a very useful tool to gain insight and facilitate understanding of

geochemical processes involved in a coal mining environment and has shown to be a very valuable in making predictions of contaminant behaviour in an aqueous environment (Maest *et al*., 2005). Numeric geochemical models allow a maximum number of interactive input variables and quick calculations (Magombedze, 2006). This greatly improves the ability to predict impacts resulting from a given mine site for which the model calibration is valid, allowing for technical supported decision making on control and management measures (Magombedze, 2006). Increased interest has been drawn to use predictive geochemical models to simulate geochemical processes over long periods of time, to conduct risk assessments, identify important parameters in geochemical systems, to manage the identified environmental impact, and design and optimize remediation strategies (Maest *et al*., 2005; Camden-Smith *et al*., 2015). Although geochemical models, especially predictive models, are associated with a great deal of uncertainty, it remains a robust method that yields insight into the behaviour of contaminants. It can therefore be used as a decision-making tool in terms of predicting potential impacts of contaminants on the environment and for evaluating remediation implications (Swart *et al*., 1998; Bethke, 2008). Geochemical modelling can therefore be used in conjunction with analytical techniques, revealing important information where the latter tend to fail (Camden-Smith *et al*., 2015; Pearce *et al*., 2016).

The owning company of the decommissioned Union Colliery, which is located north of the town of Breyten (Figure 1-1), initiated a study to evaluate the long-term mine waste drainage stability and to review possible environmental management options. The project involved various geohydrological and geochemical tools to measure present drainage chemistry and predict the potential future drainage chemistry to evaluate associated impacts on sensitive receptors. The chief component of the project involved numerical geochemical modelling and probably the most important tool being the evaluation of the geochemical changes that the mine drainage undergoes over time through the implementation of kinetic numerical models. The main purpose of the investigation was to identify potential geochemical risks posed by the geological mine waste as a product of underground coal mining and to subsequently quantify these risks and evaluate long-term mine waste drainage stability by means of forward reaction path models. Therefore, mine waste characterisation techniques, in conjunction with geochemical modelling have been applied to evaluate the present drainage chemistry and predict the potential quality of drainage that will be generated by Union Colliery mine waste components over time.
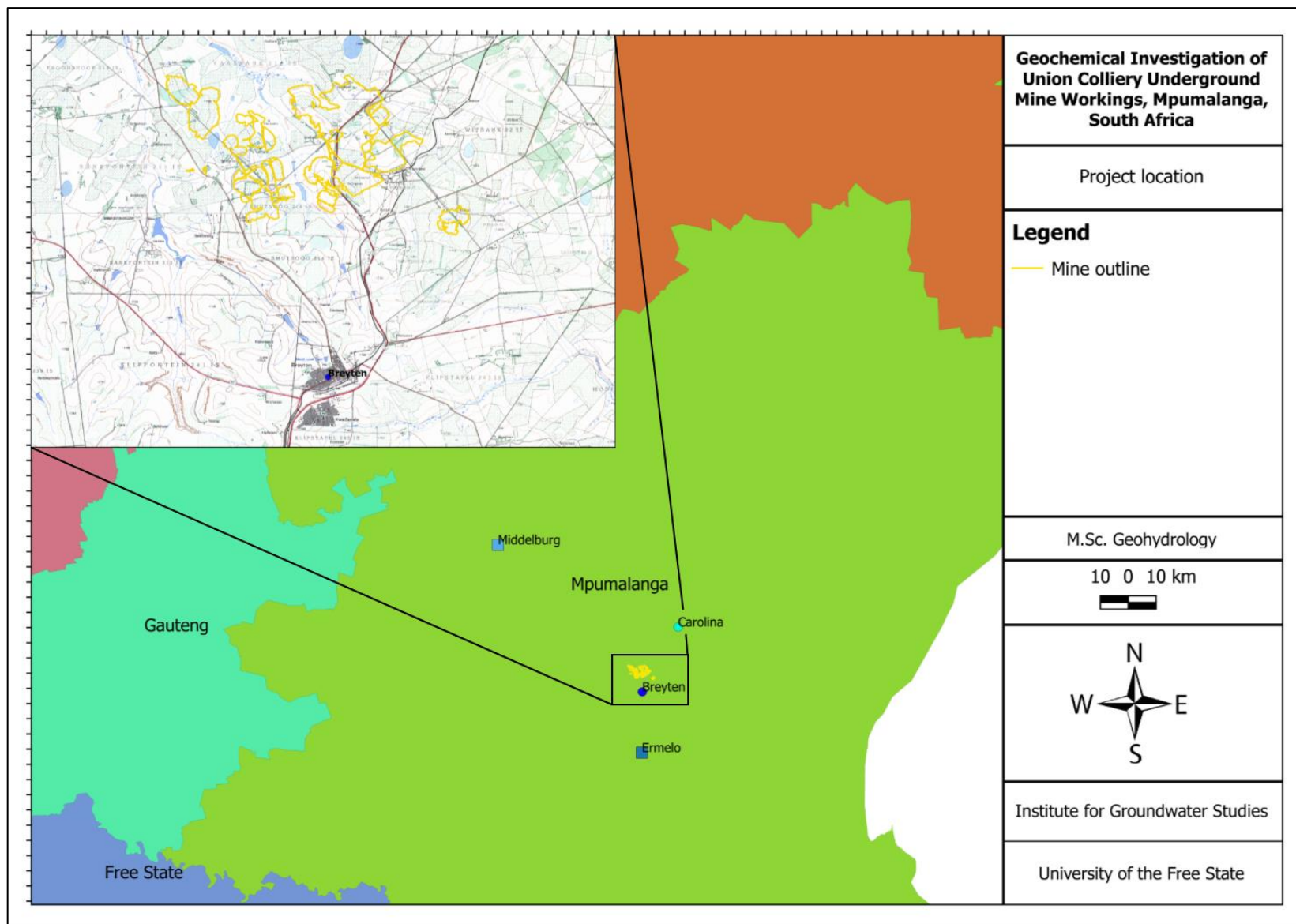
Figure 1-1: Regional map showing the project area location.

1.3 PROBLEM STATEMENT

The defunct Union Colliery, for which the responsibility lies with South 32 CSA, is seeping and decanting mining-influenced waters after decades of mining activities into the upper reaches of the Boesmanspruit and Vaalwaterspruit without any measures to prevent or control acid generation. The mine has however made attempts to investigate a small pilot treatment system having a barium carbonate [$BaCO_3$] dispersed alkaline substrate for use in the at least partial remediation of mine drainage. Potential surface seepage and leaching from existing rehabilitated coal discard dumps further creates a challenge for post mining groundwater use. Contrary to a previously accepted view that in this semi-arid climate, prolonged dry spells and re-vegetating mine waste dumps will prevent water quality deterioration, the mine is indicating contamination problems relating to acid mine drainage (AMD) and metal(loid) contamination from both the underground operations and coal discard dumps (Hodgson & Vermeulen, 2002a, 2002b, 2008; Golder Associates, 2016a, 2016b).

It is widely accepted that the quality of drainage emanating from mine wastes is primarily a function of mine waste composition and the availability of water and oxygen. Furthermore, it is understood that the drainage quality varies with time and distance along its flow path. These conditions are variable even within a mine site (Magombedze, 2006). The evolution in the geochemistry of mine impacted waters as it disperses from the primary source minerals until final discharge is subject to site specific influences and thus necessitates site specific evaluation. This research was formulated on the basis that there is currently no sufficient scientific information on studies done at the Union Colliery in terms of the quantification of risks, the evaluation of long-term mine waste drainage stability and to guide the ways the owning company operate in controlling and managing contamination caused by the mine drainage.

1.4 STUDY SPECIFIC AIMS AND OBJECTIVES

The aim of this study is to assess and predict changes in mine waste drainage quality over time for the purpose of determining the current and anticipated impacts on groundwater and surface water quality.

Objectives:

  i.   To characterise and classify the mine water, groundwater and surface water chemically using classical hydro-chemical methods.

  ii. To identify potential geochemical risks from the geological mine waste resulting from underground coal mining.

  iii. To quantify these risks and evaluate long term mine waste drainage stability by means of a forward reaction path model.

iv.   To review various remediation options in order to provide a rational basis for the recommendation of the most appropriate strategies.

1.5   RESEARCH FRAMEWORK

The approach followed for predicting mine drainage chemistry during this study was that as prescribed by Price (2009). The research framework consists of three main tiers of which the first is to review the general properties of the project and site. Second, any existing monitoring chemistry data with additional hydro -and geochemical data will be assessed, then potential future drainage chemistry predicted. Third, simulations from the previous steps will constantly be checked or calibrated against the monitoring data sets where any significant information gaps will be identified and highlighted.

The strategy adopted in this study is thus that of an integrated, multidisciplinary approach that recognises certain key aspects associated with risk identification and quantification. This includes field site assessment and characterisation, waste characterisation by means of laboratory geochemical assessments, and geochemical modelling where both the field and laboratory data are used to support forward reaction path models. The author aimed to hydro-chemically characterise the different hydrogeochemical systems or components of the study area and to geochemically characterise the mine waste which is vital for a well-defined conceptual model. Once detailed conceptual site models are developed, the author would then be able to model the systems and to recommend appropriate management strategies for the site.

The framework used to maintain the aim of this study is illustrated in Figure 1-2. The following sections ascertain the specific goals of the main components of the study.
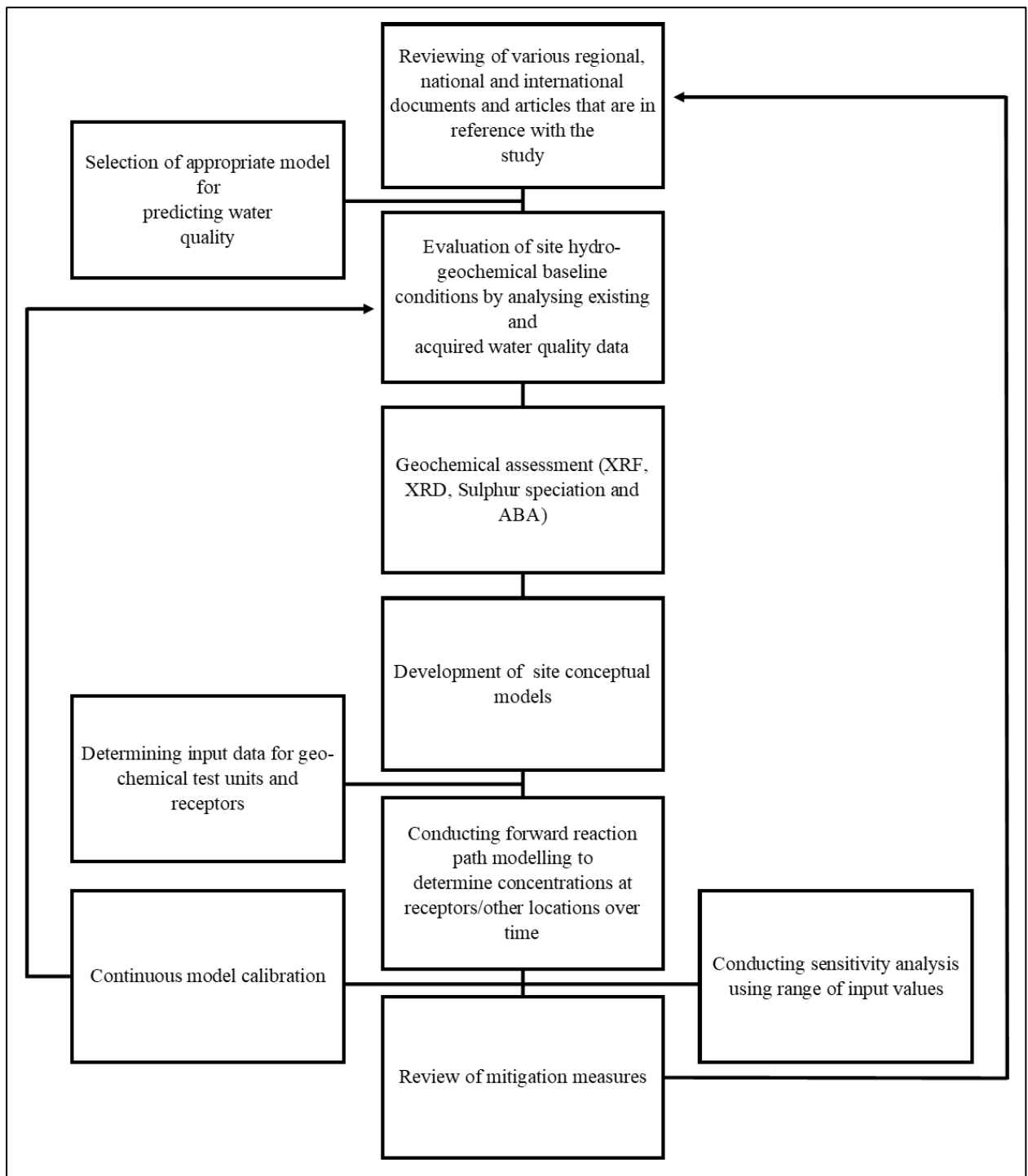
Figure 1-2: Research framework followed to achieve the aim of this study.

1.5.1 Site assessment and characterisation

The specific goals of the site assessment and characterisation are to:

- Ascertain hydrological data, climate and topography from current measurements and historical mine records.

- Conduct a hydrocensus and additional field campaigns to identify the types of mine waste material and locate and sample monitoring and mine boreholes together with additional relevant locations.

- Assess the sources and pathways for acid and metal(loid) release, and evaluate the quality of mine water, surface water and groundwater believed to be affected by mine waste drainage.

- Determine hydrogeochemical baseline conditions for different components in the area incorporating historical and current monitoring data so that future changes in water quality can be quantified.

1.5.2 Geochemical assessment tests

The purpose of geochemical assessment and characterisation tests are to:

- Ascertain the mineralogy and chemical composition of the mine waste with a view to recognise neutralising and acid generating components in the mine system.

- Conduct acid base balance through static prediction tests to obtain a general indication of the acid generation -and neutralisation potentials of the coal discard -and coal material.

1.5.3 Geochemical modelling

The principal modelling goal is to evaluate long-term mine waste drainage stability and thereby predict variation in contaminant characteristics of mine drainage from the different site components, e.g. coal discard dumps and underground operations, based on its unique combination of site conditions and design. The modelling code, The Geochemist's Workbench (Bethke, 1996), here after referred to as GWB, has been selected for this purpose.

1.6 LIMITATIONS TO THE CURRENT RESEARCH

The Union Colliery demonstrates the type of limitations typically encountered in the study of decommissioned AMD-generating sites, such as difficult or no access to relevant areas due to unstable, unknown and closed mine workings, sparse, accurate historical records and uncertainty regarding the metal(loid) and sulphate load to adjacent water bodies. The absence of detailed records of mine plans

and mine waste disposal practices prevents the a priori identification of acid-generation 'hotspots' within the mine waste components (Younger & Robins, 2002).

1.7   DISSERTATION STRUCTURE

The dissertation is divided into ten chapters wherein **Chapter 1** provides a brief background to mine waste drainage and management challenges both globally and in South African collieries. Furthermore, the associated research objectives during this study, which will be addressed within the dissertation itself, is presented.

Chapter 2 presents a review on the literature of national and international case studies, articles, books and reports within the context of the aspects involved in the research topic and geochemical modelling.

Chapter 3 introduces the study area in which the methods were performed. Mining history and general mine infrastructure, geology, geohydrology, climate, surface topography and drainage, and an overview of previous studies conducted at the Union Colliery is presented.

Chapter 4 provides a description of the project data sources and test methodology used to achieve the aforementioned objectives. Data sources described in this chapter will be evaluated and discussed in the following chapters.

Chapter 5 presents the statistical and hydro-chemical characterisation of the components in the research area to infer hydrogeochemical baseline ranges for the different areas within the study area.

Chapter 6 presents the main laboratory test results and discussion as obtained from the geochemical assessments of the mine wastes.

Chapter 7 presents the conceptual models developed for the underground operations and the surface coal discard dumps, considering the main aspects discussed in Chapter 5 and Chapter 6 which includes the hydrogeochemical baseline characterisation (Chapter 5) as well as waste characterisation (Chapter 6).

Chapter 8 provides a description of the forward reaction path model setup, modelling scenarios and results giving a clear guide to the processes and elements involved in a geochemical assessment of mining waste.

Chapter 9 discusses modelling simulations and research results and review potential mitigation and management options and their implications in context with the current study outcomes.

Chapter 10 summarises the major findings of this study and provides recommendations for future research.

CHAPTER 2:
LITERATURE REVIEW

In this chapter, a review of available literature in the fields of mine water and mine waste characterisation are presented. Principally this serves to establish an understanding of the potential environmental issues associated with mine closure and the discharge of contaminated water, as well as the main controlling processes influencing mine drainage chemistry. Numerous authors have reported on the specific geological (Grobbelaar *et al*., 2004; Jeffrey, 2005; Hancox & Gotz, 2014) and geohydrological (Grobbelaar *et al.,* 2004; Vermeulen & Usher, 2006a) setting of the Mpumalanga Coalfields within the Ecca sediments of the greater Karoo Supergroup. The following sub-sections will thus focus on specific water quality issues faced in most coal mining environments.

The author has conducted a literature review of information available within the public domain in consideration of the following aspects of the study:

- Water quality in mining environments
- Threats posed by mining waste and associated deterioration of water quality
- Overview of prediction methods with specific emphasis on kinetic geochemical modelling as an assessment tool of future water quality

2.1 WATER QUALITY IN MINING ENVIRONMENTS

From South African and international experience, it is well known that coal mining has pronounced impacts on surface -and groundwater resources in terms of both quality and quantity (Bester & Vermeulen, 2010). The promulgation of laws like the National Water Act (Act No.36, 1998) and the Mineral and Petroleum Resource Development Act (Act No.28, 2002) which focuses more on sustainability and equality, have however led to the considerable transformation of water management and protection aspects in South Africa in the last few years (Usher, 2003). According to Postma and Schwab (2002) the impact of these laws is manifested by aspects such as waste discharge costs and the polluter pays principle that have become important focuses of water management in the South African collieries (Usher, 2003). However, despite the new emphasis placed on groundwater and surface water quality by regulatory authorities, the effects and associated impacts of coal mining on water resources and other sensitive receptors are still poorly understood (Gupta & Nikhil, 2016).

The state of water resources remains a major concern with respect to surface and underground mining in South Africa's Coalfields. An understanding of the key drivers on water quality in South African collieries is crucial to deal with these issues. According to Sherlock *et al*. (1995), and Usher (2003) there are numerous factors that will influence the observed water quality in the short and long-term at any

coal mine and these factors need to be considered to fundamentally understand the system dynamics within a mined area.

2.1.1   Risks posed by mining wastes: an overview

Small-scale mining activities can be associated with large scale consequences. Gupta and Nikhil (2016), Ahanger *et al*. (2014), and Salomons (1995) explained that although exploitation directly affects only a limited area of terrestrial land, its associated impacts due to failed management attempts on the environment as well as on public well-being, may be detectable at greater distances from the source and may persist for many years. Environmental impacts linked to mining activities can be identified from exploration to the decommissioning phase (Gupta & Nikhil, 2016). However, mining impacts at decommissioned mine sites, especially at older mines, are more pronounced due to a previous lack of accountability and liability now detailed in the newly promulgated laws.

Banks *et al*. (1997a), and Pulles *et al*. (2005) explained that a major environmental concern relating to mining in many parts of the world is uncontrolled discharge of contaminated water (decant) from defunct and abandoned mines. Given the long history of coal mining in South Africa, some deposits have been worked out and mines closed. According to Oelofse (2008) the discharge of contaminated water from defunct, abandoned or ownerless mining sites is common in South Africa where mining started prior to the promulgation of environmental legislation. The immediate concern is thus the threat posed by decanting mine water, which poses potentially severe environmental and safety impacts on the receiving sensitive receptors and concomitant surface areas (Coetzee *et al*., 2010). Mine water decant can be associated with numerous environmental problems relating to acid mine drainage (AMD) (Chon *et al*., 1999; Usher, 2003; McCarthy & Humphries, 2013), high salt loads (Vermeulen & Usher, 2006b; Haunch, 2013) and non-compliant metal(loid) concentrations (Evangelou & Zhang, 1995; Salomons, 1995; Oelofse, 2008; McCarthy & Pretorius, 2009). The impact of decanting mine water on receiving watercourses have been investigated and reported by numerous authors (Hodgson & Krantz, 1998; Luis *et al*., 2009; Ochieng *et al*., 2010; McCarthy, 2011; McCarthy & Humphries, 2013). While South Africa has made significant progress in directing policy frameworks to address mine closure and mine water management, and the mining industry has changed its practises to conform to new legislation and regulation, vulnerabilities in the current system remain (Oelofse, 2008).

During mine closure, pumping of underground water is terminated and a new water table within the voids are created with new flow vectors, allowing oxygen and water to mix with sulphides, resulting in AMD which then seeps to surface (Coetzee, n.d.). Studies by various authors (Swart *et al.*, 1998; Hattingh *et al*., 2002; Vermeulen & Usher, 2006b; Jarvis & Gandy, 2010; Mack *et al*., 2010; Huisamen & Wolkersdorfer, 2016; Aphane & Vermeulen, 2011) have revealed that poor quality seepage associated with the mining of sulphide containing ores generally arises from the oxidation of sulphide minerals, particularly pyrite [FeS_2], which is exposed by the mining processes. The subsequent chemical reactions

can lead to the discharge of often acidic, iron [Fe] and sulphate [SO_4^{2-}] rich waters. The term "mining-influenced waters" (MIW), which were introduced by Schmiermund and Drozd (1997), will be referred to in this document. Mining-influenced waters are affected by the weathering of rocks and minerals exposed by mining activities and may be associated with one or more of the characteristics of low pH, high sulphate, elevated metal(loid)s, and high turbidity (Schmiermund & Drozd, 1997; Smith, 2007). ERMITE (2004) further defines mine water as "water in mined ground including waste rock/tailings repositories and/or draining into an adjoining body of water including streams, lakes, aquifers, wetlands, and oceans".

Most underground mines are characterised by undulating coal floors which may be in the form of small variation in slopes or large regional structures. Grobbelaar *et al.* (2004) explained that water in underground mined out voids will flow along the coal floor and finally accumulate in low-lying areas. Mine water flow will generally be restricted by either natural or artificial barriers but will display an overall flux in the direction of the decanting points or conduits, which generically refers to adits, weak geological structures or sinkholes (Vermeulen & Usher, 2006a, 2006b). Mine discharge usually occurs at the lowest interconnections between the surface and the mine. Significant elevation differences exist across the Mpumalanga Coalfields and regional highs can often be recognised (Grobbelaar *et al.*, 2004). As most of the adits are dug into the side of the hills, this creates pathways for the discharge of MIW. Vermeulen and Usher (2006a, 2006b) provides numerous examples of different decanting scenarios of partially flooded underground mines. They report on mines decanting before it is totally flooded due to an outcrop and seepages along weak geological structures and adits. Decanting of flooded underground -and opencast mines will not be discussed, and the reader is referred to Vermeulen and Usher (2006a).

Oelofse (2008) explained that the effect of mining and the uncontrolled discharge of MIW on the environment includes the release of many chemical contaminants into water resources, environmental damage that can persist for decades to centuries, and the health and safety of nearby communities being compromised. The South Africa Environment Outlook Report (DEAT, 2006) highlighted elevated salinity and acidification as specific water quality problems from defunct mines which result in large scale ramifications. Mine water decant phenomena and associated AMD conditions in South Africa's West Rand in the Gauteng Province have been reported on by various authors (Coetzee *et al.,* 2003; Oelofse *et al.*, 2007; Oelofse, 2008; McCarthy, 2010) and it emphasises profound, generally irreversible destruction of ecosystems due to the discharge of MIW. In many cases contamination have progressed to such a stage that the sites may never be fully restored due to the persistent nature of AMD (Younger, 1997). A study by Naicker *et al.* (2003) revealed that the groundwater in the mining district of Johannesburg, South Africa, is heavily contaminated and is characterised by acid pH values and elevated metal(loid) concentrations as a result of oxidation of pyrite contained in the tailings impoundments. It was further observed in soil profiles that the upper soil layers are heavily contaminated with excess metal concentrations which may be due to the capillary rise and evaporation of shallow groundwater. Moreover, MIW discharges into surface streams which involuntarily lead to stream water acidity.

Naicker *et al*. (2003) further pointed out that the effect of mine water can persist distances greater than 10 km beyond the source.

An article written by Davies (2014) of the Centre of Environmental Rights, titled "Mpumalanga crisis: why is nobody listening" addresses some dire warnings issued by scientists, academia, conservation organisations, tourism authorities and non-governmental organisations (NGO's). A Coal and Water Futures in South Africa report released by WWF-SA (2011) discussed the rapid degradation of the critical Olifants River catchment due to coal mining and the unabated release of contaminated mine drainage. Furthermore, a pilot study released by the Bureau for Food and Agricultural Policy (BFAP) (2012) regarding the impact of coal mining on agriculture revealed that approximately 46% of South Africa's total high potential arable soils are found in the Mpumalanga Province. The study concluded that at the current rate of coal exploitation approximately 12% of South Africa's total high potential arable land will be transformed and that the effects of coal mining and associated MIW discharge on agriculture are "immense and some effects are irreversible". McCarthy and Humphries (2013) highlighted concerns of AMD when the Boesmanspruit Dam, which is a potable water supplier to Carolina, underwent rapid deterioration following a large rain event in January 2012. The dam water displayed pH values as low as 3.7 with accompanied elevated levels of sulphate, iron, aluminium [Al] and manganese [Mn]. Studies revealed that the source of contamination originated from the Witrandspruit sub-catchment where seepage from coal mine waste had accumulated in a wetland located upstream of the Boesmanspruit Dam. During the heavy precipitation experienced in those months, water holding ponds, in which contaminated runoff from coal mine waste repositories have accumulated, overtopped and flushed the contents of the wetland into the dam.

As mentioned before, surface sources of AMD present the greatest threat to the surrounding environment and include coal discard dumps and other repositories. Subsurface impacts are generally associated with flooding of underground mine operations with the attendant threat of decant providing a source of spoiled mine water for potential migration into surface water streams and groundwater sources (Banister *et al*., 2002; Oelofse, 2008). During a study by Younger (2001) a survey of all known mine water discharges in Scotland were undertaken and showed that abandoned workings were responsible for approximately 98% of cases, whereas surface repositories only contributed relatively 2% to the total. Younger and Robins (2002) explained that in the longer term, more environmental damage is wrought by contaminated drainage from defunct and abandoned mine workings than from surface repositories.

The detrimental effects of MIW on streams and river ecosystems are well documented (DeNicola & Stapleton, 2002; Luis *et al*., 2009). Surface water and groundwater regimes are affected through not only acidity, which is generally accompanied by the release of metal(loid)s associated with coal, but also through ferric iron [Fe^{3+}] precipitation (primarily iron hydroxides) (Dills & Rogers, 1974; Letterman & Mitsch, 1978; Scullion & Edwards, 1980; DeNicola & Stapleton, 2002) and oxygen depletion. Metals usually associated with AMD include aluminium, copper [Cu], lead [Pb], manganese,

silver [Ag], uranium [U], and zinc [Zn]; and metalloids most commonly include arsenic [As] and selenium [Se] (Usher, 2003; Oelofse, 2008).

It is therefore recognised that mining activities have resulted in unavoidable environmental consequences that in many cases arose from poor or simply the lack of environmental and water management decisions and in many cases in the South African Coalfields, AMD (Chon *et al*., 1999; Usher, 2003; McCarthy & Humphries, 2013). Acidic mine drainage from abandoned and decommissioned coal mines is a well-documented phenomenon and poses major socio-economic challenges and environmental concerns, specifically for the long-term sustainability of the country's supply of fresh water (Younger & Robins, 2002; McCarthy & Humphries, 2013; Camden-Smith *et al*., 2015; Goerke-Mallet *et al*., 2016). Evangelou and Zhang (1995) captured the essence of AMD as they described it as "an economic and environmental burden". The legacy of mining continues to affect groundwater and surface water resources till this day. These impacts not only highlight the need for fundamental understanding of the main controls driving the observed water quality but necessitates it.

There are various of parameters and processes that affect site specific drainage chemistry from sulphidic mine wastes materials (Price, 2009). The following sections discuss the more important processes from a hydro-chemical and geochemical perspective. Detailed discussions regarding the specific reactions will follow in Chapter 7 of this dissertation.

2.1.2   Deterioration of water quality

Understanding of processes leading to the generation and development of acidic water, including rock weathering, pyrite oxidation, inorganic and microbial processes as well as processes affecting the mobility of metal(loid)s in surface and ground waters, has shown considerable improvement over the last two decades (Nordstrom, 2015). With the previous mentioned definition of MIW in mind, water quality deterioration as a result of mining activities will further be discussed.

According to Nordstrom *et al*. (2015) the quality of mine waste drainage is collectively affected by various processes including different physical, geochemical, microbiological and electrochemical processes. The effect of the specific geochemistry is of primary concern as it is generally the key source of poor-quality drainage containing elevated contaminant concentrations (Muniruzzaman *et al*., 2018).

According to Wood *et al*. (1999) contaminant loadings in MIW as well as the evolution of mine water chemistry are influenced by several factors and numerous processes that may either be time dependent or time independent. The most dominant processes affecting the final drainage quality are completely site specific and is typically determined by the characteristics of the waste materials and the prevailing environmental conditions in the specific area.

The coal resources of South Africa occur in layers within the sedimentary succession of the Karoo Supergroup (Grobbelaar *et al.,* 2004; Hancox & Gotz, 2014). Pyrite occurs in coal seams, host rocks

and associated mining waste which can potentially oxidise upon exposure to atmospheric oxygen and water to produce sulphuric acid (Nordstrom, 1982; Evangelou & Zhang, 1995; Evangelou, 1998; Nordstrom & Alpers, 1999; Oelofse, 2008; Muniruzzaman *et al.*, 2018). Pyrite is the most important sulphide mineral found in South African coal mines (Vermeulen & Usher, 2006b). It was explained by McCarthy and Humphries (2013) that sulphide oxidation is a natural process within undisturbed rock, it however occurs at a rate that is typically neutralised by the natural occurring neutralising minerals such as carbonate minerals. Increased surface areas of these sulphide-bearing rocks are exposed during mining activities (Evangelou & Zhang, 1995), therefore accelerating acid generation beyond the neutralising capabilities of the local environment (Nordstrom, 2015). The resultant acidic drainage is associated with elevated metal(loid)s (Campaner *et al.*, 2014) due to increased metal(loid) solubility and mobility under the acidic conditions (Nordstrom, 2015), which may render the groundwater and surface water toxic (McCarthy & Humphries, 2013).

The water quality in the Mpumalanga Coalfields have extensively been reported on in many specialist reports to the owning companies and the Water Research Commission (WRC). Some of these documents include those by Hodgson and Krantz (1998), Hodgson *et al.* (2007) and Griffin *et al.* (2014). It is clear from these reports that in terms of water quality in mines, the main issues to consider are the geochemistry of the host rocks and coal layers, the mining type, the degree of flooding, and the through flow rate of infiltrated fresh water.

Water quality over the short -and long-term is very difficult to predict with a degree of accuracy due to site specific dynamic processes which leads to very complicated systems. However, deterioration of mine water quality generically follows empirical rules which will be addressed in the following sub-sections. Note that the following sub-sections aim to briefly introduce some processes that may contribute to mine water quality evolution. These processes are discussed in more detail in Chapter 7 of this dissertation as part of the site conceptual models.

2.1.2.1   Acid generation

As already established, a number of environmental problems arise as a result of coal mining, of which acid generation is precursor for many subsequent impacts. According to Grobbelaar *et al.* (2004) all the collieries located within the Mpumalanga Coalfields have the potential to acidify with time and the neutralisation potential varies between and within collieries. Not only the mineralogy of the coal seams and country rock determines the acid generation and neutralisation potential, but also the specific mining method employed. Zhao *et al.* (2010) stated that spatial variability observed in water chemistry is most likely controlled locally by the geochemistry of different underground compartments or between different mine sites.

Grobbelaar *et al.* (2004) found that upon initial pyrite oxidation the drop in the pH of the water is sudden and values below 3.0 have been observed which is the conversion point of ferrous [Fe^{2+}] and ferric iron

[Fe^{3+}]. Extremely acidic mine waters with pH values as low as 0.52 (Williams & Smith, 2000) and -3.6 (Nordstrom *et al.*, 2000) have been reported on. Grobbelaar *et al.* (2004) described the pH evolution of mine water over time through computer simulations using GWB software and is presented in Figure 2-1.
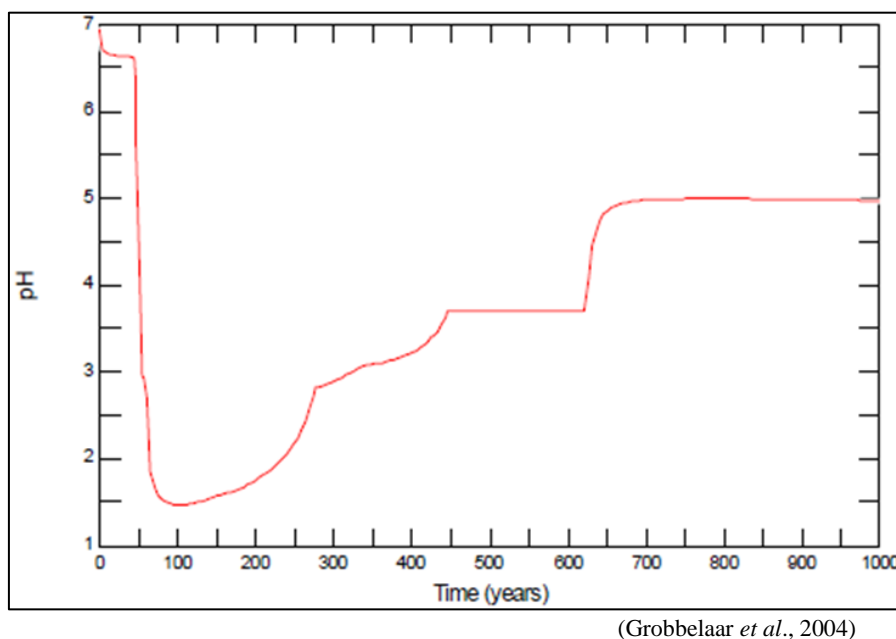
Figure 2-1: Typical reaction path pH-conditions for rocks and coal mined in the Mpumalanga Coalfields.

The reaction path presented by Grobbelaar *et al.* (2004) (Figure 2-1) is typical of what would be found in all Mpumalanga Collieries. The time scale should however be ignored, and the slope and shape of certain sections will differ for all mines as the pH is related to the site-specific mineral composition and flow dynamics at the specific site. The pH evolution over time is related to the actual mineral composition of a specific rock in the larger context of the coalfields. Each of the pH dips or rises corresponds to certain mineral dissolution and buffer capacity. Drops in pH values at or below 2.0 have been observed in Mpumalanga collieries (Grobbelaar *et al.*, 2004). Waters displaying these low pH values may be characterised by sulphate concentrations exceeding 10 000 mg/L as well as elevated metal(loid)s (Grobbelaar *et al.*, 2004; Campaner *et al.*, 2014).

Acidification is generally initiated in patches where microclimates for acid production is favoured. Acid production therefore initially dominates in isolated areas (Grobbelaar *et al.*, 2004). Acid production in underground mines usually start in the moist areas on the outside of coal pillars, particularly where the neutralisation potential of the coal and rock is leached by the dynamic flow of mine water. This might start as soon as mining activities has altered the country rocks and coal seams. Water that flows over these patched oxidised areas will contribute as acid water to the bulk of the mine water. Flooding of areas impacted by patched pyrite oxidation will usually result in neutral pH drainage. Flooding causes water, which is circum-neutral in nature, to saturate both the country rock and coal. Grobbelaar *et al.* (2004) cited various mine sites such as New Largo, Minnaar (Vermeulen & Usher, 2006b), Transvaal

Navigational Colliery (TNC), and Ermelo (Vermeulen & Usher, 2006b) where acid water was encountered during the operational phase. Following mine closure, mine water however displayed neutral conditions after partial and complete flooding. The degree of flooding within underground operations is a controlling factor in terms of long-term stability of the neutral pH conditions.

Studies reported by Grobbelaar *et al.* (2004) indicated frequent correlation between neutralisation potential and the degree of weathering of the rock. This may be ascribed to the oxygen dependency of pyrite. Pyrite will thus only oxidise when it occurs above the groundwater table. These sediments are usually moderately to highly weathered and sometimes devoid of pyrite through oxidation over many years. Neutralisation through carbonate dissolution is not dependent on oxygen and it dissolves upon contact with circulating groundwater since the water is generally undersaturated in terms of its carbonate components. Circulating groundwater occurs naturally within the top 10 to 40 m of the Karoo strata in Mpumalanga and very little groundwater circulation takes place deeper down, where the sedimentary rocks are tightly packed under natural conditions.

As mentioned before, some mines can be completely flooded, whereas other mines may only become partially flooded due to water levels being controlled by decant elevations through adits and geological conduits. In mines that are only partially flooded, the unflooded portions will continue to produce acidic water due to exposed pyritic surfaces which oxidises in the presence of oxygen and moisture. The products are then transported by circulating groundwater as well as infiltrated rainwater following precipitation events. The acidic mine water will subsequently drain into the flooded areas, where it progressively depletes the neutralisation potential (Grobbelaar *et al.,* 2004). Once the mine water is acidic (pH below ~3.0) acid production becomes a self-sustaining reaction through electron transfer and is independent of the presence of oxygen (more comprehensive discussions follow in Chapter 7).

Observed coal mine drainage in South Africa varies widely in composition, from acidic to alkaline, generally displaying elevated concentrations of sulphate, iron, manganese, and aluminium and other more common elements such as calcium [Ca^{2+}], magnesium [Mg^{2+}], sodium [Na^+], and potassium [K^+] (Usher *et al*., 2003). According to Usher *et al.* (2003) coal mine drainage is usually associated with a pH in the ranges of 3.0 to 4.5 or 6.0 to 7.0, with fewer intermediate or extreme values, reflecting a bimodal distribution. Bimodal pH distributions in coal mine water have also been reported by Brady *et al*. (1997), Cravotta *et al*. (1999), Nordstrom and Alpers (1999), Azzie (2002), and Castillo *et al*. (2015). Although acidic drainage resulting from sulphide oxidation has received much attention, it is not just acidic drainage that poses an environmental concern. Elevated concentrations of metal(loid)s in drainage with a near-neutral to alkaline pH may also pose severe risks to the receiving environment (Price, 2009). The following sub-sections highlight AMD and neutral mine drainage conditions and associated risks.

2.1.2.1.1   *Acid Mine Drainage (AMD)*

Acid mine drainage is a significant and costly environmental impact of the mining industry worldwide (Evangelou & Zhang, 1995; Udayabhanu & Prasad, 2010). According to Usher *et al.* (2003) AMD is a

widespread phenomenon which affects the quality of both surface -and groundwater at many South African collieries. Qian *et al*. (2017) describes AMD that originates from mine wastes as a global environmental issue which remains an expensive economic and social challenge for the international mining sector. This may be ascribed to the lasting impacts of mining activities on surface -and groundwater sources long after mining operations have ceased. Acid mine drainage is a problem that numerous defunct and abandoned mine sites around the world have in common (Anon, 2011; Feris & Kotze, 2014).

Johnson and Hallberg (2005a, 2005b) stated that it is imperative to consider the potential long-term threat posed by mine waste as AMD generation may continue in perpetuity even after mine sites are decommissioned. Chon *et al*. (1999) recognises AMD from underground coal mines and coal refuse piles as the probable cause of one of the most persistent industrial problems as it has the ability to cause significant continuing contamination of the surrounding environment that could potentially persist for hundreds of years (Pearce *et al*., 2016). Younger (1997) ascertained the persistent nature of AMD and explained the two-fold components of AMD evolution over time. The short-term component is associated with vestigial acidity, which is generated during initial water ingress into underground workings that declines over a period of 10 to 40 years. The long-term component is associated with the production of juvenile acidity, which is formed in the zone of water level fluctuation after partial flooding, which may persist for centuries until the mineral sources are depleted.

As mentioned before, AMD occurs as the result of weathering reactions between sulphide bearing rocks, moisture (water) and oxygen which leads to the oxidation of sulphide minerals, particularly pyrite (Durkin, 1995. Usher *et al*., 2003; Qian *et al*., 2017; Muniruzzaman *et al*., 2018). This results in the generation of sulphates, toxic metal(loid) ions, and acidity that can have manifold environmental consequences (Nordstrom, 1982; Foos, 1997; Stumm & Morgan, 1996; Nordstrom & Alpers, 1999; Nordstrom, 2000; Williams & Smith, 2000; Cravotta, 2007, 2008; Campaner *et al*., 2014). Waste rock and tailings that are produced at the surface is exposed to the effects of water infiltration and oxygen diffusion which leads to the oxidation of sulphide minerals (Singer & Stumm, 1970; Blowes & Ptacek, 1994). The excavation process during mining not only exposes sulphide minerals in the walls and pillars of underground operations but also disturbs the host rock and hydrological regime around the mined-out areas, allowing the ingress of water and oxygen. It is therefore of extreme importance to the mining industry and to the relevant mining company to be aware of and recognise the characteristics and capacity of the mine waste repositories and roof and floor sediments of the underground voids to produce AMD. The fact that many mines in South Africa are located in or close to urban areas and local agricultural lands, necessitates mining companies to address the already established and pending issues of AMD (Anon, 2011).

A direct consequence of AMD is the leaching of many elements as acidic mine waters, generated by pyrite oxidation, reacts with country rock and mobilises metal(loids)s built in rock and coal structures

(Hem, 1985; Blowes & Jambor, 1990; Lottermoser *et al*., 1999). Many of these metal(loid)s may be transported as either free ions or complexes. Other metals, especially iron and aluminium, may be quickly removed from the water by precipitation as solid phases, depending on the physicochemical conditions along the flow path. The role of these precipitates to remove metal(loid)s through adsorption and co-precipitation have been studied and reported on by Benjamin (1983), Johnson (1986) and Stumm and Sulzberger (1992). A fundamental understanding of the chemical behaviour of these constituents is therefore necessary. More comprehensive discussions of the reactions involved during pyrite oxidation will follow in Chapter 7.

2.1.2.1.2 *Neutral mine drainage*

Haunch (2013) explained that the timing and relationship between pyrite oxidation, neutralisation provided by carbonate buffering and secondary mineral formation reactions all mediates the contaminant potential of MIW. In the South African Coalfields there are co-existing carbonates such as calcite [$CaCO_3$] and dolomite [$CaMg(CO_3)_2$], which help neutralise the acidity generated. The result of this is that MIW are not necessarily acidic, but often high in dissolved salts and potentially toxic metal(loid)s (Brady *et al*., 1998; Banks *et al*., 2002; Usher, 2003; Vermeulen & Usher, 2006b; Bester & Vermeulen, 2010). Net-alkaline mine waters with circum-neutral pH have been described by many authors (Younger, 1995; Banks *et al*., 1997b; Younger, 2001; Cidu *et al*., 2009).

Banks *et al.* (2002) and Brady *et al*. (1998) found that circum-neutral to alkaline mine drainage may either be due to:

- Sulphide mineral deficiency (lower sulphate concentrations is expected);

- the presence of mono-sulphides rather than pyrite or marcasite;

- large pyrite grain sizes which limits the rate of oxidation;

- neutralisation of acid by carbonate or basic silicate minerals (one would expect elevated calcium concentrations);

- engineering factors which includes introduction of lime dust for explosion prevention or cement or rock flour during construction of the workings;

- neutralisation of acidic waters by naturally occuring highly alkaline groundwater;

- circulating water not coming into effective contact with sulphide minerals; and

- oxygen not coming into direct contact with sulphide minerals or influent water being highly reducing.

Banks *et al.* (2002) illustrated the occurrence and chemistry of alkaline mine drainage water in various case studies including those at coal mines on the Arctic Archipelago of Svalbard, coal mines in the Abakan basin of Siberia and iron ore mines in the Sayan and Kuznetsk-Alatua Mountains of Siberia.

During these studies they identified one or more of the beforementioned factors as the possible mechanism generating circum-neutral to alkaline drainage.

Cravotta et al. (1999) reported on a wide range pH frequency distribution in coal mine drainage in Pennsylvania with modes at 2.5 to 4.0 (acidic) and 6.0 to 7.0 (near neutral). Cravotta et al. (1999) found during their study that pH values in the near neutral mode result from carbonate buffering and imply the presence of calcareous minerals so that acid produced by pyrite oxidation is neutralised. Conversely the pH values in the acidic mode result from pyrite oxidation and imply that calcareous minerals are deficient and therefore the absence of carbonate buffering result in acidic drainage. Similar observations were made by Castillo et al. (2015) during a study where drainages with different hydrogeochemical characteristics from active and abandoned mines located within the Mpumalanga Province of South Africa were evaluated.

Banks et al. (2002) ascribed changes in mine water chemistry at the same mine to the fact that considering the heterogeneity of the subsurface environment, newly opening parts or compartments of the mine might have been part of a somewhat different geological – hydro-chemical regime to the existing mine. Mine drainage that is near neutral may originate from host rock that lacks pyrite or may originate as AMD that has been neutralised along the flow path by reaction with calcareous minerals (Blowes & Ptacek, 1994; Cravotta et al., 1994; Cravotta et al., 1999). Bicarbonate [HCO_3^-] together with sulphate is significant anions in neutral mine drainage. Furthermore, concentrations of dissolved calcium and magnesium are typically elevated relative to dissolved iron and aluminium, which may precipitate as the pH increases to above ~4.0 to 5.0. Iribar (2004) studied the evolution of drainage quality of an underground sulphide mine associated with near neutral pH ranges. The importance of kinetic processes that affect pyrite oxidation, carbonate dissolution and the aging of iron hydroxides were highlighted. The changes observed in mine drainage quality at different sites and within the same site may be related with changes in mineral availability within sulphide ores or in the host rocks, and with hydrologic changes. Mineral availability can be related to mineral depletion, surface coatings or with kinetic processes (Iribar, 2004). Long-term water quality is also controlled by the availability of oxygen in the mine water system and is influenced by flow factors such as recharge into, and residence time of water in the mine voids (Vermeulen & Usher, 2006b).

Coal mine drainage whether near neutral or acidic are generally associated with elevated concentrations of dissolved solids ranging from 200 mg/L to concentrations greater than 10 000 mg/L. Mine drainage is typically characterised by having high salinity (Ca > Mg > Na), hardness, and metal concentrations such as Fe > Al > Mn and moderate to low trace metal concentrations such as Ni > Zn > Cu (Durand, 2012; Castillo et al., 2015). Groundwater and stream water in unmined areas typically reflect near neutral pH conditions and are dilute when compared to mine water (Brady et al., 1996; Rose & Cravotta, 1998).

2.1.2.2   Neutralisation reactions

As mentioned before, neutralisation potential is often provided by the presence of carbonate minerals, calcite and dolomite within the waste material and country rock (Vermeulen & Usher, 2006b; Muniruzzaman *et al*., 2018). Neutralisation capacity is only available in areas inundated with water where groundwater flow is active. This can be explained as waters acidic in nature can only be neutralised when in contact with carbonate or base minerals. Neutralising minerals present in coal pillar or hanging wall material in unflooded underground workings is therefore of little help in acid neutralisation as water is not available for dissolution. However, when underground workings become flooded, the neutralisation potential becomes available since the material becomes part of the hydraulic system and can therefore dissolve and neutralise any acid present in the mine water. Acidic water generally persists due to the often-insufficient neutralisation potential (Grobbelaar *et al*., 2004). Comprehensive discussion on carbonate and silicate neutralisation will follow in Chapter 7.

2.1.2.3   Metal and metalloid content

It is well known that the release of both major and trace elements into the receiving environment is accelerated through mining activities (Salomons, 1995; Smith, 2007; Fashola *et al*., 2016; Muniruzzaman *et al*., 2018). Metal(loid)s, which are generally present in trace concentrations in waters, may reach toxic and hazardous concentrations. Nyarko *et al*. (2008) and Carreras *et al*. (2009) classifies metal(loid)s as probably one of the most dangerous groups of pollutants due to their toxicity and persistence in the environment (Smith, 2007). Accumulation of metal(loid)s within mine waste or along flow paths may be leached from surface mine repositories or underground workings during precipitation events thereby contaminating surface streams and groundwater (Gupta & Nikhil, 2016).

A study by Mohanty *et al*. (2001) on the sequential leaching of trace elements from coal from the Talcher Coalfields in India concluded that trace elements are mostly bound to soluble oxides and sulphide minerals present in coal material. This is supported by Karbassi *et al*. (2008) who found that metal(loid)s occurring in the water often reflect the mineralogy of the area. Gupta and Nikhil (2016) explained that natural weathering processes of mineral bearing sediments is one of the major causes of metal contamination in groundwater, although anthropogenic sources are also major causes (Ammann *et al*., 2002; Nouri *et al*., 2008). As metal(loid)s occur in the earth's crust, these constituents may become solubilised and mobilised in groundwater through natural weathering processes (Karbassi *et al*., 2008). Natural weathering processes of sediments are strongly related to temperature and precipitation (Hem, 1985), however mining activities accelerate the solubilisation and mobilisation by means of artificially weathering the sediments (Gupta & Nikhil, 2016). Metal concentrations are generally orders of magnitude greater in soils and sediments when compared to concentrations observed in associated waters (Smith & Huyck, 1999). This may be ascribed to the partitioning of metals among various components of sediments and soils.

Azzie (2002) defines mobility as "the capacity of an element to move within fluids after dissolution". As mentioned, metal(loid)s may be present in the structure of primary or secondary minerals and it can also be occluded in amorphous material or in remains of animals. The mobility and occurrence of metal(loid)s is further influenced by sorption on hydrous metal oxides, organic matter and clays. (Smith & Huyck, 1999). Nordstrom (1999) explained that elements are associated with certain inherent chemical and physical properties that influence their occurrence and behaviour in natural environments. The redox conditions and pH of the system are some of the most important factors influencing dissolved metal(loid) concentrations (Nordstrom, 2011). Smith and Huyck (1999) present a summary on element properties that influences their mobility and dispersivity in nature.

Grobbelaar *et al.* (2004) investigated the availability of metal(loid)s over the whole pH range and is presented in Figure 2-2 and Figure 2-3. They observed three categories of metal(loid)s depending on their solubility characteristics at various pH levels. Firstly, iron was observed to have a variation in solubility characteristics with a drop in the pH due to the conversion of iron from its ferrous to its ferric state. They noted elements that increase linearly as the pH decreases, such as manganese, aluminium, cobalt and nickel. Moreover, there are elements that are not affected by a drop in the pH and are usually those elements whose availability is limited within the rock and coal lithologies.
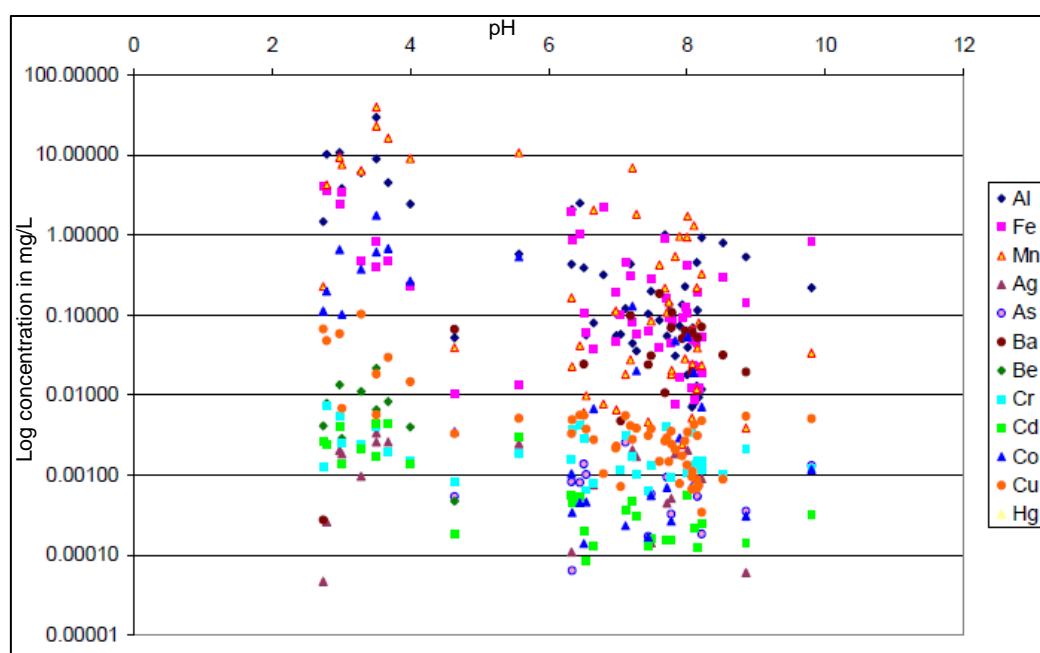
(Grobbelaar *et al.*, 2004)

Figure 2-2: Availability of elements from rock and coal material at various pH-levels.
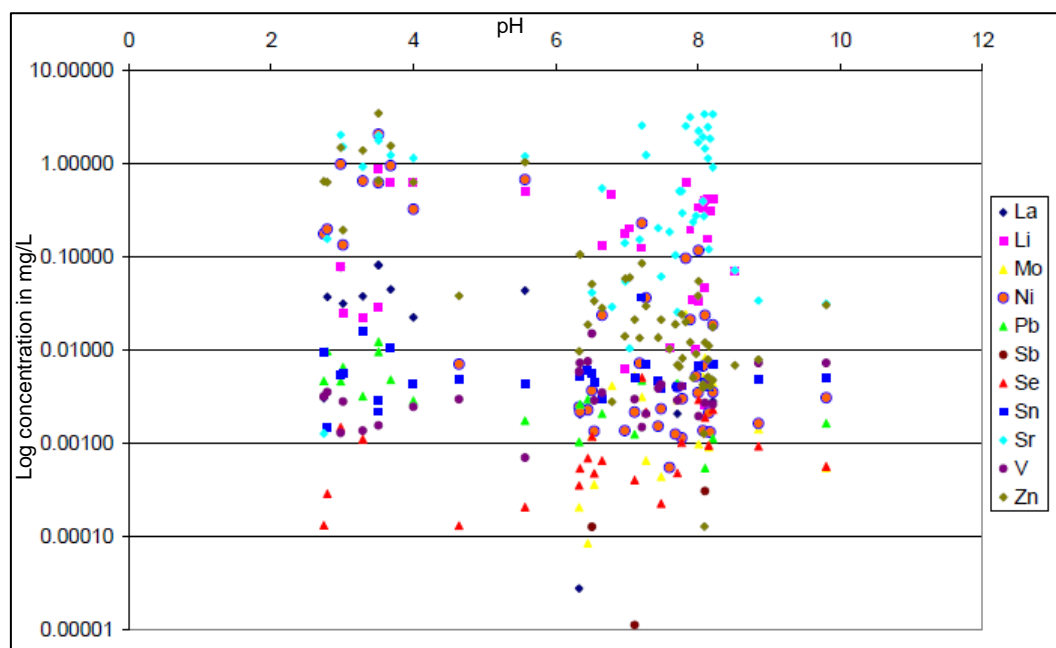
(Grobbelaar *et al*., 2004)

Figure 2-3: Availability of elements from rock and coal material at various pH-levels (continued).

The quantitative prediction of element mobility in surficial environments is challenging and the behaviour of elements under changing environmental conditions should be considered in a relative sense by empirical comparison (Grobbelaar *et al*., 2004). Rose *et al*. (1979) qualitatively discussed the relative mobility of selected elements during weathering. Langmuir and Mahoney (1984) and Smith (2007) highlighted that metal(loid) mobility is strongly impacted by geochemical and biological reaction rates since reactions involving metal(loid)s are kinetically controlled and biologically mediated. This makes reactions difficult to predict. The occurrence and principal limiting factors controlling the mobility of selected metal(loid)s in nature are referred to in the following sections.

2.1.2.3.1   *Aluminium*

According to Hem (1985) aluminium rarely occurs at concentrations greater than ~10 to 100 mg/L in natural waters. The exception may occur in very acidic water. Aluminium occurs in considerable amounts in many silicate igneous rock minerals including feldspars, feldspathoids, micas and many amphiboles. Due to aluminium's relative abundance and wide distribution, it occurs in a dissolved state in most natural waters.

When igneous rocks undergo weathering, aluminium is mostly retained in a new solid species, some of which may be greatly enriched in aluminium. Gibbsite, which is nearly a pure aluminium hydroxide, is a fairly common mineral. In environments where low pH conditions persist, aluminium may be precipitated as an aluminium hydroxy-sulphate. Clays are probably the most common sedimentary minerals enriched in aluminium. Clays are present in most natural environments and occur abundantly in most soils and in hydrolysate sedimentary rocks (Hem, 1985).

In waters associated with pH values lower than ~4.0, aluminium predominates as the cation Al^{3+}, whereas at neutral pH values, the dominant dissolved form of aluminium is the anion $Al(OH)_4^-$ (Hem, 1985). According to Smith (2007) aluminium is mobile under oxidising environmental conditions where the pH is below 3.0. Aluminium is scarcely mobile to immobile under oxidising conditions with pH above 5.0 to circum-neutral where iron substrates are limited to abundant. For waters with pH values below 4.5 to 5.0, dissolved aluminium tends to behave as a conservative ion in surface waters, whereas for waters with pH above 5.0, solubility control of dissolved aluminium by microcrystalline to amorphous $Al(OH)_3$ is apparent (Nordstrom & Ball, 1986). Such control may be caused by equilibrium solubility or by a surface reaction involving the exchange of Al^{3+} for $3H^+$ on an aluminous surface (Azzie, 2002).

According to Hem (1985) aluminium concentration reported as 1.0 mg/L or more in waters having near-neutral pH values and no unusual concentrations of complexing ions probably represent particulate matter (polymeric colloidal material). Whether the particulate matter is present as aluminium hydroxide or aluminosilicate is indeterminate. Waters displaying pH values below ~4.0 may be associated with aluminium concentrations of several hundred to several thousand milligrams per litre. This is usually a characteristic of AMD.

2.1.2.3.2   *Iron*

The oxidation intensity together with the pH of the system strongly effects the chemical behaviour of iron and its solubility in water. Igneous rock minerals including pyroxenes, amphiboles, biotite, magnetite and especially nesosilicate olivine have iron contents that is relatively high. Iron in these minerals mostly occur in its ferrous oxidation state, however ferric iron may also be present in magnetite [Fe_3O_4]. In the event of mineral weathering as a result of circulating groundwater, iron that may be mobilised is usually reprecipitated along the flow path as sedimentary species. Pyrite, which is a ferrous polysulphide, occur under reducing conditions when sulphur is available. Siderite [$FeCO_3$] may form where sulphur is less abundant. Under oxidising conditions, the sedimentary species includes ferric oxides or oxyhydroxides such as hematite [Fe_2O_3] and goethite [$FeOOH$]. Ferric hydroxide [$Fe(OH)_3$] freshly precipitated is commonly associated with poorly developed crystal structures (Hem, 1985).

Iron is a common constituent of sulphide ores and ferrous sulphide is generally associated with coal seams. Iron in solution is most commonly present in groundwater in its ferrous state. Under acidic pH conditions ferric iron may occur either as Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_2^+$ and in polymeric hydroxide forms. The predominant form and concentration strongly depend on the pH of the water as Hem (1985) reported that at pH values above 4.8, the total activity of these species in equilibrium with ferric hydroxide will be less than 10 μg/L.

Ferric oxyhydroxide surfaces have substantial adsorption capacity which may influence the concentration of minor constituents in water associated with such material. Metal ion solubilities may be controlled by redox coprecipitation processes under certain conditions (Hem, 1985). Precipitation of

ferric oxyhydroxide by oxygenation of solutions rich in ferrous iron occurs rapidly at near-neutral pH levels. Water that is fully aerated and displays a pH range between 6.5 and 8.5 should in practice not contain more than a few micrograms per litre of uncomplexed dissolved iron at equilibrium. Higher concentrations reported under these conditions are generally small particulates (Kennedy *et al.,* 1974; Hem, 1985). Lower pH and higher iron concentrations can occur in coal mine drainage water. Waters under reducing conditions may retain ferrous iron in solution at great concentrations (Hem, 1985).

2.1.2.3.3 *Manganese*

Unlike aluminium and iron, manganese does not essentially occur in common silicate rock minerals. However, it can substitute for iron, magnesium and calcium in silicate structures (Hem, 1985). Manganese precipitate in redox processes during weathering processes. It has three possible valence states in weathering environments and include Mn^{2+}, Mn^{3+} and Mn^{4+} and can form various mixed-valence oxides (Hem, 1985).

Divalent manganese [Mn^{2+}] may occur as a minor constituent in numerous igneous and metamorphic minerals and it may occur as a significant constituent of basalt, olivines and of pyroxenes and amphiboles. Furthermore, it may substitute calcium in dolomite and limestone. Divalent manganese in aqueous solutions may precipitate as a crust of Mn^{4+}-oxide when in contact with the atmosphere and at sites where the pH is relatively high. As the system becomes more oxidising, the aqueous Mn^{2+} is converted to various solid manganese forms (Lovett, n.d.). Therefore, it is less mobile in oxidising environments with pH above 5.0 (Smith & Huyck, 1999; Smith, 2007).

Under natural conditions, dissolved manganese is expected to occur in the 2+ oxidation state and the ion Mn^{2+} will predominate in most cases. Waters that have been affected by acidic drainage from coal mines is generally associated with manganese concentrations greater than 1.0 mg/L.

According to Hem (1985) manganese usually persists in stream water for greater distances from the source than iron present in the drainage inflows. During acid neutralisation as the pH becomes gradually higher, ferric hydroxide will be the first to precipitate. Manganese will disappear from solution after a longer time period. Manganese concentrations exceeding 1.0 mg/L is not uncommon in groundwaters under certain conditions and may variably be accompanied by elevated iron concentrations. Manganese has been reported to be mobile under oxidising conditions where the pH is below 3.0 (typical of AMD conditions) and under reducing conditions with a pH above 5.0 (Bricker, 1965; Hem, 1985).

2.1.2.3.4 *Cobalt and Nickel*

Cobalt ions may substitute for part of the iron present in ferromagnesian rock minerals and may occur in 2+ or 3+ oxidation states. Nickel in aqueous solutions primarily occur in the Ni^{2+} oxidation state. Coprecipitation and/or adsorption of cobalt and nickel by manganese and iron oxides are controlling factors in the occurrence of these metals in natural waters (Hem, 1985). However, Smith (1999) found that very little nickel is sorbed by hydrous ferric oxides (HFO) in oxygen deficient mine water, in low

pH water with abundant iron and other metals, and under low pH conditions with moderate iron -and other metal concentrations. Observations made by Smith (1999), and Plumlee *et al*. (1999) included that nickel tends not to sorb at all and are thus expected to be mobile in many mining areas. Cobalt and nickel have been reported very mobile under oxidising conditions where the pH is below 3.0 and less mobile in water with pH above 5.0. Nickel may also be mobile under reducing conditions where the pH is above 5.0 to circum-neutral (Hem, 1985).

2.1.2.3.5   *Lead*

Lead is relatively widely dispersed in sedimentary rocks. Its natural mobility however is low owing to the low solubility of lead hydroxy carbonates. Adsorption of lead on organic and inorganic sediment surfaces and coprecipitation with manganese oxide tend to maintain low concentrations of lead in surface streams and groundwater. Adsorption of lead by HFO have been reported by Smith (1999). The principal dissolved inorganic forms of lead include the free Pb^{2+}, hydroxide complexes and carbonate and sulphate ion pairs (Hem, 1985).

According to Smith (2007) lead is somewhat mobile under oxidising conditions where the pH is below 3.0 and its mobility increases in reducing environments where a pH greater than 5.0 prevails. Lead is scarcely mobile to immobile under oxidising conditions where the pH is above 5.0 to circum-neutral. Azzie (2002) conjectured that the overall mobility of lead is relatively low which is in part limited by precipitation with organic matter and HFO.

2.1.2.3.6   *Arsenic*

Due to the toxic nature of arsenic in very small concentrations, it is considered a highly undesirable impurity in water. Arsenic may be released in coal mining environments during the burning of coal and is a common trace element that can be extremely elevated in acid to neutral mine waters (Rait *et al*., 2010). In aqueous solutions arsenic may occur in its stable arsenate $[As^{5+}]$ or arsenite $[As^{3+}]$ oxyanions. The monovalent arsenate anion $[H_2AsO^{4-}]$ are expected to predominate between pH 3.0 and 7.0, whereas the divalent species $HAsO_4^{2-}$ are dominant from a pH of 7.0 to 11.0. Major inorganic factors that may control arsenic concentrations at very low levels in water include adsorption by HFO and coprecipitation (Hem, 1985). According to studies performed by Smith (1999) and Rait *et al*. (2010) dissolved arsenic can be strongly adsorbed to HFO's. According to Smith (2007) arsenic is mobile under oxidising acidic (pH <3.0) conditions and is less mobile under oxidising conditions where the pH is 5.0 to circum-neutral and under reducing conditions.

2.1.2.3.7   *Selenium*

According to Bailey *et al*. (2009) selenium is a trace constituent in all igneous rocks and is present in all soils. Taylor (1964) reported significantly elevated selenium concentrations in marine shale deposits, wherein selenium exists as a sulphur-substituting constituent in pyrite.

Selenium may occur in oxidising solutions either as selenite [SeO_3^{2-}] or selenate [SeO_4^{2-}] ionic species, but it can readily be reduced to elemental and relatively insoluble Se^0 (Hem, 1985; Bailey *et al*., 2009). In the presence of iron it may be coprecipitated with pyrite (Hem, 1985). Bailey *et al*. (2009) explained that the migration of selenium in the groundwater regime is governed by redox reactions, which controls the speciation of selenium, and adsorption processes that may retard SeO_3^{2-} and SeO_4^{2-}. The more oxidised forms of selenium may be adsorbed on ferric oxyhydroxides (Hem, 1985). In highly oxidising environments, selenium dominates as SeO_4^{2-} and SeO_3^{2-}, whereas Se^0 and Se^{2+} are the principle selenium constituents under reducing conditions (Bailey *et al*., 2009).

Selenium is relatively mobile under oxidising, acidic (pH <3.0) conditions as well as in pH environments of >5.0 to circum-neutral (Smith, 2007). Its mobility however decreases in reducing environments. The reader is referred to Liu and Narasimhan (1994) for the stability of selenium species with respect to Eh-pH conditions.

2.2 OVERVIEW OF PREDICTION METHODS

Substantial research effort during recent decades has been put into improving understanding of the long-term behaviour of mining wastes and the development of prediction tools for their effluents (Morin & Hutt, 1994a; White *et al*., 1994; White *et al*., 1999; Blowes *et al*., 2007; Sapsford *et al*., 2009). A large selection of forms of guidance and tools are currently available and ranges from simple laboratory tests and analyses to field-scale tests and simple geochemical or more sophisticated reactive-transport modelling (Lawrence & Day, 1997; Maest *et al*., 2005; INAP, 2009; Price, 2009; Parbhakar-Fox & Lottermoser, 2015). A comprehensive prediction programme generally combines data from all aforementioned sources (Lawrence & Day, 1997). However, predictive programmes should be in accordance with the complexity of the available data, the scale of the addressed problem and the requirements set by the regulatory decisions made at that point (Maest *et al*., 2005).

Numerous studies have reviewed and evaluated methods and models applied in the prediction of drainage quality as a result of mining activities (Lappako, 2002; Usher *et al*., 2003; Usher, 2003; Maest *et al*., 2005; Zhao *et al*., 2010). Various authors also already studied the prediction of post-mining water quality in underground mines (Banks, 1994; Younger, 2000, 2001; Younger & Robins, 2002; Appelo & Postma, 2005; Gzyl & Banks, 2007). These studies highlight the necessity of site-specific evaluations and waste characterisation as the geochemistry of the mining waste will ultimately influence the quality of discharging water from the waste material.

Laboratory and field tests and hydrogeochemical models used for prediction purposes are continually undergoing modifications; however, the basic characterisation and modelling approaches have undergone few changes over the last three decades (Maest *et al*., 2005). The effectiveness of the different

methods and approaches together with the associated advantages and limitations have been discussed in length by aforementioned authors.

Maest *et al.* (2005) made it clear that the prediction of water quality drainage as a result of mined wastes is very challenging due to technical complications and inherent uncertainties. Mine wastes, in terms of their quantity and characteristics, are probably the most important determinants of water quality at mine sites. Mine waste may refer to and include the extraction areas of open pits and underground workings, waste rock, unprocessed lean ore, heap or dump leach piles, tailings and metallurgical processing wastes (Maest *et al.*, 2005).

Sherlock *et al.* (1995) pointed out that control and regulation of acidic mine drainage in practice are closely interrelated with prediction. This implies that cost effective management and mitigation strategies and the promulgation and implementation of fair regulations and guidelines relies on the ability to predict drainage quality emerging from mine wastes. Prediction techniques at abandoned and decommissioned mines are aimed to inform development of plans for control, remediation and final closure (Usher, 2003; Maest *et al.*, 2005).

Kania (1998) recognises the ongoing debate between those who must predict post-mining water quality and which of the predictive methods should be performed and hence be the most contributing. Kania (1998) simply stated that an appropriate approach should be that, where possible, all the predictive tools should be used so that each contribute to create a fundamental understanding of the system dynamics. Maest *et al.* (2005) introduced a "toolbox" approach, adapted from work done by Plumlee and Logsdon (1999), for reviewing and evaluating methods and models that can successfully be used to predict water quality at mine sites. They describe two "toolboxes" that include the range of geochemical characterisation methods and modelling approaches. Geochemical characterisation generally includes field and laboratory methods and tests that is applied to assess and predict water quality and acid generation. These methods heavily rely on methods used for geologic and mineralogical characterisation of material.

According to Lawrence and Day (1997) mechanisms and reactions of acid generation and the controls that yield the measured water quality can vary significantly. The main challenge in predictive methods lies therein that all the test results with accompanied uncertainties have to be extrapolated into the future. Therefore, predictive capability is best achieved when using a combination of tools, rather than relying on any single procedure (Usher *et al.*, 2003; Usher, 2003, Maest *et al.*, 2005). Various mine waste characterisation techniques, in conjunction with geochemical modelling incorporating relevant existing data have been applied by various authors to evaluate and predict the quality of drainage generated by mine wastes over time (Hattingh *et al.*, 2002; Huisamen & Wolkersdorfer, 2016; McKeown *et al.*, 2017).

Predictive programmes of water quality should therefore consist of various integrated and iterative tests, analyses and procedures to assess the future behaviour of mine wastes. These tests inherently vary in complexity of methodology, data interpretation, time frames and cost. Combinations of these tests are

recommended and required to provide reliable interpretations since it is highly unlikely that a single test can yield all the information needed to properly evaluate mine wastes. Usher (2003) describes certain steps that should form part of any prediction programme. However, site specific conditions and factors guides the scope of a prediction programme and therefore the whole array of predictive tools are rarely consistently performed at mine sites. According to Usher (2003) steps in water quality prediction are inconsistently applied in South Africa. This results in mine drainage prediction programmes that vary greatly with non-uniformity applied in the interpretation of results. However, the One Environmental System was promulgated in 2014 to try to solve these issues.

Maest *et al.* (2005) recognises one of the biggest challenges inherent in water quality prediction as the estimation of the long-term geochemical behaviour of mine waste. Mine waste drainage may take years to several decades to evolve and are subject to climatic and seasonal variability in concentrations and flow. To improve water quality predictions, laboratory and field geochemical testing and hydrologic and meteorologic data at the site over time is required.

According to Banwart *et al.* (2002) laboratory data are useful for understanding the development of water quality and its temporal trend. Mineralogic characterisation is a powerful, yet underutilised tool in the prediction of the geochemical behaviour of mine waste. Static tests and short-term leach tests are not designed to simulate long-term behaviour of mine waste. It should therefore only be aimed to provide estimates of the acid-generating and acid-neutralising ratio that the material exerts and to simulate short term interaction between water and weathered mine material (Younger & Sapsford, 2004; Meast *et al.*, 2005; Huisamen & Wolkersdorfer, 2016). According to Jambor *et al.* (2000a) the common application of static tests, especially acid-base accounting (ABA), in AMD prediction has been justified based on historical and generally successful applications to North American Coalfields. The minimum screening method for the potential contamination of groundwater by mining wastes in South Africa is often ABA (Wimberley *et al.*, 2007; Huisamen & Wolkersdorfer, 2016). ABA methodology is particularly employed in Mpumalanga, where most of South Africa's coal reserves are mined (Pinetown *et al.*, 2007; Huisamen & Wolkersdorfer, 2016). Results obtained from static tests are useful as an initial screening method to ascertain which materials should be subjected to additional tests.

Kinetic tests (column and humidity cell tests) are designed to estimate longer term geochemical behaviour of mine waste. These tests are associated with various problems, most of which is related to particle size and length of the tests. According to Maest *et al.* (2005) due to these issues, kinetic tests are often poor predictors of long-term water quality. Crawford (1999) further explained that owing to issues associated with the degree of complexity and time scales involved it is not always possible to conduct sufficiently realistic laboratory experiments to observe and understand the long-term behaviour, beyond a few decades, of most geochemical systems. Geochemical models, however, can be used to interpret and predict processes that may occur over longer time scales that are not directly achievable in experiments.

Mine waste characterisation results can be utilised in drainage quality prediction by the widely used thermodynamic equilibrium modelling approach, or the more complex kinetic modelling approach (Declercq *et al.*, 2017). During the kinetic modelling approach, dissolution and precipitation of the possible mineral phases present in the waste are allowed over a selected time period. This is achieved based on the mineralogy, the reaction rates and reactivity equations for each mineral, temperature, particle-size distribution and reactive surface area parameters (Declercq *et al.*, 2017). Modelling techniques performed at mine sites mostly include forward modelling which refers to the modelling of future conditions. Predictive modelling at mine sites is an evolving science with inherent uncertainties.

2.3 GEOCHEMICAL MODELLING FOR LONG-TERM WATER QUALITY PREDICTION

In the field of environmental protection and risk analysis, interest is increasingly being focused upon predicting how geochemical systems will evolve over long periods of time (Crawford, 1999). According to Alpers and Nordstrom (1999) geochemical modelling is a powerful tool for evaluating geochemical processes and has been increasingly considered as the method of choice for the prediction of long-term drainage quality particularly in mining environments.

Crawford (1999) explained that although modelling and computer simulation is by no means a substitute for experiment, it is a valuable predictive tool that can be used to gain a greater understanding of laboratory experiment outcomes, field observations, and the long-term behaviour of geochemical systems. When properly constrained and cautiously applied, modelling can provide valuable insights into processes controlling the release, transport, and fate of contaminants in mine drainage. It should however be born in mind that modelling is not an exact science and its application is associated with numerous drawbacks, uncertainties and limitations. Crawford (1999) highlighted that a model is more or less by definition a simplification of reality and should always be treated as a powerful heuristic tool rather than a source of abslute truth.

Usher (2003), and Perkins *et al.* (1997) described typical objectives when modelling AMD from mine wastes and the typical range of tasks performed that corresponds to the level of detail required (Li, 2000). Oreskes *et al.* (1994) explained that computer modelling should principally be used to obtain better understanding of inconsistencies between observed data and simulated results, test hypotheses regarding the major controls on the mobility of selected contaminants (Alpers & Nordstrom, 1999), conduct sensitivity analyses, and explore different scenarios.

The modelling approach can be used to gain considerable insight into processes that may be occurring at a contaminated mine, and to assess the probable consequences of various remediation strategies without costly field experiments (Alpers & Nordstrom, 1999). It was pointed out by Lupankwa *et al.* (n.d.) that predictions of mine water quality are very useful in selecting cost-effective rehabilitation and

remediation strategies to reduce future risks associated with AMD and metal leaching (ML), henceforth to limit long-term impacts. Lichtner (1996) made the observation that although models and computer simulations cannot provide direct quantitative descriptions and answers, it provides far better qualitative understanding of the geochemical and physical processes under investigation.

Geochemical models incorporate numerous chemical and physical parameters to describe the chemical reactions commonly associated with acid generation, microbial catalysis and transport of the weathering products (Scharer *et al*., 1991; Crawford, 1999; Usher *et al*., 2003; Usher, 2003). Forward modelling in the form of forward reaction path models simulates the consequences of particular geochemical reactions given assumptions regarding the initial state of a system and its boundary conditions. The consequences of specific geochemical reactions can be computed from user-supplied reactions with associated thermodynamic data and assumptions regarding equilibrium. Reactions that may be modelled include for example mineral dissolution and precipitation, oxidation-reduction, gas-evolution and sorption (Alpers & Nordstrom, 1999). However, microbial assessment was not part of this study.

Detailed site-specific information can be used to develop representative conceptual models of the specific mine site which is in reality a reflection of current condition or conditions in the recent past. A well-defined conceptual model results in increased levels of confidence and can be used to develop a model to simulate future site conditions (Mayer *et al*., 2003; Maest *et al*., 2005). Einstein and Infeld (1938) had the following additional remark: "We cannot compare our theories with the real world; we can only compare the predictions from our theories with our theory-laden observations of the world". It is therefore incorrect to state that models are based or compared to reality. Only the consequences of models are compared with independent observations and those observations are not devoid of concepts and theories, they come with their own conceptual framework (Nordstrom, 2012; Hansen, 2018). According to Nordstrom (2012) a geochemical model is always a simplification, an idealisation, a picture of how we think about some aspect of physical phenomenon. It can be debated that model predictions are always incorrect, because it is never complete or exact, however in another sense, it may be correct as it might be our best understanding at a particular time in history (Nordstrom, 2012).

The following sub-sections briefly highlight the uncertainty inherent in geochemical modelling and briefly review The Geochemist's Workbench software as modelling code. Since a full evaluation of several commonly used modelling codes is available (Crawford, 1999; Zhao *et al*., 2010) and guidance in terms of the advantages, uncertainties, requirements and output from geochemical models have been presented by several authors (Crawford, 1999; Usher, 2003; Zhao *et al*., 2010), it was felt that the repeating of this exercise would be redundant.

2.3.1 Uncertainty in geochemical modelling

Younger and Robins (2002) recognises the difficulty in applying standard geochemical modelling packages to real mine water cases and that significant areas of uncertainty remain with regard to

hydrogeological and geochemical processes in and around mining environments. The uncertainties must be addressed if challenges in developing robust mine water management strategies are to be realised. Also, a thorough understanding of the strengths and limitations often encountered during modelling exercises will place the results and answers obtained from such models in context (Usher, 2003).

Usher (2003) describes a model as a simplified version of reality which is constructed built on various assumption manifested during the development of the conceptual model. As most models are built on several assumptions it involuntary provides uncertainty regarding the accuracy of the results. Bethke (1996) considers uncertainty as an integral part of modelling and therefore it requires much attention. Usher (2003) explained that the degree of confidence of modelling results is very important to all the affected and interested parties in mine drainage prediction, since these results inform long-term water management strategies.

Numerous uncertainties dealt with during geochemical modelling have been addressed by Scharer *et al*. (1993) and Usher (2003). Maest *et al.* (2005) described certain small to large scale factors that yield uncertainty in drainage quality predictions. Firstly, dissolution of minerals present in the mine waste as well as secondary reactions among solutes, gas phases and solid surfaces influences the quality of drainage emerging from mine wastes. Mineral surface areas available for reaction can be very difficult to quantify and the reaction rates of minerals and other contributing processes in a complex system are not well known (Younger & Robins, 2002; Bowell, 2002). Furthermore, geology, climate, mining methods and mineral processing, and mine waste management approaches may vary among and within mine sites. This variability implies that characterisation and results are unique to an operation or operational component. This inevitably limits the degree to which information from one site can be applied to another. Moreover, when laboratory results are extrapolated to operational scale certain factors needs to be addressed like differences in particle size, environmental conditions, water and gas transport, and how these variables affect drainage quality over extended periods of time. The general lack of these field information provides for uncertainty in predictions (Maest *et al*., 2005).

Li (2000) and Usher (2003) highlight several input parameters typically required in geochemical models, all of which may be a source of uncertainty. Input values to geochemical models probably provide for most of the uncertainty associated with modelling. A model used to predict water drainage quality should be representative of the site (stresses the importance of an adequate conceptual model) and should accordingly be applied at a level of complexity that considers the available data and regulatory decisions that must follow. Maest *et al.* (2005) emphasises that site specific values used as inputs to geochemical models should reflect an accurate range of conditions at the mine site and should account for seasonal and temporal variability.

Several methods have been developed and successfully applied to account to some extent for the uncertainties inherent in modelling. Some of these methods include Monte Carlo analysis, other stochastic methods and evaluating a range of model input values to deliver a range of outcomes. A range

of water quality outcomes can therefore be generated for a given receptor. These methods support parameters being better described with a probability distribution, rather than being well described by a single value. Therefore, potential contaminant concentrations at receptors are better presented in ranges rather than absolute values to reflect the inherent uncertainty in predictive modelling. However, it should be noted that these methods do not address inaccurate conceptual models, which highlights once again the importance of adequate and representative conceptual models.

The predictions should always be evaluated and compared to site-specific water quality information (Maest *et al*., 2005). However, Oreskes *et al*. (1994) stated that because natural systems are most often open systems, and because hydrologic and geochemical model inputs are typically incomplete and uncertain, and because of scaling problems in natural systems, models used to simulate natural processes cannot be verified.

2.3.2 Hydrogeochemical modelling considerations and software

According to Maest *et al.* (2005) hydrologic and geochemical codes today still solve the same basic equations and reactions that were identified and described decades ago. Improvements in operating systems and graphic interfaces that is more user friendly and provide better visual output of the modelling results are some of the more notable changes. Certain individual codes are associated with slight advantages and disadvantages which ultimately depends on its applications. However, Maest *et al.* (2005) explained that the experience of the modeller, the choice of input parameters and data, and the interpretation of the modelling results are more important than the choice of modelling code itself.

2.3.2.1 The Geochemist's Workbench and software motivation

The Geochemist's Workbench (Bethke, 1996) is a commercial software package that consists of various programme packages and are typically applied to model environmental geochemical reaction processes and thermodynamics. The Geochemist Workbench software is therefore commonly applied in the environmental, geological, biochemical, geohydrological and pollution management fields. This software package consists of numerous tools which can be used to manipulate chemical reactions, calculate stability diagrams and the equilibrium states of natural waters, tracing reaction processes, modelling reactive transport, plotting results from these calculations and storing related data (Van Coller, 2013; Bethke & Yeakel, 2016a).

The specific tools and capabilities of GWB have been described in depth by Bethke and Yeakel (2016b, 2016c). The modelling capabilities of GWB enables researchers to develop a system where the processes are built and specified from the beginning to the end with integrated thermodynamic and geochemical databases to complete reaction paths and yield results that reflect the processes involved in the simulated system (Van Coller, 2013). At the end of modelled simulations, the results can be represented on various diagrams and graphs directly from the simulated interface, which is lacking in other software packages.

Work performed by Pabalari and Sabido (2007) regarding model validation exercises of trends and results between GWB Version 6.0 database and the various calculational methods revealed good agreement. They further found that the code is correctly and consistently applying the underlying geochemical theorems and algorithms needed to evaluate the equilibrium and kinetic behaviour of geochemical systems (Van Coller, 2013).

2.4   MITIGATION IMPLICATIONS

As mentioned by Younger and Robins (2002) one of the most problematic aspects of effective mine site management is the mismatch between a 21st century environmental consciousness and the often-undocumented realities of site evolution over periods of decades to centuries. Even when a mineral deposit has only been mined within the last few decades, the legacy of mining decisions made by previous mine owners in the past can act as serious restrictions on post-closure management and re-use of a site. Problems like these are intensified where frequent changes in site management or mine ownership have resulted in the loss of all non-statutory records of mining and mine waste disposal practices.

According to Usher (2003) accurate water quality predictions inform cost-effective means of mitigating and minimising the impact of mine drainage on the environment and the associated costs by allowing advanced planning for prevention and control. A prediction programme should be aimed to reduce uncertainty to such a level where potential risks and liabilities can be identified. The latter should steer the selection of effective waste handling and mitigation and monitoring strategies.

In terms of water quality management, many strategies have been proposed and used to solve low pH and salinity related problems. Numerous authors have reviewed and proposed various water quality mitigation and management strategies and include reviews and studies done by INAP (2003), Gunther *et al*. (2006), DWAF (2007), Hobbs *et al*. (2008), and Mey and Van Niekerk (2009), to only name a few.

Grobbelaar *et al.* (2004) refers to management strategies that falls in one of three groups, namely: 1) "on the spur of the moment solution" in which a systems-thinking approach and the wider picture is not considered; 2) solutions that are acceptable to regulatory institutions; and 3) future technology solutions. According to Grobbelaar *et al.* (2004) strategies that make provision for 50-year in advance solutions have rarely been investigated or applied in the mining industry. Secunda Mines and New Denmark Colliery are probably furthest along the line of finding and applying strategies directed towards the future.

According to Younger and Robins (2002) it is often found that the cost associated with preventative strategies in relation to post-closure water pollution from mines is small compared with that of the potential damage and cost of amelioration (Younger & Harbourne, 1995). Most often long-term and lasting solutions are not considered or applied due to resistance from both the government and mining

company sectors. The governing bodies (including the Department of Water Affairs (DWA)) are cautious, and the mining companies would like to minimise current expenditure. However, the government and mining companies should constructively work towards a common goal in finding and applying long-term management strategies and solutions (Grobbelaar *et al*., 2004). Plentiful information to plan management strategies to minimise mine waste drainage outflows and to provide for future systems through which impacts can be minimised exists. Some of the options available, specifically in light of the Union Colliery situation, will be detailed in Chapter 9 of this dissertation.

2.5 CONCLUDING SUMMARY

This chapter reviewed and compiled a wide range of various data and literature sources with relevant national and international references. Chapter 2 served as a literature study to gain understanding of various processes and factors to consider in the research project and hydro -and geochemical assessments as well as geochemical models. The following main conclusions can be drawn from discussions in preceding sections:

- Underground mining activities invariably disturbs the hydrogeological environment since the groundwater level has to be lowered, hence, to dewater the mine. Then, once mining activities have ceased, subsequent flooding contributes to recovery of the water level from the previously developed cone of depression and may lead to significant contamination of the surrounding environment.

- The oxidation of sulphide minerals, such as pyrite, during the dewatering phase will give rise to acid or neutral waters, depending on neutralisation reactions, that pose potential risks to the environment in that it is commonly associated with elevated metal(loid) concentrations. The leached metal(loid)s may however also be sorbed on or co-precipitated with solid phases.

- The main risks as a result of mining is associated with the uncontrolled discharge of often acidic and highly contaminated water which may impact on sensitive receptors. Mining-influenced water (MIW) discharged from mine sites create high level risk environmental impacts due to its low pH and high dissolved metal(loid) content, especially if not managed or mitigated appropriately.

- From various studies on AMD and neutral coal mine drainage and factors influencing aqueous geochemistry, the following processes were focussed on:

  o Acid generation

  o Neutralisation reactions

  o Selected metal(loid)s' speciation and mobilisation

- The ability to predict pH and dissolved metal(loid) concentrations and speciation following discharge of mine waste drainage which may impact receiving water courses is useful to gain understanding of the controlling processes and to eventually manage the environmental impacts.

- Given the complexity of natural systems, multidisciplinary, integrated research approaches incorporating various water quality prediction methods have been described where geochemical modelling serves as an invaluable tool for the interpretation of complex systems as well as prediction and anticipation of how geochemical systems evolve over time.

CHAPTER 3:
PROJECT SITE DESCRIPTION

Because prediction of drainage chemistry requires a great deal of site-specific information, this chapter lists and discusses many important aspects of the project site conditions to pave the way to address the study key objectives. The main objective of this chapter is to provide relevant information regarding the mining history and current infrastructure at the Union Colliery and to describe the location, topography and drainage, and geological and geohydrological setting of the area under investigation. Numerous specialist geohydrological studies have been performed at the Union Colliery and only information augmenting the conceptual understanding of the system components will briefly be discussed. The information presented in this chapter was sourced mainly from aforementioned studies and literature survey.

3.1   SITE HISTORY

The Union Colliery started as a Trans Natal Coal Mine in the early 1900's and continued until the late 1970's, early 1980's (IGS, 2017). The Union colliery has changed hands between owning companies many times and is currently the responsibility of South 32 CSA. It can be assumed that during changes in ownership, mine related information was lost in the process. This resulted in very sparse information regarding the mining history and mining plans as well as the different phases of the site. Underground coal mining activities started in the year 1900 as known today as the eastern operations, where after mining was directed west of these operations from 1945 to 1970. The eastern and western operations were simultaneously mined from 1945 to 1970. An isolated, smaller area was mined further south-east of the eastern operations from 1980 to 1985 (Hodgson & Vermeulen, 2008).

3.2   PREVIOUS STUDIES

Numerous geohydrological and specialist studies have been conducted at the Union Colliery mostly by personnel of the Institute for Groundwater Studies (IGS) as well as Golder Associates. Hodgson and Vermeulen (2002a, 2008) investigated the geohydrology, water holding capacity and water chemistry of the Union Colliery as well as the groundwater pollution potential from the coal discard dumps (Hodgson & Vermeulen, 2002b). Golder Associates (2016a) reported on the geochemistry aspects of related mine closure planning of the Union and related collieries as well as surface water impacts and related closure planning by means of a catchment water quality model (Golder Associates, 2016b). Allwright (2018) investigated and verified the sources, pathways and volumes of water ingress into the mine workings. A numerical groundwater flow and transport model as well as a water balance for the

mine compartments were focused on during the study. IGS (2017) estimated volumetric calculations for the Union Colliery underground operations.

3.3   STUDY AREA LOCATION

The Union Colliery underground workings is situated approximately 7 km north of Breyten in the Mpumalanga Province, South Africa (Figure 1-1). Figure 3-1 shows the mining layout with the many distinct and separately mined compartments indicated.
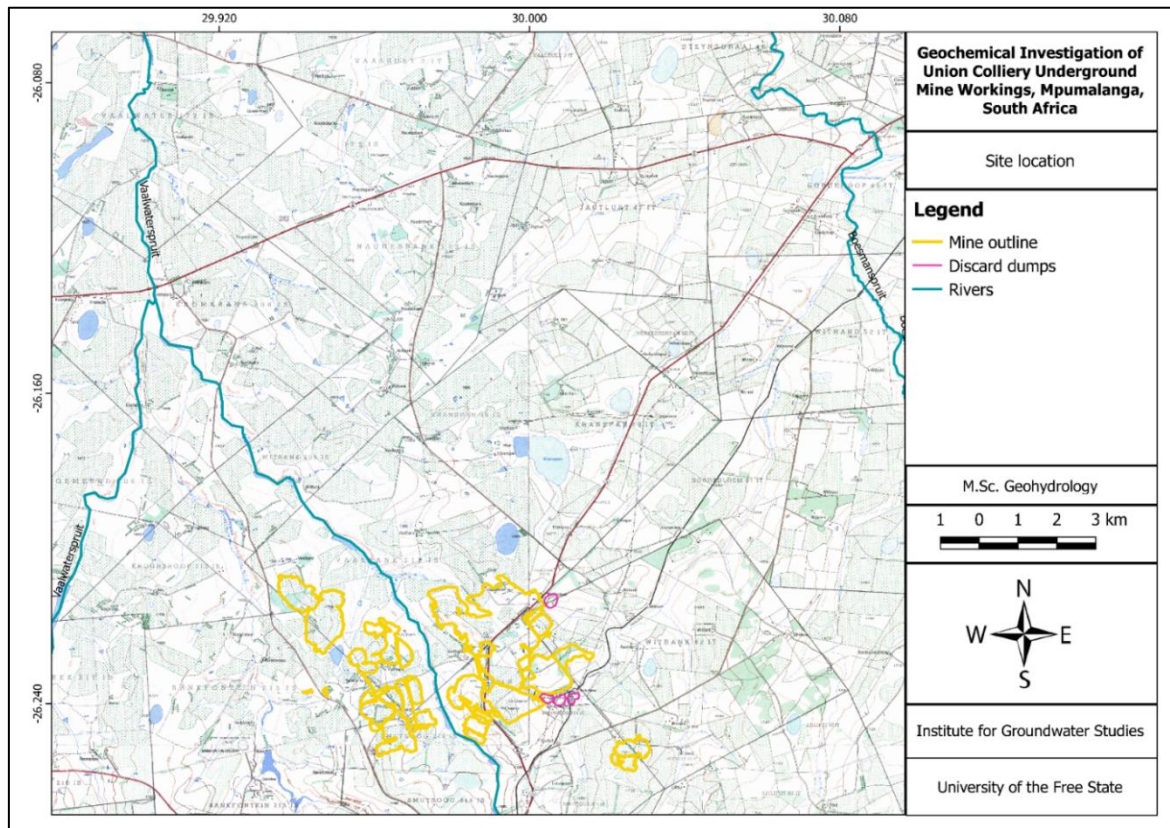
Figure 3-1: Project area location displayed on a topographic map showing the main surface water features.

3.4   GENERAL MINE INFORMATION

The Union Colliery consists of many decommissioned underground coal mine workings and coal extractions started in the early 1900's to the 1980's. Many mining areas are present within and around the Union Area (refer to Figure 3-6), of which South 32 has environmental responsibility for western operation blocks, W1–W4, and eastern operation blocks, E1–E4, and the Susanna Area (Figure 3-2). The Union Colliery consists of a total mined area of 1 370 ha and the surface areas of the underground compartment/s are presented in Table 3-1.

Table 3-1: Name and area of the Union underground workings.

Underground operations	Surface area (ha)
W1	194
W2	28
W3	75
W4	220
E1, E2, E3, and E4	795
Susanna	58

(Hodgson & Vermeulen, 2002a, 2008)

Four coal discard dumps, all of which have been rehabilitated, exist in two areas at the Union Colliery and their positions relative to the underground workings are shown in Figure 3-2. These are the so-called Union (more south) and Black Diamond (located north) dumps. Rehabilitation processes commenced in 2007 and included the use of topsoil for the establishment of vegetation cover (South 32, 2017).

Mining dates provided by South 32 for the various compartments are displayed in Figure 3-3. As mentioned, active mining activities started as early as the year 1900 in the Eastern blocks and ceased in 1985 in the Susanna compartment.
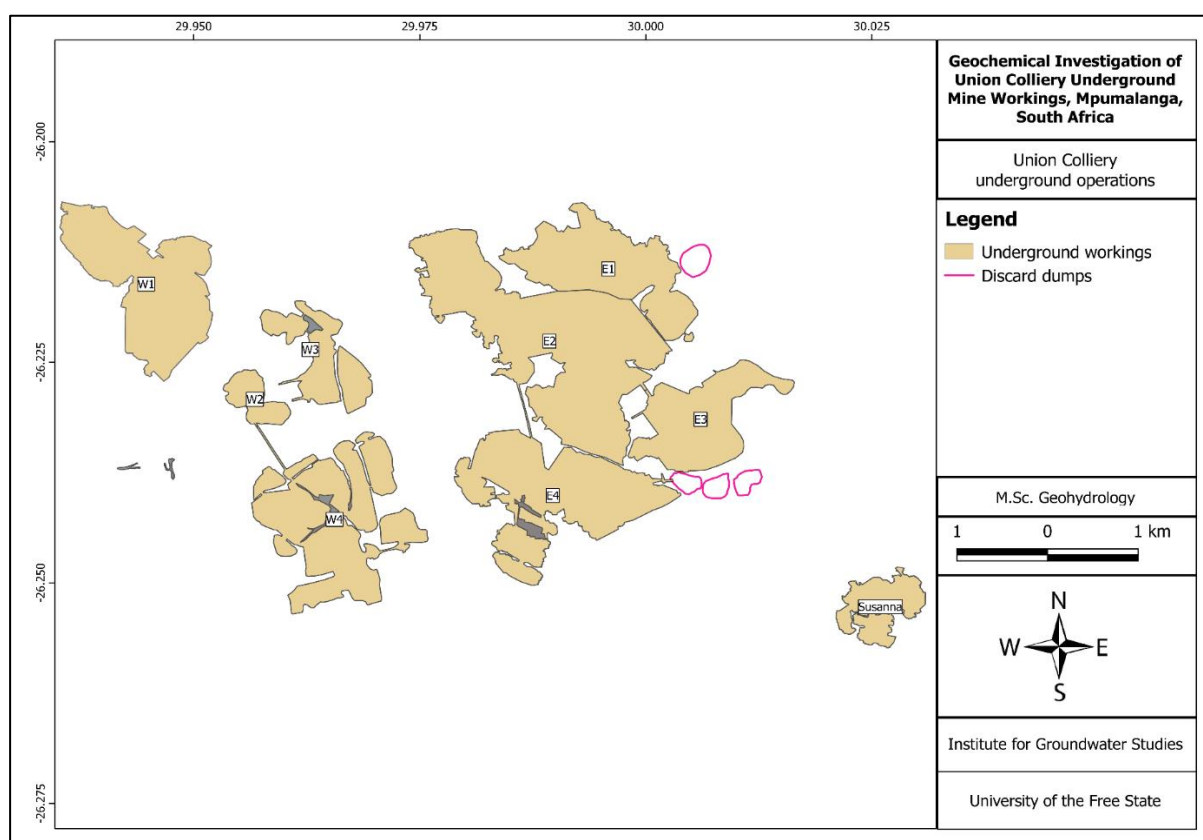
Figure 3-2: The Union Colliery underground operations for which South 32 are responsible.
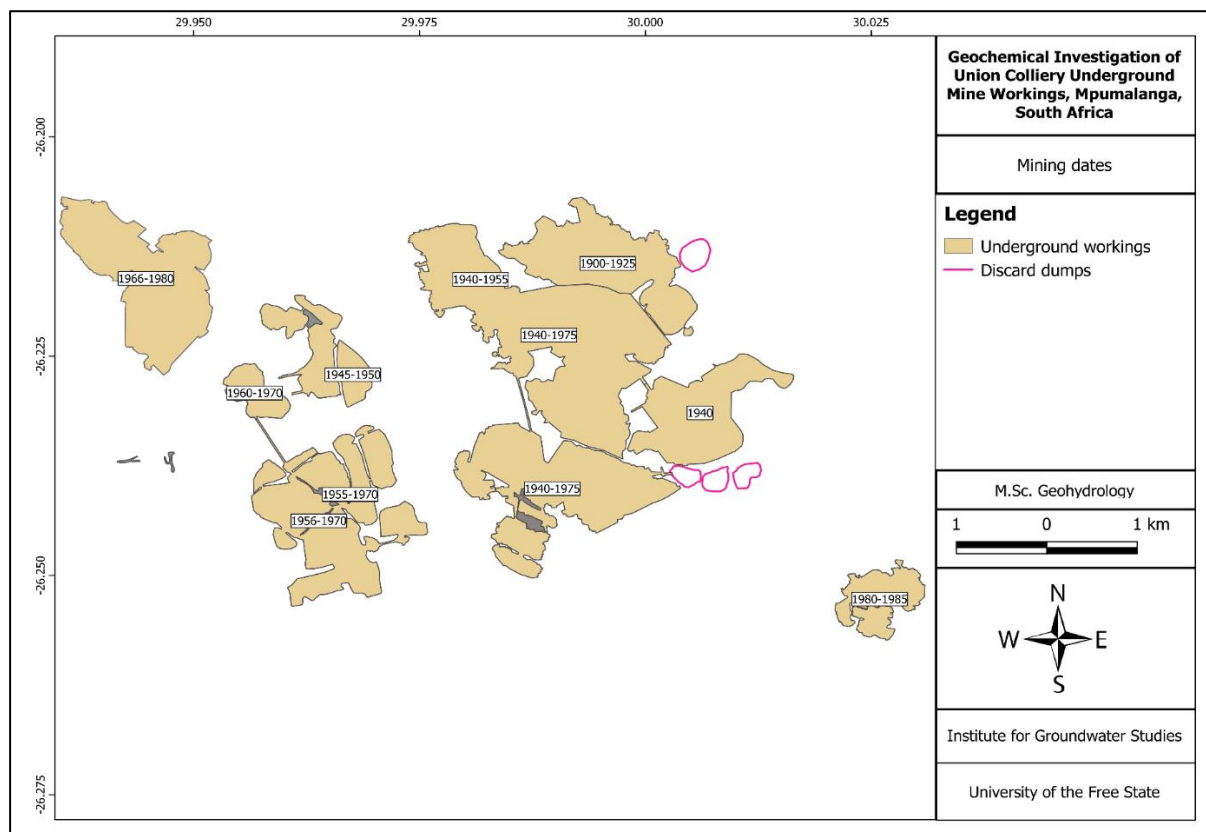
Figure 3-3: Mining dates for the different underground operations which consists the Union Colliery.

The main mining method employed was bord-and-pillar mining methods with pillar robbing in a few areas, such as in the E4 block. Mining was often very shallow, especially along the perimeter of the mines. Although mining depths range between 10 and 75 m, most of the mining was less than 30 m below surface and occurs in the zone where active groundwater circulation is common (Hodgson & Vermeulen, 2008). Mining depths as shallow as 10 m are not uncommon, and an average mining height of 2 m was maintained throughout the workings (Hodgson & Vermeulen, 2002a; 2008).

The surface topography cuts into the central portion of the area with the result that coal is only present in the hills (Hodgson & Vermeulen, 2008). A three-dimensional view of the surface with the mine layout super imposed can be seen in Figure 3-4. Therefore, water that accumulates in the mine workings has ample opportunity to discharge from the mine workings towards the local streams.
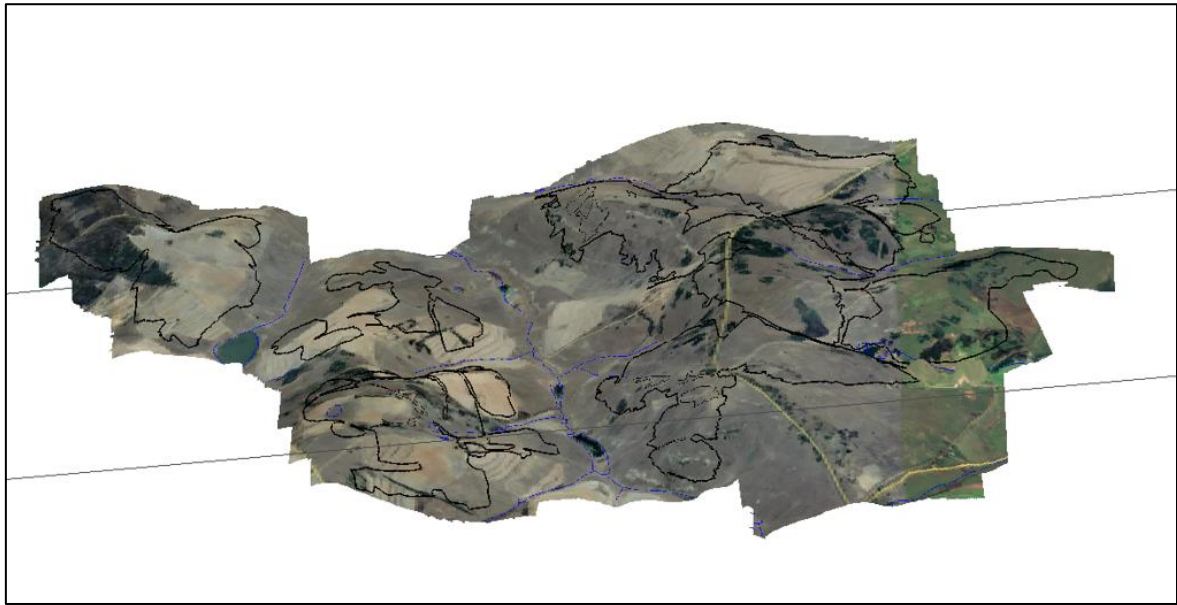
Figure 3-4: Three-dimensional view of the Union Colliery with the outline of the compartments super imposed.

In the past, entrance to the underground workings were gained through horizontal or inclined shafts usually dug into the sides of the hills. The positions of known shafts in the area are displayed in Figure 3-5. Hodgson and Vermeulen (2008) verified that most of the adits have been sealed and fitted with drainage pipes to allow for controlled release of excess water that accumulates within the underground workings. Flooding of the underground mine workings, representing more than 80 years of mining, culminated in the decant of acidic mine drainage (AMD) from the western operations (Hodgson & Vermeulen, 2002a, 2008; Golder Associates, 2016a). Currently there are seven known decant positions at the Union Colliery (Figure 3-15).
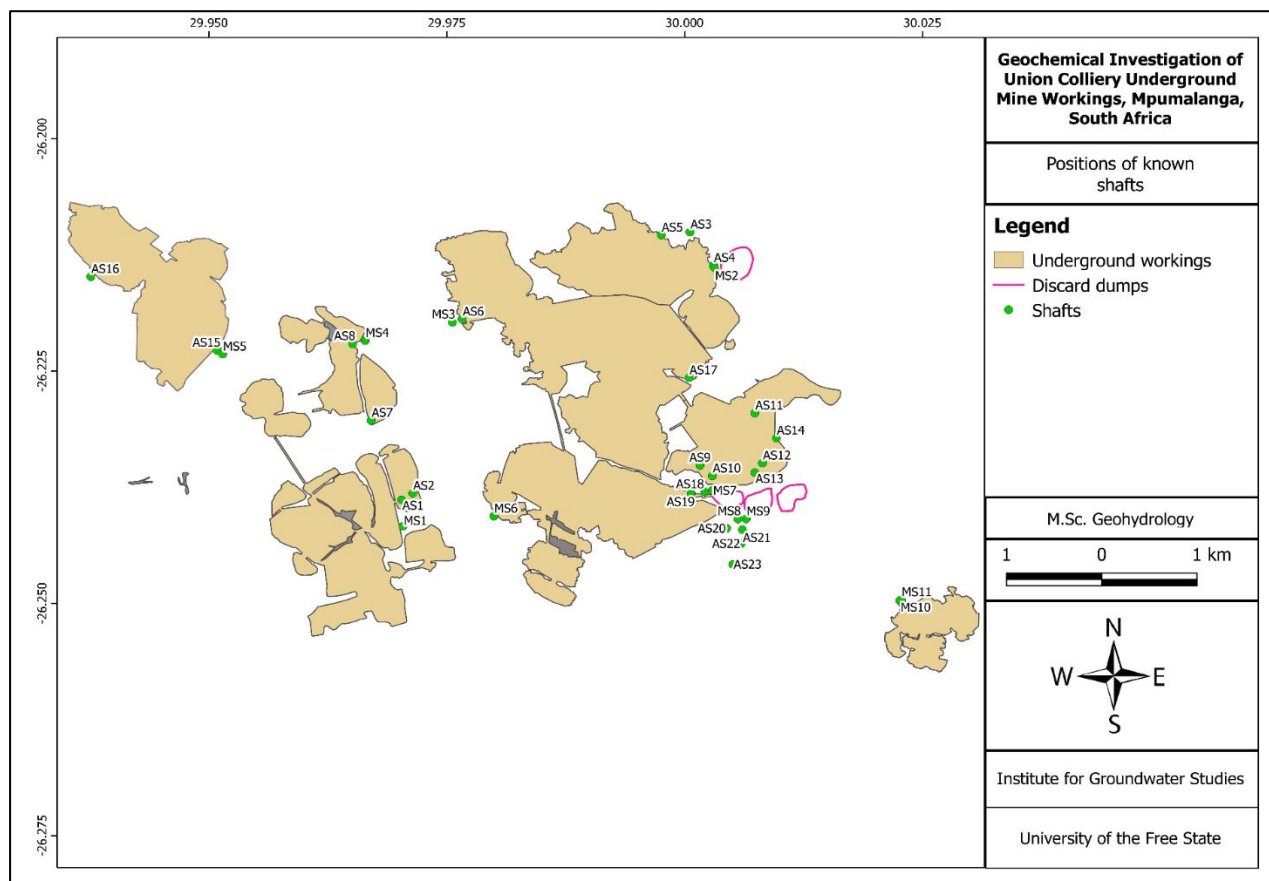
Figure 3-5: Positions of known shafts at the Union Colliery.

Seepages and mine decant in well-defined flow channels occur from adits, sinkholes, and geological structural weaknesses (Hodgson & Vermeulen, 2008; Allwright, 2018). Should the seals and drainage pipes be sealed off, water would emanate along other pathways such as geological structural weaknesses, within the weathered strata and sinkholes. Decant discharge volumes at the Arcadia Adits, Fourie Decant, Butter Adit Decant and Duck Pond Decant (measured at Union V-notch), are measured intermittently as a height in mm at a V-notch installation and converted to a discharge in m^3/d (Allwright, 2018). The average daily calculated discharge flows from the decant points fitted with a V-notch are presented in Table 3-2. Allwright (2018) investigated if relationships exist between the discharge measured from November 2012 to August 2017 and the monthly rainfall to infer if decant is recharge driven. Overall there seemed to be no distinct correlation between measured decant volumes and the amount of rainfall, however some decant points showed small relationships with rainfall.

Table 3-2: Average calculated discharge flows from decant points fitted with a V-notch.

Decant point	Average calculated outflow per day (m^3/d)
Butter Adit Decant	130
Arcadia Adit No.1	275
Arcadia Adit No.2	<50
Fourie Decant	260
Duck Pond Decant	40-200

(Hodgson & Vermeulen, 2008)

According to Hodgson and Vermeulen (2002a) numerous sinkholes, most of which have been rehabilitated, occur mainly along the perimeter of the mined areas where the coal seam is at its shallowest due to topographic differences and in stooped areas. However, not all sinkholes are associated with shallow mining conditions as sinkholes are also found in areas where mining exceeds 60 m in depth. Substantial stooping has been performed in the Arcadia area which may also account for sinkholes in the area.

A monitoring programme was established at the Union Colliery in the year 2000. Sixteen boreholes were drilled to intersect the mine voids for water level and water quality monitoring within the mine voids (Hodgson & Vermeulen, 2008). Furthermore, nine boreholes to detect and monitor pollution plumes caused by the surface coal discard dumps were installed in 2002 (Hodgson & Vermeulen, 2002b). The locations of these boreholes are presented in Figure 4-7. The current monitoring strategy includes monthly water level and decant V-notch measurements as well as monthly surface water (decant and stream water) sampling and quarterly groundwater sampling. The monitoring network and current protocol employed at the Union Colliery will further be discussed in Chapter 4 under section 4.3.1 of this dissertation.

3.5 ENVIRONMENTAL SETTING

3.5.1 Topography and drainage

The Union Colliery is located within the upper reaches of the Komati Drainage System (Figure 3-6), and forms part of the Inkomati-Usuthu Water Management Area (WMA). The Union Colliery operations are located between two quaternary catchments, namely X11A and X11B. Compartments, E1, E3 and Susanna, fall within quaternary catchment X11B, while the W1-W4, E2 and E4 compartments are located within the X11A catchment (Figure 3-8).

(IGS, 2017)
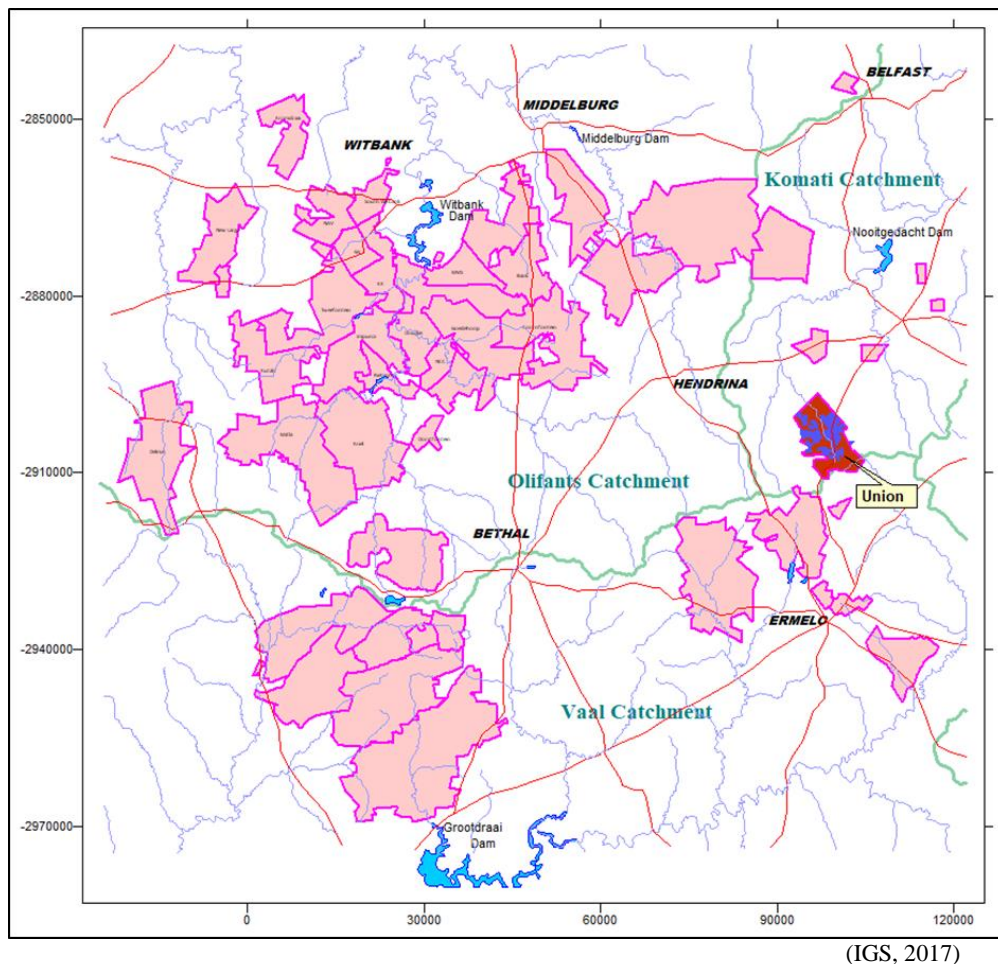
Figure 3-6: Mine lease area for the Union Colliery with respect to other mining areas and catchments in the Mpumalanga Province.

Elevations over the quaternary catchment (extracted from SRTM 30 m digital elevation data) display that the topography generally decreases towards the north (Allwright, 2018). It further indicates the local topographical trends within each quaternary catchment (Figure 3-7). As stated before, the Union Colliery is located on a topographical high where surface water drains to three neighbouring streams (Allwright, 2018). The landscape is very undulating with an average height of 1 600 mamsl and occasional peaks with elevations of up to 1 793 mamsl.

The surface water drainage of the area is controlled by two main non-perennial streams, namely the Vaalwaterspruit and the Boesmanspruit. Both of these streams drain towards the Nooitgedacht Dam (Figure 3-8). The Boesmanspruit and Vaalwaterspruit streams are significant due to their location within the Komati River catchment. The Boesmanspruit discharge into the Boesmanspruit Dam, which is a source of raw water supply for Carolina, and on to the Nooitgedacht Dam (Golder Associates, 2016a). The Vaalwaterspruit directly discharges into the Nooitgedacht Dam, which is of strategic importance as it supplies the Eskom Power Stations located in the Olifants Catchment. Deterioration of the water quality in this dam has significant financial implications for water users and the power stations (Golder Associates, 2016a).

The landscape and topography allow for regional dendritic drainage patterns. An upper tributary of the Boesmanspruit runs along the eastern side of the eastern mine compartments (E1–E4) and west of the Susanna compartment. Tributaries of the Vaalwaterspruit drain the central and the western mine areas (W1–W4) (Figure 3-8).

The Vaalwaterspruit and Boesmanspruit only flows during rain events in the summer months and demonstrate water quality dominated by sulphate, iron and manganese which may reflect the impact of further upstream mines and the seepages and surface decant from the Union Colliery mining wastes (Golder Associates, 2016a, 2016b). This results in increased dependence on groundwater resources due to the unavailability of sustainable surface water reservoirs in the immediate vicinity of Breyten.
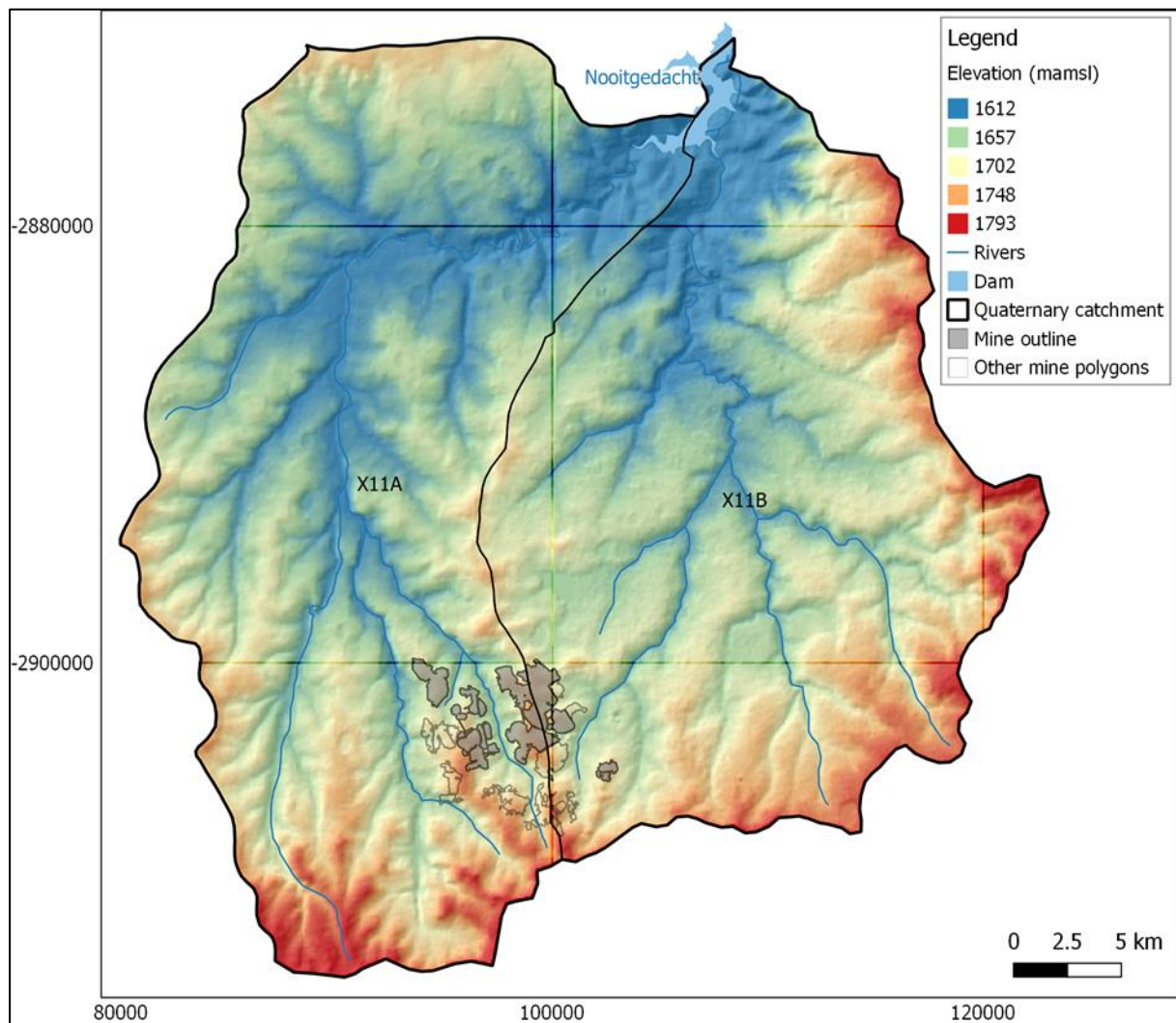
(Allwright, 2018)

Figure 3-7: Digital Elevation Model (DEM) of the study area, showing the quaternary catchments and surface water features.
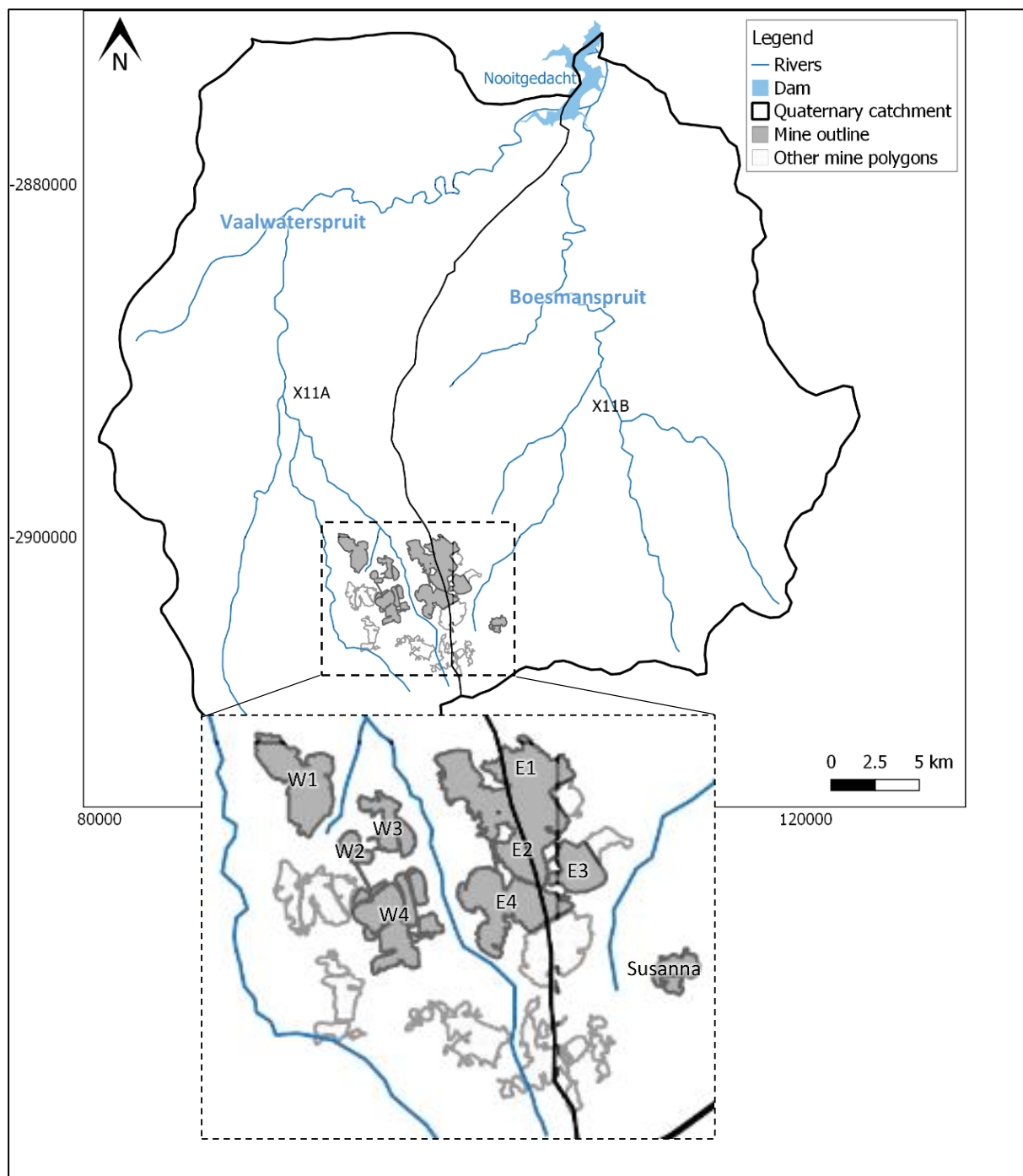
Figure 3-8: Surface water features and drainage within quaternary catchments X11A and X11B, showing the Union Colliery mine outline and the compartments for which South 32 are responsible.

3.5.2   Climate, rainfall and groundwater recharge

The climate of the area is typical of a mild, temperate climate with warm and dry winters and hot and wet summers. The average maximum temperature in summer is approximately 24°C and the average minimum temperature is 15.2°C. The average maximum temperature in winter is 15.2°C and the average minimum temperature is 4°C. Frost is a common occurrence during winter.

Monthly rainfall data collected from the DWS Nooitgedacht Dam station (X1E003), combined with rainfall data supplied by Golder Associates (2016b), is presented in Figure 3-9. The average rainfall is 740 mm/a, the 95th percentile is 940 mm/a and the 5th percentile is 530 mm/a. Daily rainfall collected from the DWS Nooitgedacht Dam station (X1E003) from January 2000 to July 2017 is presented in Figure 3-10.
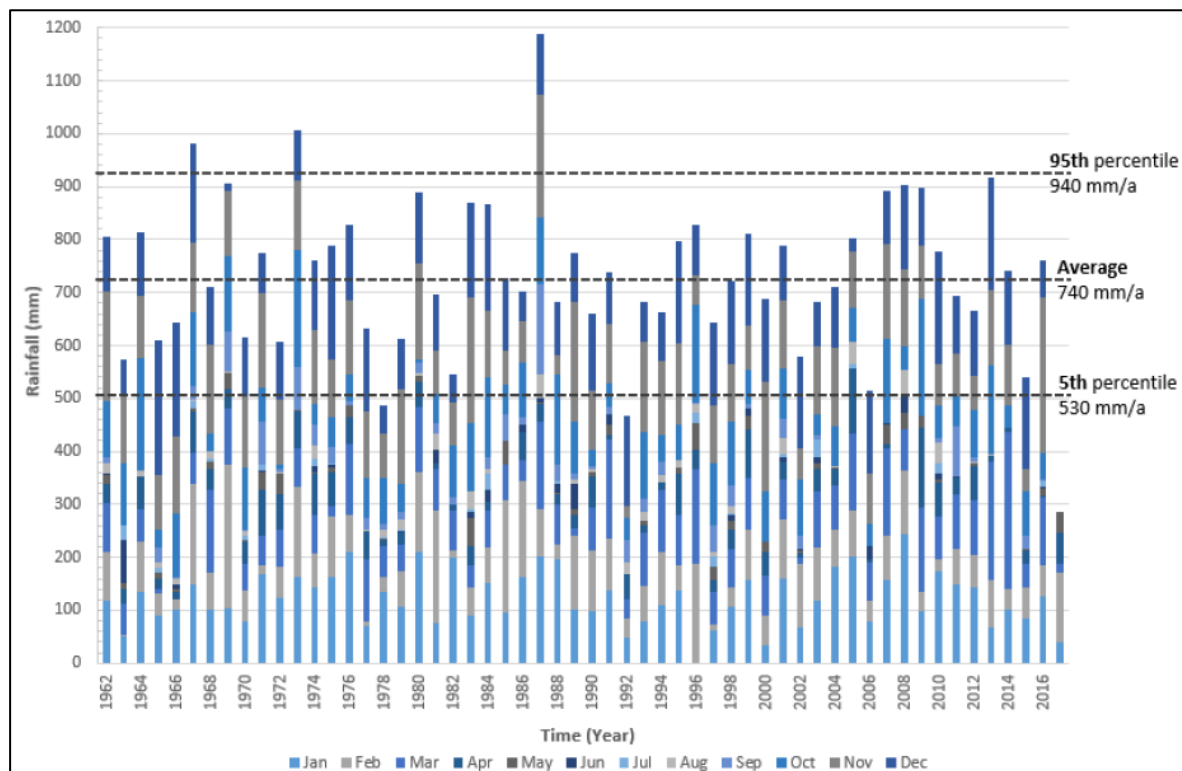
<div align="right">(Allwright, 2018)</div>

Figure 3-9: Monthly rainfall data from the DWS Nooitgedacht Dam station (X1E003), combined with the rainfall data given by Golder Associates (2016b), from January 1962 to April 2017.
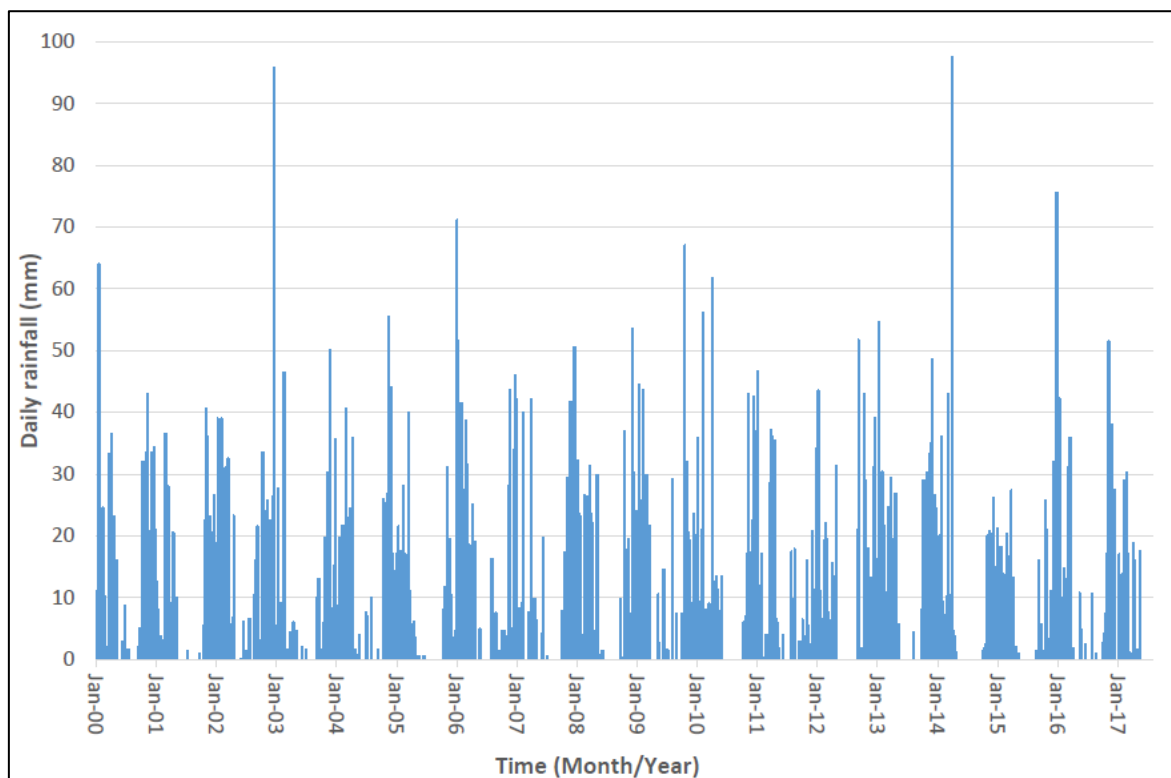
(Allwright, 2018)

Figure 3-10: Daily rainfall measured at the DWS Nooitgedacht Dam station (X1E003) from January 2000 to July 2017.

Over the past 40 years, an empirical relationship has been established in Mpumalanga between the depth of mining and influx of water into underground bord-and-pillar mining where recharge into undisturbed Karoo sediments varies between 1–3%. It is known that the permeability of the Karoo sediments and dolerite dykes decrease with depth. This may be ascribed to the dissolution and leaching of calcium carbonate, which is the binding material between the grains of sand (sandstone) and mud (shale), by circulating groundwater from the top 40 m of sediments. All the compartments are very shallow with an average depth less than 60 m. Based on roof thickness and due to the presence of rehabilitated sinkholes the recharge is estimated at 9% (Hodgson & Vermeulen, 2008; IGS, 2017).

3.5.3   Geological setting

Broadly, the geology of the area is typical of Karoo sediments of the Dwyka and Ecca groups. The Union Colliery underground mine workings falls within the Ermelo Coalfield, which extends from Carolina in the north to Dirkiesdorp in the south covering a surface area of approximately 11 250 km^2 (Hancox & Gotz, 2014). Five coal seams occur within this coal field and are alphabetically numbered from A (top) to E (bottom) and the distribution of these coal seams are mainly affected by the topography of the pre-Karoo basement and the present-day erosional surface.

The area is characterised by consolidated sedimentary layers which consists mainly of sandstone, shale, siltstone and coal beds of the Vryheid Formation of the Ecca Group and is underlain by the Dwyka

Group of the larger Karoo Supergroup (Figure 3-11). The Ecca Group comprises of sediments deposited in shallow marine and fluvio-deltaic environments where coal accumulated as peat in swamps and marshes that was often associated with these environments. The generally horizontally disposed sediments of the Karoo Supergroup are generally undulating with a gentle regional dip to the south.

Jurassic dolerite intrusions occur throughout the area in the form of dykes, and a continuous sill. Outcrops are found throughout the whole study area. The dolerite sill is typically encountered at depths between 15–30 mbgl. Displacements as a result of dolerite sill intrusions are common. Dolerite intrusions within the Ecca sediments are abundant which comprise off sills that vary from being concordant to transgressive in structure. Although these structures serve as aquitards and tend to compartmentalise the groundwater regime, the contact zones with the host geological formations also serve as groundwater conduits. There are common occurrences of minor slips or faults, particularly in close proximity to the dolerite intrusives.

(Allwright, 2018)
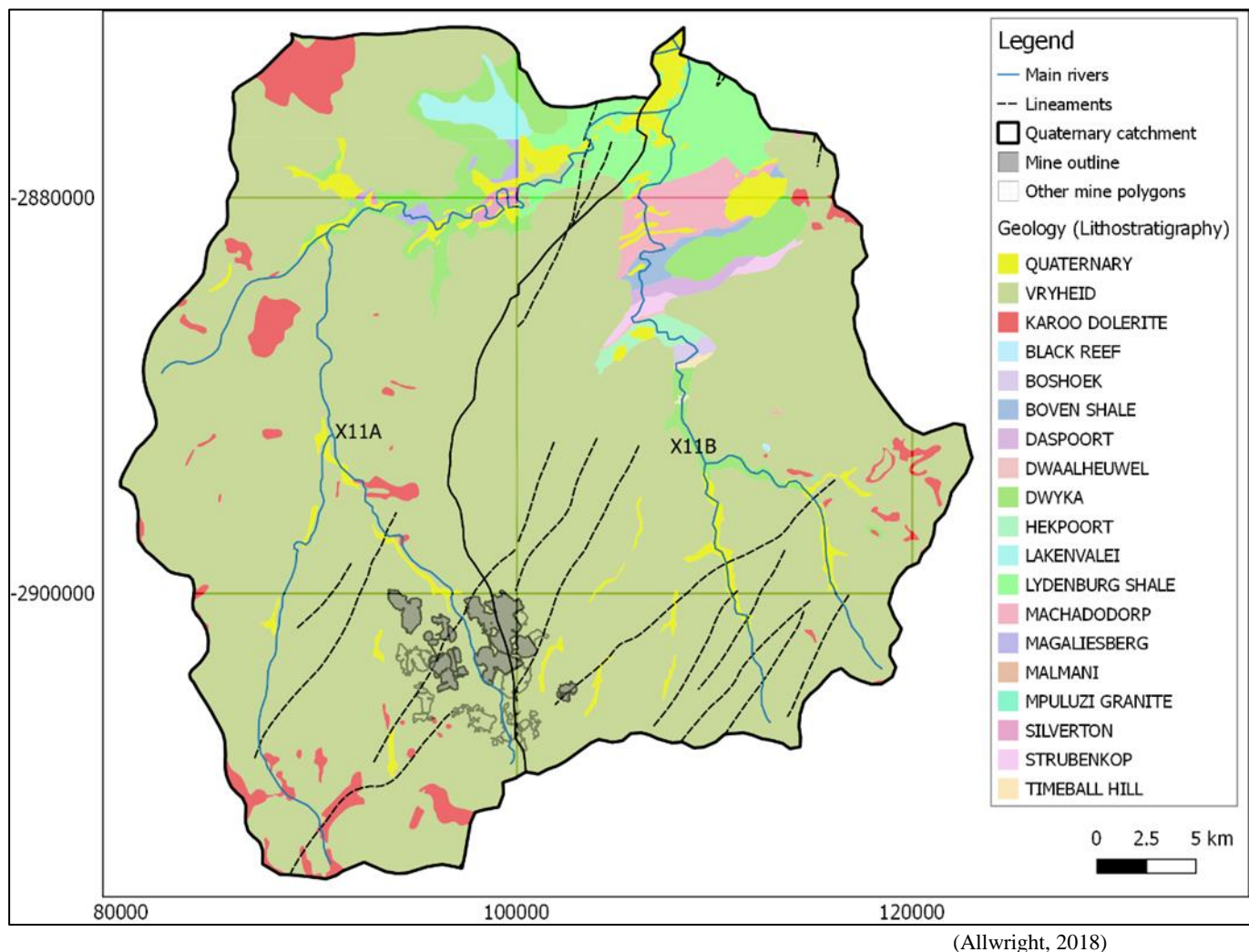
Figure 3-11: Geology outcrops on the surface within the X11A and X11B quaternary catchment area.

3.5.4   Geohydrological setting

Three superimposed aquifers typically occur within this region under natural conditions, namely the upper weathered aquifer (5-12 mbgl), fractured Ecca aquifer (15-30 mbgl), and the fractured basement aquifer, also referred to as the pre-Karoo aquifer (Grobbelaar *et al.*, 2004).

The area is characterised by inter-granular weathered and fractured aquifers (Figure 3-12). The inter-granular weathered aquifer is characterised by loose unconsolidated material whereas the fractured aquifer is characterised by hard compact rock formations in which fractures, fissures and joints are capable of storing and transmitting water (Grobbelaar *et al.*, 2004). Water is stored in the inter-granular part and transmitted mainly through the fractured part of the aquifer systems. Both lithology and the geological structures like faults and dykes define the occurrence and flow paths of groundwater. The sandstone and coal layers are typically reasonable aquifer systems, whereas the shale layers can be considered as aquitards. Perched aquifer systems on the relative impermeable shale is not uncommon in such sequences (Allwright, 2018).

According to the South African aquifer system management classification the aquifers found in this area are classified as minor aquifer systems and the borehole yields in the area typically range from 0.1 to 2 L/s (Hydrogeological Map Series of the Republic of South Africa, 2003). The groundwater resources in the vicinity are mainly used for domestic purposes and stock watering.
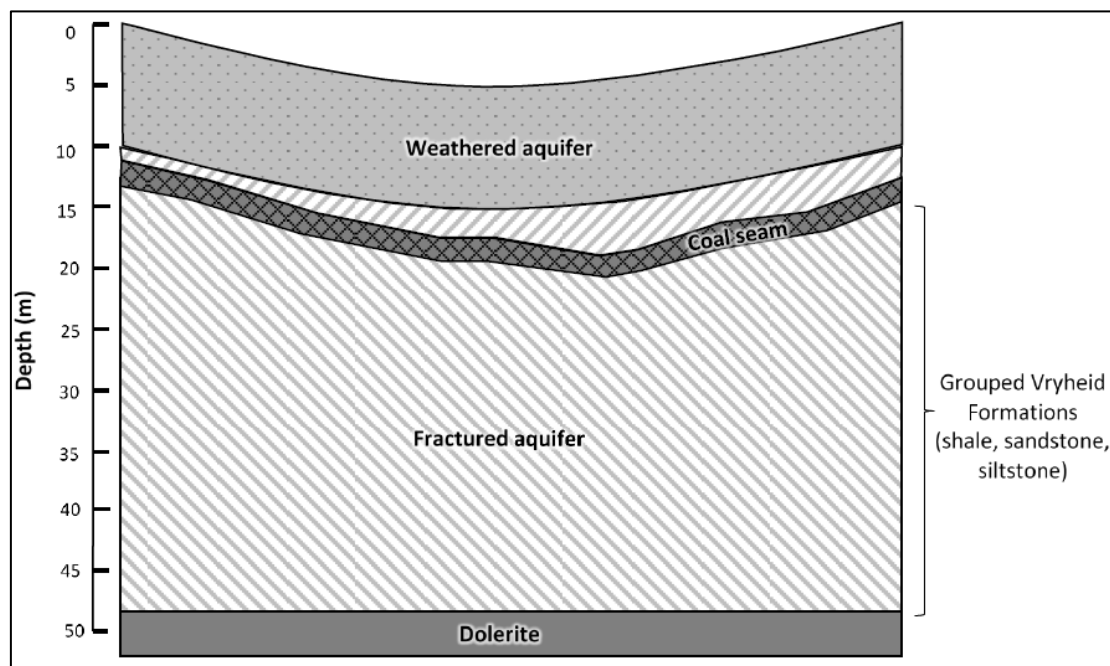
(Allwright, 2018)

Figure 3-12: Hydrostratigraphic units, where an upper weathered aquifer is defined, underlain by a fractured aquifer. The coal seam is found within the fractured aquifer and the dolerite sill below.

3.6 WATER HOLDING CAPACITY OF MINE VOIDS

The coal floor is undulating with distinct gradients present. Recharged water therefore accumulates in lower areas (IGS, 2017). The capacity of the mine workings to hold water is however limited by the shallow mining conditions and the undulating nature of the surface and coal floors (Hodgson & Vermeulen, 2002a). Water levels within the mine voids will thus rise until decant elevations are reached or until seepage through the weathered strata balances the rate of recharge (Hodgson & Vermeulen, 2008).

As mentioned before, a monitoring network consisting of 16 boreholes intersecting the mine voids were initiated in the year 2000 and water levels have been recorded since (Hodgson & Vermeulen, 2008). The localities of these boreholes are shown in Figure 3-13. The mine boreholes giving an indication of the mine water levels within the underground mine voids include boreholes BH2, BH3, BH5, BH7, BH8, BH9, BH10, BH11, BH13, and BH15. The measured mine water levels in these boreholes from July 2009 to July 2017, indicate that an equilibrium has been reached within the mine water levels. Boreholes BH5, BH9, BH11 and BH15 all have stable mine water levels, and are located in mine compartments that are currently decanting. However, the mine water levels within boreholes BH3, BH8 and BH13 have not been stable, where BH8 and BH13 are currently rising (Allwright, 2018). Borehole BH3 located within the W2 compartment had a stable water level from July 2009 to January 2011 and displayed a steady increase to a new equilibrium in February 2015. Borehole BH13, located within the Susanna compartment, indicates a slowly increasing mine water level. This could indicate that this underground working has not yet reached its new equilibrium. Rising water levels in boreholes BH8 and BH13 suggest that water levels in the W4 and Susanna compartments have not reached decant elevations yet. However, rising water levels could potentially reach decant elevations in the future. Borehole BH15 and BH5 have the same mine water level, while borehole BH3 is much higher, indicating that W2 and W3 compartments are not interconnected, while the W3 block forms a single reservoir. Borehole BH6 was drilled with the intention of intersecting the underground mine void of the W4 compartment, but it has since been deduced that this is not the case (Allwright, 2018). This is evident in the seasonal fluctuations in the measured groundwater levels (Figure 3-13).

According to a recent specialist study (IGS, 2017), the total amount of water within the underground voids is $8.78 \cdot 10^6$ m^3 (Figure 3-14), which is $3.98 \cdot 10^6$ m^3 more than the $4.80 \cdot 10^6$ m^3 reported by Hodgson and Vermeulen (2008). The entire water holding capacity of the underground voids are $26.88 \cdot 10^6$ m^3, therefore the mine is currently filled 32.66% of its total holding capacity. Complete flooding of the underground workings is improbable due to the shallow mining conditions and the undulating surface topography (IGS, 2017; Hodgson & Vermeulen, 2008). However, the question if the mine has reached its maximum water holding capacity remains as it is clear from the measured water levels that new equilibrium water levels can be reached within certain mine voids.
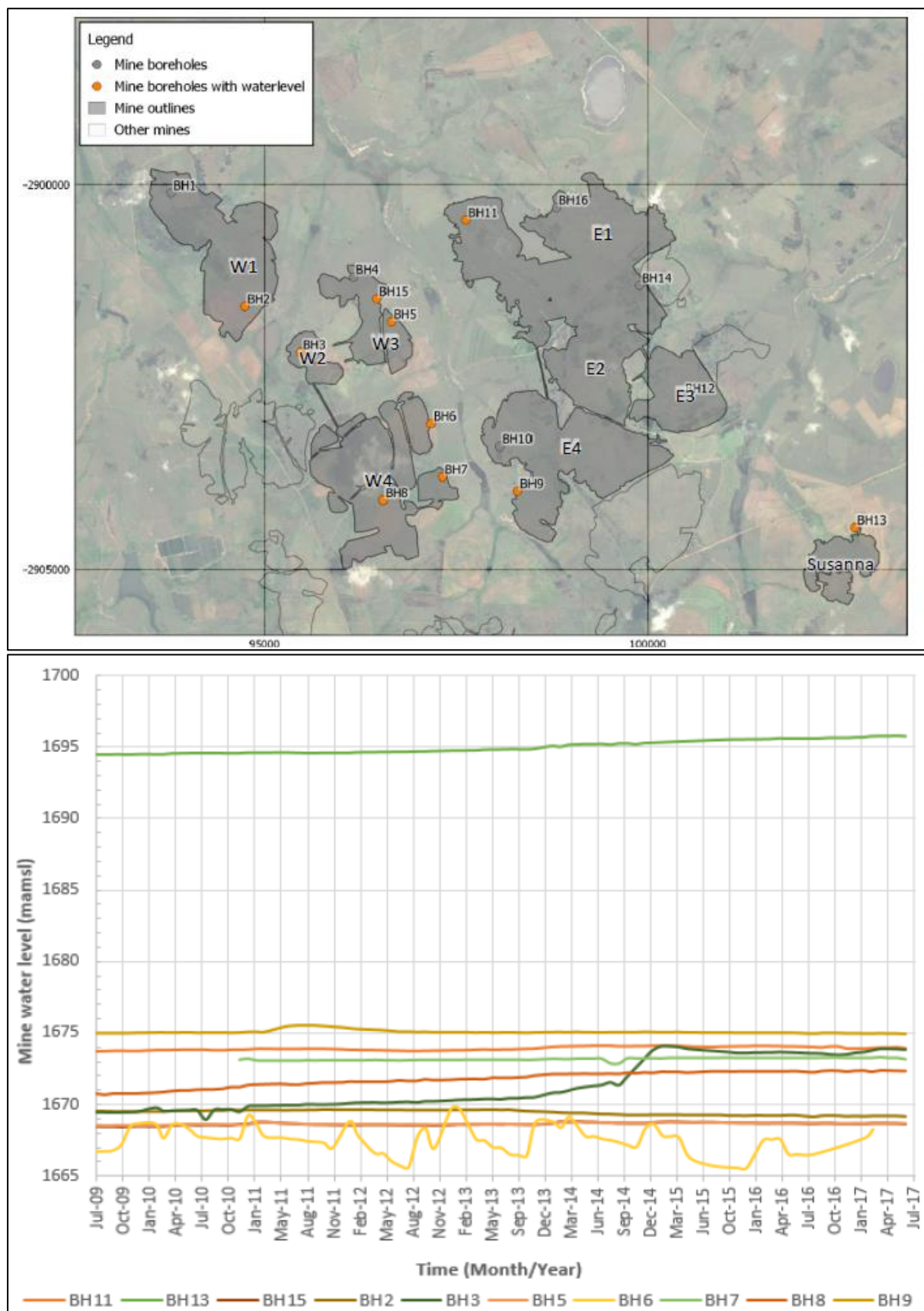
Figure 3-13: Location of mine boreholes with a plot of measured mine water levels over time from July 2009 to July 2017.
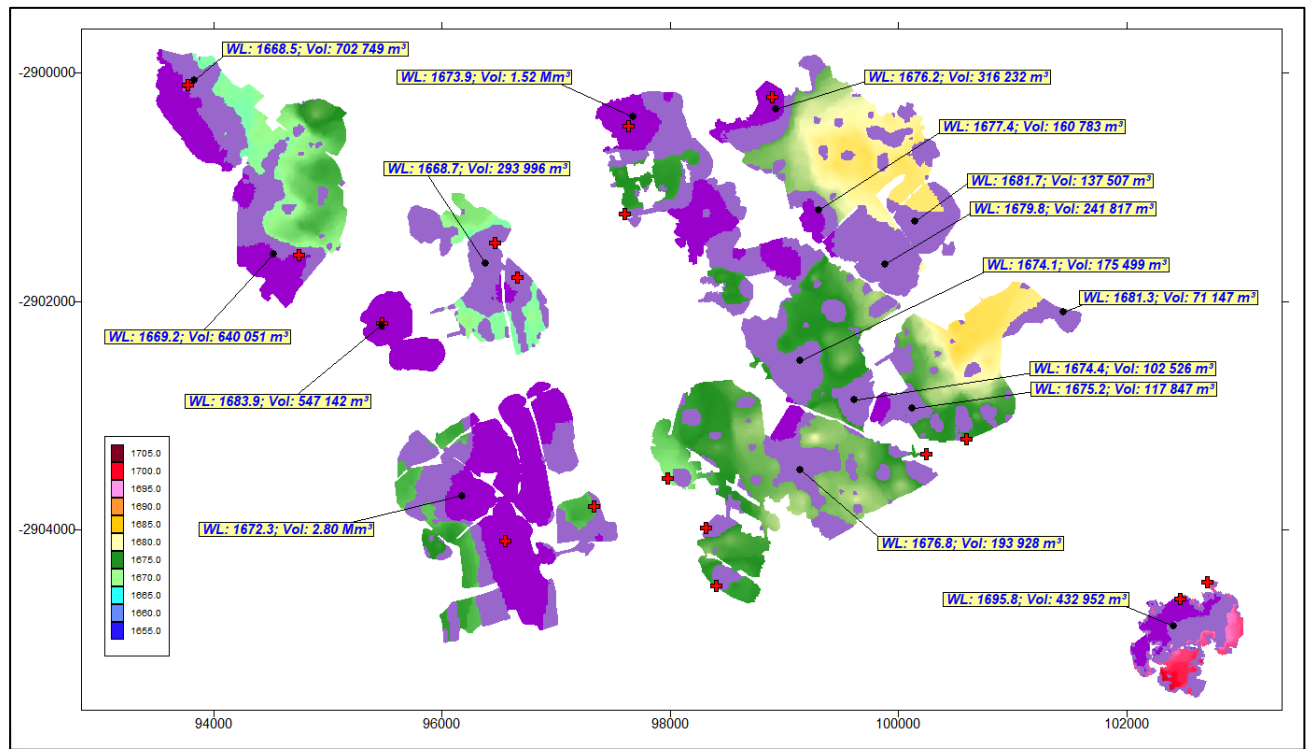
Figure 3-14: Partially flooded compartments with a total of 8 777 ML (8.78·10⁶ m³) water inside the workings.

As mentioned, mine water discharges at the surface at seven known positions. These include two decant positions in the western operations and five positions in the eastern operations (Figure 3-15). According to Hodgson and Vermeulen (2008) the Union Adit has been sealed and fitted with drainage pipes which feeds water to the Reyneke Dam, where it mixes with natural storm water runoff. Similarly, the Duck Pond Decant and the Arcadia Adit No.1 is closed to stop entry, however mine water seeps from the adits. The Susanna shaft has been closed and fitted with pipes to drain the water, should it eventually become necessary. According to Hodgson and Vermeulen (2008) sealing the current outflow paths is not an option due to the shallow mining conditions. Mine water will therefore emanate along other pathways including geological structural weaknesses and weathered strata. Although efforts have been directed to curtail the decant water to pollution control dams, especially at the Butter Adit Decant, contaminated water still makes its way into the streams.
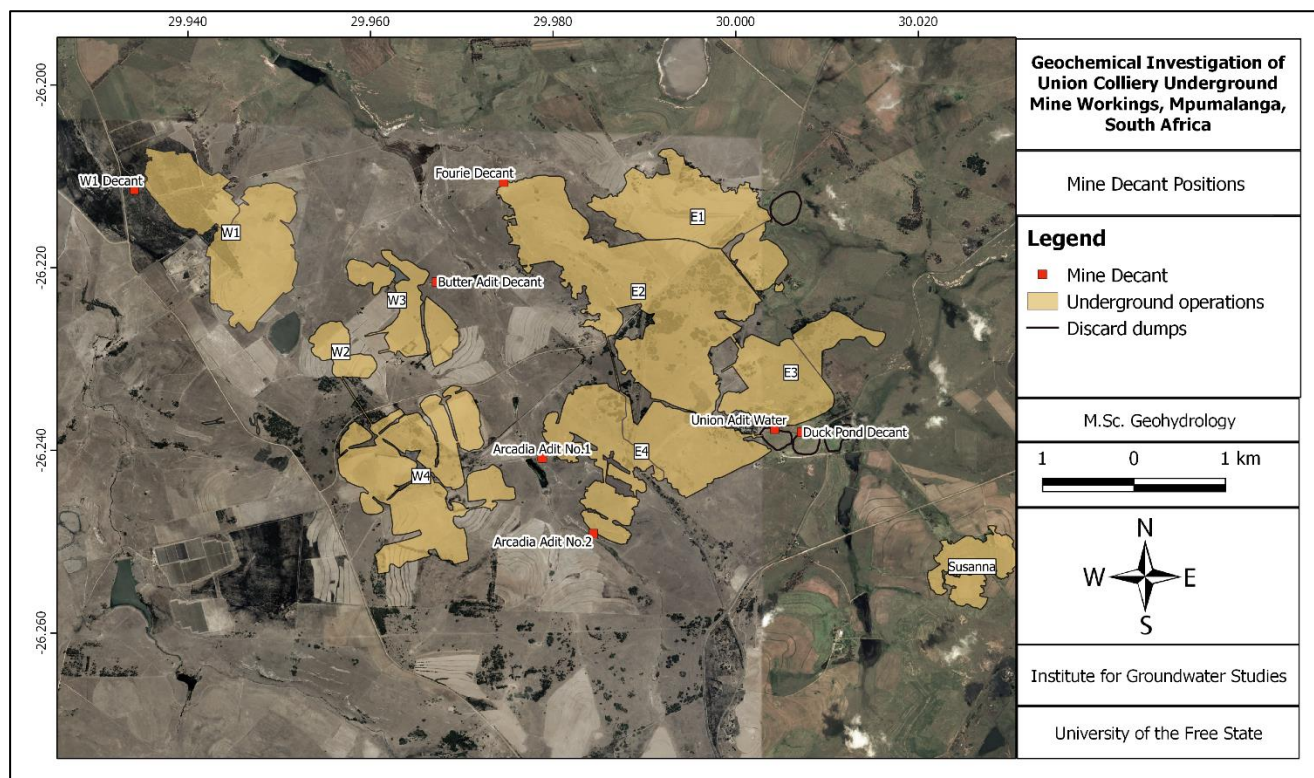
Figure 3-15: Location of current mine water decant positions within the Union Colliery operations.

3.7 NUMERICAL GROUNDWATER TRANSPORT MODEL

The aim of this section is to give a brief overview of the main findings of a recently performed specialist study (Allwright, 2018) which focused on contaminant transport from the underground extraction areas and surface coal discard dumps by groundwater flow. Note that only the information considered supplementing to this study will be mentioned in this section.

The developed flow model was applied to develop a non-reactive numerical groundwater transport model to simulate and evaluate the existing and potential extent of the mining impacts on the groundwater regime. The combined impacts of the underground extractions areas as well as the surface coal discard dumps were simulated. The assigned contaminant sources were considered continuous and constant over time, and any natural attenuation processes were neglected. The transport simulation is therefore considered conservative. However, the simulation is not conservative from a surface water perspective, because the model only considered movement within the groundwater system (only governing groundwater equations in the software). Thus, movement of contaminants once discharged from the groundwater system cannot be considered. The model does not reflect the impacts associated with the decant water that moves along the land surface at a faster rate to the river systems (Allwright, 2018).

In summary, the groundwater transport was simulated over a total period of 100 years. The scenario-based prediction of groundwater transport was limited by the assumption that limited data for the study

area can be extrapolated over time. The predictions are uncertain, especially considering the longer time-period considered. The simulation started from an assumption of recently re-established equilibrium conditions (correspond to roughly the 1980s). The 50-year simulation approximates the current (2017-2018) situation at the Union Colliery, while the 100-year simulation represents the transport to occur within the next 50 years (Figure 3-16).

The model results indicate that there are large areas of contaminant seepage along low-lying areas, instead of contaminants being limited to specific decant areas (Figure 3-16). The currently measured water quality within the Vaalwaterspruit and Boesmanspruit correspond to the 50-year simulation where contaminant plumes have already reached these rivers. The model highlights that contaminants will increase in both their area of influence and concentrations within the next 50 years. The model further indicates that subsurface seepage extends to such an extent that it influences both groundwater and stream water quality. It should therefore be controlled and monitored separately (Allwright, 2018).

The simulations of the mass concentration distribution with the influence of the coal discard dumps, indicate that the Black Diamond dump shows minimal contaminant movement from the dump area. However, the Union dumps are found to be directly influencing the Boesmanspruit tributary. It was mentioned by Hodgson and Vermeulen (2002b) that the coal discard dumps have been in existence for many years, however the groundwater pollution plume has not migrated a significant distance from the dump sites. This may be due to a combination of geohydrological factors, the most important of which is the absence of noticeable groundwater in the weathered zone. Computer simulations confirmed field observations and suggest that the pollution plume will not migrate significantly from its current location.
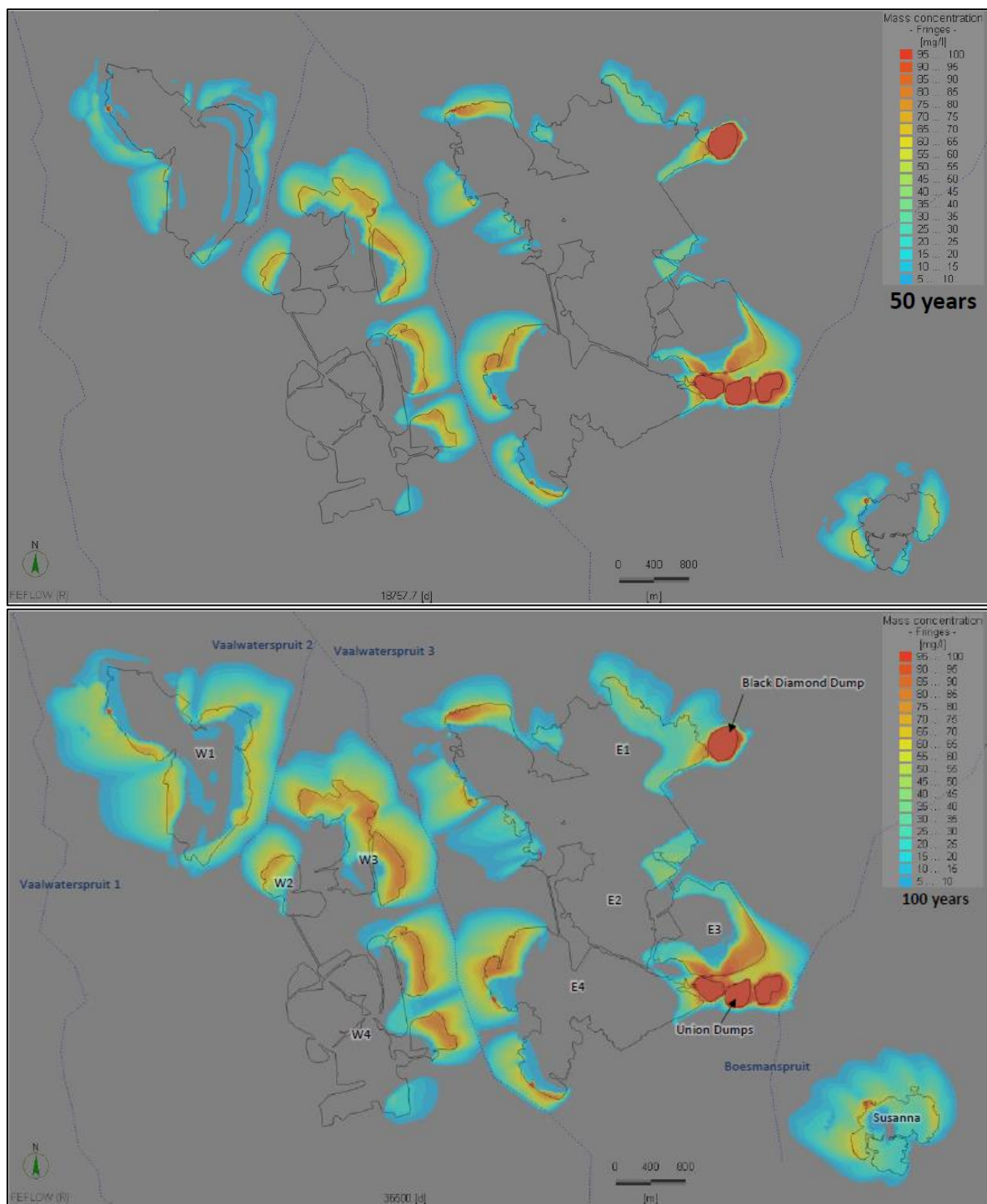
(Allwright, 2018)

Figure 3-16: Simulated mass concentration distribution of a generic 100% concentration at the ground surface with the influence of the coal discard dumps, at 50 years and the final time of 100 years. Planar view of the ground surface.

3.8 CONCLUDING SUMMARY

Chapter 3 characterised and described the study area, which was vital to create context during the various assessments and for site conceptualisation, with the following main conclusions from the site assessment:

- The Union Colliery is a decommissioned underground coal mine located just north of the town, Breyten and all active mining activities ceased in 1985.

- The study area falls within the X11A and X11B quaternary catchments with the main draining channels being the Boesmanspruit and the Vaalwaterspruit.

- The study area has a temperate climate with characteristically warm, wet summers and cold, dry winters. The summer rainfall area has an average rainfall of 740 mm/a and the recharge over the area was estimated at 9%.

- The main geology of the area includes coal seams (Vryheid Formation) and consolidated sedimentary layers of the Ecca Group of the larger Karoo Supergroup. Displacements as a result of dolerite sill intrusions that vary from being concordant to transgressive in structure are common. The dolerite intrusives are frequently associated with the occurrence of miner slips and faults, particularly in close proximity to the dolerite intrusives.

- The area is characterised by inter-granular weathered and fractured aquifers. The sandstone and coal layers are typically reasonable aquifer systems, whereas the shale layers can be considered as aquitards.

- The measured mine water levels in the mine void monitoring boreholes, from July 2009 to July 2017, indicate that mine water levels have reached an equilibrium within certain mine voids. However, new equilibrium water levels can be established in the future as indicated by rising water levels in W4 and Susanna compartments.

- The total volume of water within the underground voids is $8.78 \cdot 10^6$ m^3. The total water holding capacity of the underground voids are $26.88 \cdot 10^6$ m^3, therefore the mine is currently filled 32.66% of its total holding capacity.

- Seven distinct decants in well-defined flow channels exist at the Union Colliery which impact the local streams.

- Complete flooding of the underground workings is improbable due to the shallow mining conditions and the undulating surface topography. However, the question if the mine has reached its maximum water holding capacity remains as water levels appear to still be rising in several compartments.

- The numerical groundwater transport model simulation indicates that there are large areas of contaminant seepage along low-lying areas, instead of contaminants being limited to specific

surface decant areas. The model highlights that contaminants will further increase in both their area of influence and concentrations within the next 50 years. Thus, subsurface seepage extends to such an extent that it influences both groundwater and stream water quality. It should therefore be controlled and monitored separately.

With the conclusions of Chapter 3, allowing the reader a broader hydrogeological understanding of the study area, this information will be considered during the conceptualisation, setup and simulation of the geochemical models as will be discussed in Chapter 7 and Chapter 8 of this dissertation.

CHAPTER 4:
PROJECT DATA AND METHODOLOGY

The approach followed during the study centred around a risk-based approach with the aim to combine mineralogical, geochemical and hydrogeological characteristics of the mine site into well-defined conceptual models. The objectives of this research required a multifaceted research approach which included fieldwork, lab work, statistical analysis, and geochemical modelling techniques. Several groundwater and surface water monitoring data sets, geochemical data sets as well as supplementary data collected during field campaigns were used during the hydro -and geochemical assessments and subsequent predictive geochemical modelling.

The main objective of this chapter is to describe data sets and sources used in assessments as well as sampling and collection methods followed during the field campaigns. Moreover, geochemical characterisation techniques and associated methods together with data analysis tools employed to summarise the large data sets will be discussed. Note that hydro-chemical -and geochemical evaluations were done to augment site conceptualisation which serves as the foundation for geochemical modelling. Comprehensive interpretation and discussion of the acquired data will follow in Chapter 5 and Chapter 6 of this dissertation.

4.1   DATA SETS AND SOURCES

As described by several authors (Perkins *et al.*, 1997; Usher, 2003; Price, 2009) crucial considerations and requirements for quantitative geochemical modelling of mine drainage chemistry are reliable and complete data sets. Water chemistry data, mineralogical properties and additional geochemical data forms a fundamental part of the input parameters used to develop the kinetic geochemical models.

Table 4-1 presents the data sets with complementary sources made available during this study. Two main data sets which comprise historic and more recent water quality data were supplied by South 32. The parameters measured and analysed during these monitoring periods are listed in Table 4-1. Additional data sets included a compilation of historical reports of geohydrological and specialist studies performed at the Union Colliery as well as geochemical characterisation data which included sulphur speciation, X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses. These data sets will further be discussed under section 4.3.

Table 4-1: List of data sets and sources.

Data set	Source	Description	Parameters
Compiled excel file of groundwater, surface water and mine water monitoring data	South 32 monitoring database	Macro and micro chemistry data from January 2000 to December 2007	Continuous: pH, EC, Ca, Mg, Na, K, Total Alkalinity, F, Cl, $NO_3(N)$, PO_4, SO_4, Al, Fe, Mn Occasional: $NO_2(N)$, Br, Ag, As, Ba, Be, Cr, Cd, Co, Cu, Li, Mo, Ni, Pb, Sb, Se, Sr, V, Zn
Compiled excel file of groundwater, surface water and mine water monitoring data	South 32 monitoring database IGS monitoring database	Macro and micro chemistry data from July 2012 to June 2017	pH, EC, TDS, SS, Total Alkalinity, Total Hardness ($CaCO_3$), Turbidity, $NH_3(N)$, Ca, Mg, Na, K, F, Cl, $NO_3(N)$, $PO_4(P)$, SO_4, Al, Fe, Mn, Si
Historical reports	South 32	Geohydrological and specialist reports	
Sulphur speciation	Metron Laboratory (Pty) Ltd	Laboratory results (Metron Laboratory (Pty) Ltd)	%C, %S (2 200°C), %S (1 000°C)
XRD data	UFS Department of Geology	Laboratory results (UFS Department of Geology)	wt% quartz, hematite, microcline, plagioclase, ankerite, gypsum, kaolinite, mica, calcite, pyroxene, pyrite, smectite, goethite, amphibole
XRF data	UFS Department of Geology	Laboratory results (UFS Department of Geology)	wt% SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, MnO, CaO, K_2O, P_2O_5

4.2   METHODOLOGY

These sections present the specific methods performed during the collection of water -and waste solid samples and the subsequent static geochemical tests performed.

4.2.1   Hydrocensus and sample collection

According to Brady *et al*. (1994) groundwater and mine affected water at coal mines generally display spatial and temporal variations due to physical and chemical heterogeneity of the sites. A systematic water quality monitoring and evaluation programme at representative sites should therefore be a primary objective when conducting fieldwork.

With aforementioned in mind, the author of this study was involved in hydrocensus surveys as well as additional field campaigns during the duration of the project. As part of the hydrogeochemical assessment, a hydrocensus was conducted to acquire the geographic positions of mine monitoring

stations as well as other relevant monitoring sites in the area. Water samples were collected at selected sites. A total of 59 sites were visited which included 35 mine monitoring stations of which only 27 were sampled (Figure 4-1). Sampling mostly included that of mine void water as well as decant mine water for the respective eastern -and western operations. The main purpose of the sampling exercises was to obtain current and representative mine water chemistry data for the inaccessible eastern -and western compartments. Twenty-six additional sites, of which 17 were sampled, located on farms in and around the mined areas also formed part of the hydrocensus (Figure 4-2). The purpose of the groundwater sampling was to assess water chemistry of groundwater unaffected by the mining activities which may be used to infer baseline water quality conditions for the groundwater in the unmined areas. The sampling geographic locations are presented in Table 4-2.

The water columns of the monitoring boreholes were hydro-chemically profiled by means of an Aquaread Aquaprobe (model AP-1000) for the purpose of detecting possible pollution plumes and to ensure that the boreholes were sampled on a representative basis. The groundwater levels were measured by means of a Solinst dip-meter before any equipment was introduced in the boreholes. Flow-through bailing equipment was used to obtain depth specific samples. All water samples were taken in accordance with methods prescribed by Weaver *et al*. (2007) and Venter (2000). Clean sampling procedures as recommended by Benoit (1995) and U.S. Geological Survey (2003) were undertaken at each sampling site to minimise cross contamination and maintain the integrity of the trace element levels in the samples collected. The sampling tasks were assigned between two people where one only had contact with the sample, while the other managed all the measuring and sampling equipment. The sampling equipment were rinsed thoroughly with deionised water after each collected sample.

Volumetric sample bottles (1 Litre plastic bottles) were used to collect the water samples at each site. Certain parameters are difficult to preserve during storage and were measured in the field using an Aquaread Aquaprobe (model AP-1000). The parameters measured in the field included temperature, pH, EC (Electrical Conductivity), and DO (Dissolved Oxygen). The instrument was calibrated with reference buffer solutions of pH 4.0 and 7.0. The EC and DO electrodes were checked and calibrated against the manufacturer's supplied solution and instructions. Due to the significant amounts of suspended solids and total dissolved solids in the collected mine water and groundwater, no preservations were added to the water samples as on-site filtering was not practical (Zhao *et al*., 2010).

Water samples were stored and cooled in a cooler box, before being submitted to IGS Laboratory Services, Bloemfontein, where they were analysed within seven days. All collected samples were analysed for metal(loid)s, major and minor ions. Analysis for cations and metal(loid)s (Ca, Mg, Na, K, Al, As, Ba, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn) were done using a Teledyne Leeman Prodigy 7 ICP-AES, and a Dionex DX-120 Ion Chromatograph (IC) was used for the anions (F, Cl, $NO_2(N)$, Br, $NO_3(N)$, PO_4, SO_4). A Schott–auto titrator was used to determine the Total Alkalinity and a colorimetric Skalar segmented flow analyser to determine $NH_3(N)$.

Table 4-2: Sample collection geographic locations and descriptions.

Site Name	Latitude	Longitude	Location description	Date collected
			Groundwater samples	
UN01/02	-26.23973	30.01001	Downstream of Union Dump 1 and 2	7-Feb-17
UN02/02	-26.23764	30.00998	Downstream of Union Dump 1 and 2	7-Feb-18
UN04/02	-26.23656	30.00934	Upstream of Union Dump 1, 2, and 3	7-Feb-17
UN05/02	-26.23416	30.01488	Further downstream of Union Dump 3	7-Feb-17
UN06/02	-26.23556	30.01367	Downstream of Union Dump 3	7-Feb-17
BD01/02	-26.21085	30.00607	Upstream of Black Diamond coal discard dump	9-Feb-17
BD02/02	-26.21519	30.00760	Directly downstream of Black Diamond coal discard dump	9-Feb-17
BD03/02	-26.21666	30.01041	Further downstream of Black Diamond coal discard dump (Artesian)	9-Feb-17
Fourie H1	-26.22430	29.98179	Borehole on Fourie farm	14-Mar-17
Fourie H4	-26.22801	29.98184	Borehole on Fourie farm	14-Mar-17
Butter F1	-26.23091	29.96387	Fountain on Butter farm	14-Mar-17
Butter H2	-26.23408	29.96307	Borehole on Butter farm	14-Mar-17
Butter H3	-26.22885	29.95995	Borehole on Butter farm	14-Mar-17
Butter H4	-26.23952	29.96539	Borehole on Butter farm	14-Mar-17
VA-H1	-26.20715	29.98967	Borehole on Van Aswegen farm	15-Mar-17
VA-H2	-26.20797	30.00133	Borehole on Van Aswegen farm	15-Mar-17
VA-H3	-26.20834	29.98834	Borehole on Van Aswegen farm	15-Mar-17
Mnisi F1	-26.25797	29.95023	Fountain on Mnisi farm	15-Mar-17
Mnisi H1	-26.25746	29.95180	Borehole on Mnisi farm	15-Mar-17
PP.H1	-26.21792	30.00894	Borehole on Piet Prinsloo farm	16-Mar-17
Mos H1	-26.23211	29.99759	Borehole on Zwane farm	16-Mar-17
Mos H2	-26.23017	29.99070	Borehole on Zwane farm	16-Mar-17
Mos H4	-26.22543	29.99809	Borehole on Zwane farm	16-Mar-17
BACK1	-26.25236	29.98062	Newly drilled borehole on Shongwe farm	1-Jun-17
VIN1	-26.20273	29.93688	Borehole on Vincent farm	1-Jun-17
			Mine water samples	
BH1	-26.20913	29.93827	W1 compartment	1-Jun-17
BH2	-26.22243	29.94806	W1 compartment	8-Feb-17
BH3	-26.22777	29.95537	W2 compartment	8-Feb-17
BH5	-26.22410	29.96723	W3 compartment	8-Feb-17
BH8	-26.24497	29.96632	W4 compartment	9-Feb-17
BH11	-26.21208	29.97690	E1 compartment western lobe	8-Feb-17
BH13	-26.24775	30.02796	Susanna compartment	7-Feb-17
SUS1	-26.24910	30.02561	Susanna compartment (newly drilled)	2-Jun-17
BH15	-26.22142	29.96530	W3 compartment	8-Feb-17
BH16	-26.20968	29.98944	E1 compartment eastern lobe	2-Jun-17
Arcadia Adit No.1	-26.24028	29.97907	E4 compartment decant	9-Feb-17
Arcadia Adit No. 2	-26.24856	29.98467	E4 compartment decant	9-Feb-17
Butter Adit Decant	-26.22100	29.96751	W3 compartment decant	8-Feb-17
Duck Pond Decant	-26.23746	30.00750	E3 compartment decant	7-Feb-17
Fourie Decant	-26.21007	29.97485	E1 compartment decant	8-Feb-17
Union Adit Water	-26.23711	30.00454	E3 compartment decant	7-Feb-17
W1 Decant	-26.21091	29.93440	W1 compartment decant	8-Feb-17
			Surface water samples	
Arcadia Dam	-26.24056	29.97709	Dam between W4 and E4 compartments within the Vaalwaterspruit (middle)	9-Feb-17
Union V-notch	-26.23699	30.00961	Stream flowing past Union coal discard dumps	7-Feb-17
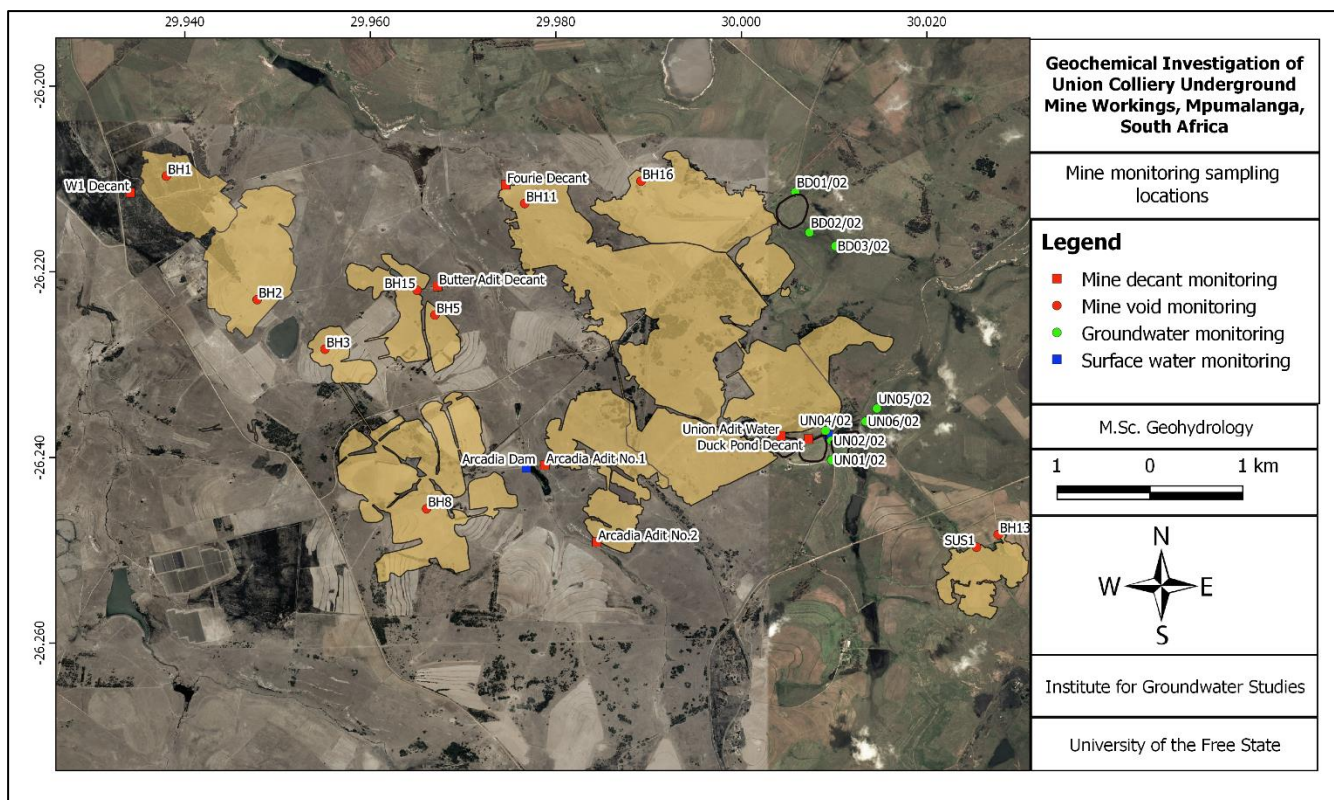
Figure 4-1: Sampling locations at current mine monitoring stations during the hydrocensus.
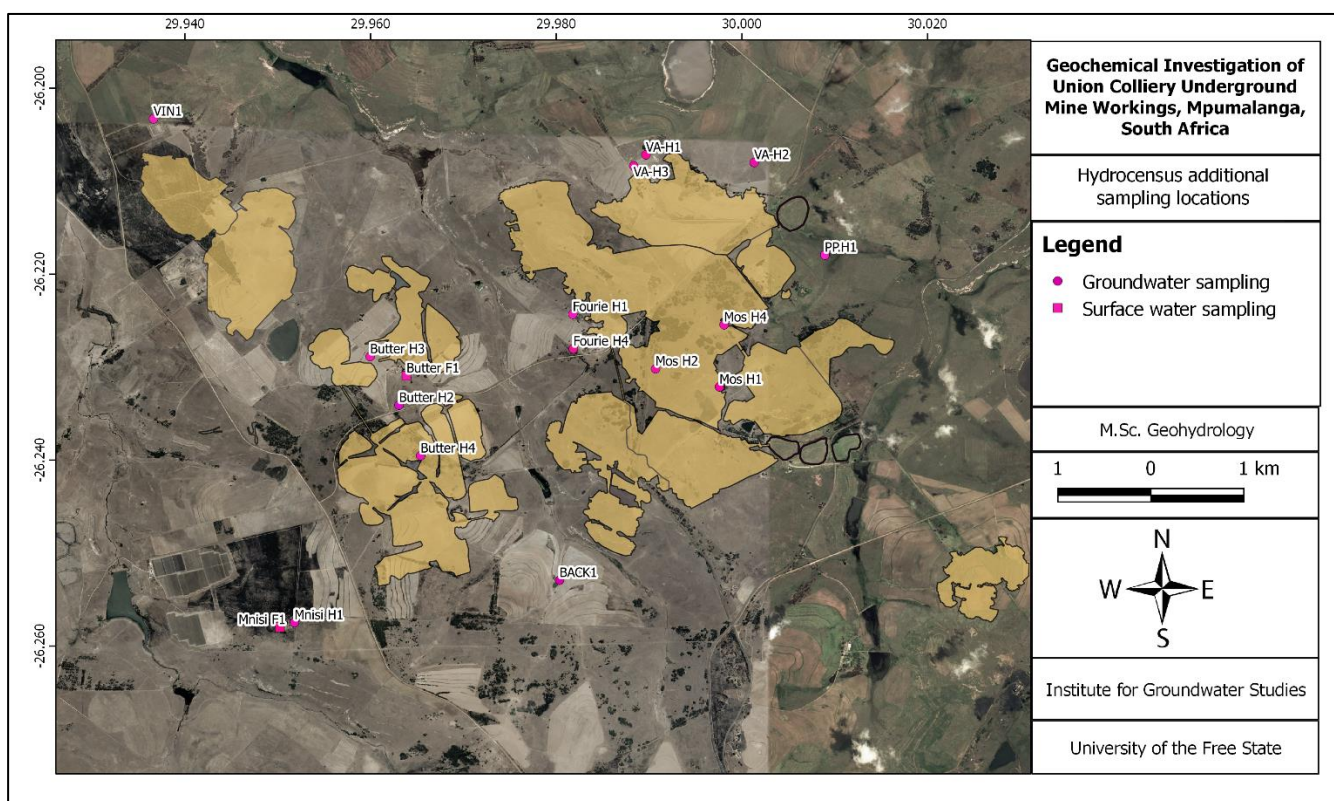
Figure 4-2: Sampling locations located on farms in in and around the Union area during the hydrocensus.

4.2.1.1 Quality Assurance and Quality Control analysis (QA/QC)

This section presents the reliability assessment of the samples collected during the hydrocensus and additional field campaigns. The main objective of the QA/QC was to indentify field sampling or laboratory errors and to provide the basis for future validation and use of the analytical results to interpret the results correctly. When the parameters or samples presented high uncertainty or exceeded minimum precision requirements, they were used with caution in subsequent analyses to secure more stable results.

4.2.1.1.1 *Charge balance*

Charge balance was used to assess the analytical quality of the chemical data. Chemical analyses of all water samples were evaluated for charge balance using the GWB software package. The charge balance error for the analyses ranged from ±0.28 to ±12.53. The charge balance error for each sample is presented in Appendix B: Water Quality Data and is provided on request.

4.2.2 Laboratory geochemical evaluation and prediction tests

An overview of prediction methods was given in section 2.2 of this dissertation, therefore the following sections will focus more on the specific geochemical assessments performed during this study which included static geochemical tests.

Prediction tests are described by numerous authors (Bethke, 1996; Usher, 2003; Usher *et al.,* 2003; Maest *et al.*, 2005; Zhao *et al.,* 2010) as a collection of integrated approaches aimed at determining the geochemical behaviour of mine waste in advance for new, operating and decommissioned mines. One of the objectives of such studies is generally associated with the determination of the acid generating potential of the mine wastes and the evaluation of the associated impacts and risks so that wastes can be better handled and managed.

As mentioned in section 2.2, several methods have been developed to predict the acid generating characteristics of mine waste material. Price (2009) gives a broad overview of static and kinetic tests used to augment in drainage chemistry prediction. In general, testing programs utilise a two-step approach of acid-base accounting (ABA) which was originally developed by Sobek *et al.* (1978). Generally, static tests on numerous samples are initially performed to identify potentially acid-generating geologic units. Kinetic tests are then performed on samples identified as important and deemed likely to generate acid by the static tests (Price, 2009). Static assessments are so referred because each involves a single measurement in time without considering or reporting on the speed or kinetic rate of the reactions producing or consuming acid (Usher, 2003; Usher *et al.*, 2003; Maest *et al*, 2005). Static tests are designed to measure the quality and quantity of different mineral constituents in a sample at a specific point in time (Price, 1997; Magombedze, 2006). Static procedures include amongst others, analyses of elemental sulphur, sulphur species, neutralisation potential, pH measurements, and mineralogical analysis (Mogombedze, 2006). These tests are typically simple, easily executable,

inexpensive procedures to prove a preliminary assessment of the potential of mine waste to generate acid mine drainage (AMD) (Zhao *et al.*, 2010).

To aid in the assessment of the acid-generating potential and associated risks posed by the coal discard -and coal material to the local environment, ABA and net acid-generating (NAG) tests were performed for all solid samples collected at the Union Colliery. Since the main purpose of the geochemical evaluation was to examine the balance between the acid-generating and acid-neutralisation components of the coal discard -and coal material with the aim to identify current risks, static tests were considered adequate. The static test methods applied during this study were not performed to answer questions regarding the future behaviour of the mine wastes or the rate of acid generation, only to augment the evaluation of the current risks. The geochemical evaluation therefore did not include kinetic tests.

Acid-base accounting should be viewed as a first-order classification procedure whereby the acid-neutralising potential and acid-generating potential of solid samples are determined. The difference or ratio between these potentials can then be calculated to classify the samples as either potential acid generators or unlikely acid generators. The net neutralisation potential (NNP) and the ratio of neutralisation potential to acid-generation potential (NPR) are compared with predetermined values, or set of values, to classify samples into categories that either require, or do not require, further determinative test work (Zhao *et al*., 2010). Acid-base accounting therefore indicates the overall balance of acidification potential (AP) and neutralisation potential (NP). Static tests provide the worst-case and best-case scenario of the likelihood of current and potential AMD generation and is associated with numerous limitations and assumptions. Some of these limitations and assumptions will be mentioned in section 4.2.3.1.

To further the geochemical characterisation of the mine waste, samples collected were submitted for mineralogical and geochemical analyses which is discussed under section 4.3 of this dissertation. According to Paktunc (1999), the mineral composition of mine waste will ultimately give a reflection of the different mineral species' contribution in the system as a whole. As geochemical modelling techniques were used as a tool during this study, mineralogical determinations were a vital component in the evaluation. The mineralogical analysis was focused on the identification and quantification of the major sulphide minerals as the potential source for acid generation and carbonate minerals and anorthite as potential sources of neutralisation potential. The information yielded by the mineralogical analysis were subsequently used to establish the relative reaction rates of the minerals which contribute to acid and alkalinity generation in the system (Zhao *et al*., 2010). Mineralogical results were further used to reduce the uncertainties during the interpretation of the ABA results.

The collection of geological solid samples for the static tests were concentrated on the rehabilitated coal discard dumps. As mentioned, the aim of the testing was to determine any disposition for acid generation in the coal -and coal discard material, and whether there is sufficient neutralisation potential in the waste

materials to counteract acid generation. The static tests included 21 coal discard samples and coal sampled from the hanging wall of the Susanna compartment (eastern operations).

4.2.2.1   Collection and preparation of solid samples

Solid samples were collected from the Union Colliery waste components and submitted to several SANAS accredited laboratories for geochemical characterisation tests. Sampling focused on obtaining representative samples with respect to the chemical characteristics of the waste material. The overall aim of the sampling exercise was to provide useful information for mineralogical and geochemical evaluation which is vital for the geochemical characterisation of the mine waste and the overall conceptualisation of the systems. As mentioned, the results obtained from sampling and laboratory analyses were used for geochemical modelling for long-term mine drainage chemistry prediction.

Characterisation of mine waste material is quite challenging due to the heterogeneity in the structure, physical nature, mineralogical and chemical characteristics in especially surface repositories. According to Williams *et al*. (2003) variation in such properties is caused by factors such as geology, construction technique, weathering rates, climate and several other factors. However, it was assumed during this study that the coal discard material was discarded homogeneously on the dumps.

According to Usher (2003) determining the number of samples to be collected and the representativeness of the sample set are critical considerations. Random coal discard samples were collected by walking over the entire coal discard dumps, collecting samples from the sidewalls, crest and toe of the dumps. The primary goal of the sampling technique was to determine the average properties and average geochemical behaviour to provide a rapid classification of the mine waste materials regarding acid-generating potential. Coal discard samples were collected by first removing the vegetation cover at the sample location by scrapping away with a trowel. A 10 cm diameter hand auger was used to excavate through the topsoil layer to reach the coal discard material. The hand auger was further advanced to a depth of at least 50 cm where after the sample was extruded directly into plastic sampling bags. Approximately 500 g of sample were collected during each sampling exercise. The auger holes were backfilled after each sample collection. The auger was thoroughly washed after each sample collection to prevent cross-contamination especially between the different coal discard dumps. In total, 22 samples were collected which included 21 coal discard samples (Figure 4-3and Figure 4-4), and one coal sample collected from the Susanna compartment hanging wall. The hanging wall sample was collected during the drilling of a new monitoring borehole that intersects the mine void. The samples' geographic locations and descriptions are presented in Table 4-3.

A major limitation to the current study was that floor and roof coal samples could not be collected at the various compartments due to inaccessible adits and shafts. The project was also limited to the drilling of a single monitoring borehole intersecting the mine voids. Mineralogical data was therefore limited to the coal discard material and the one roof coal sample collected at the isolated eastern compartment,

which is Susanna. Alpers and Nordstom (1999), and Perry (2001) demonstrated that water chemistry analysis together with geochemical modelling become the principal tools to study mine water origin and evolution, especially when sufficient geochemical characterisation data of the mine waste is lacking.

As mentioned before, the collected solid samples were returned and submitted to several laboratories for geochemical tests and analyses. The samples were submitted to UFS Department of Geology where it was crushed (coarse crusher) and milled (swing mill) to a powder of 300 mesh. The samples were then subjected to XRD and XRF analyses. The bulk of the milled samples were returned for geochemical static tests (ABA and NAG) to IGS Laboratory Services where the assessments were performed by the author of this dissertation. Given the different forms in which sulphur can occur in mining wastes and their different potentials for acid generation, sulphur speciation was most beneficial. Representative composite samples of approximately 20 g were mixed for each coal discard dump. The composite coal discard samples as well as the collected coal sample were submitted to Metron Laboratory for sulphur speciation determination.
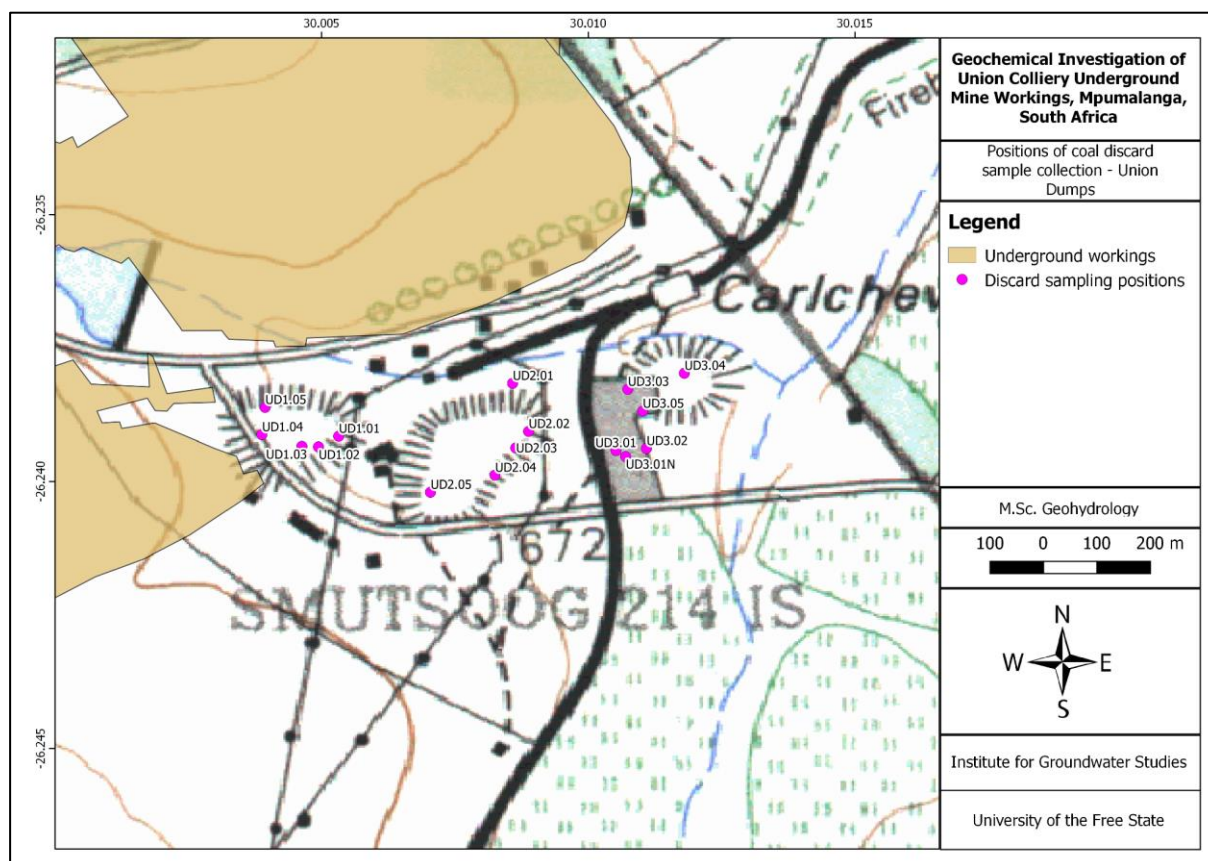
Figure 4-3: Union coal discard dumps sampling positions together with the underground workings displayed on a topographic map.
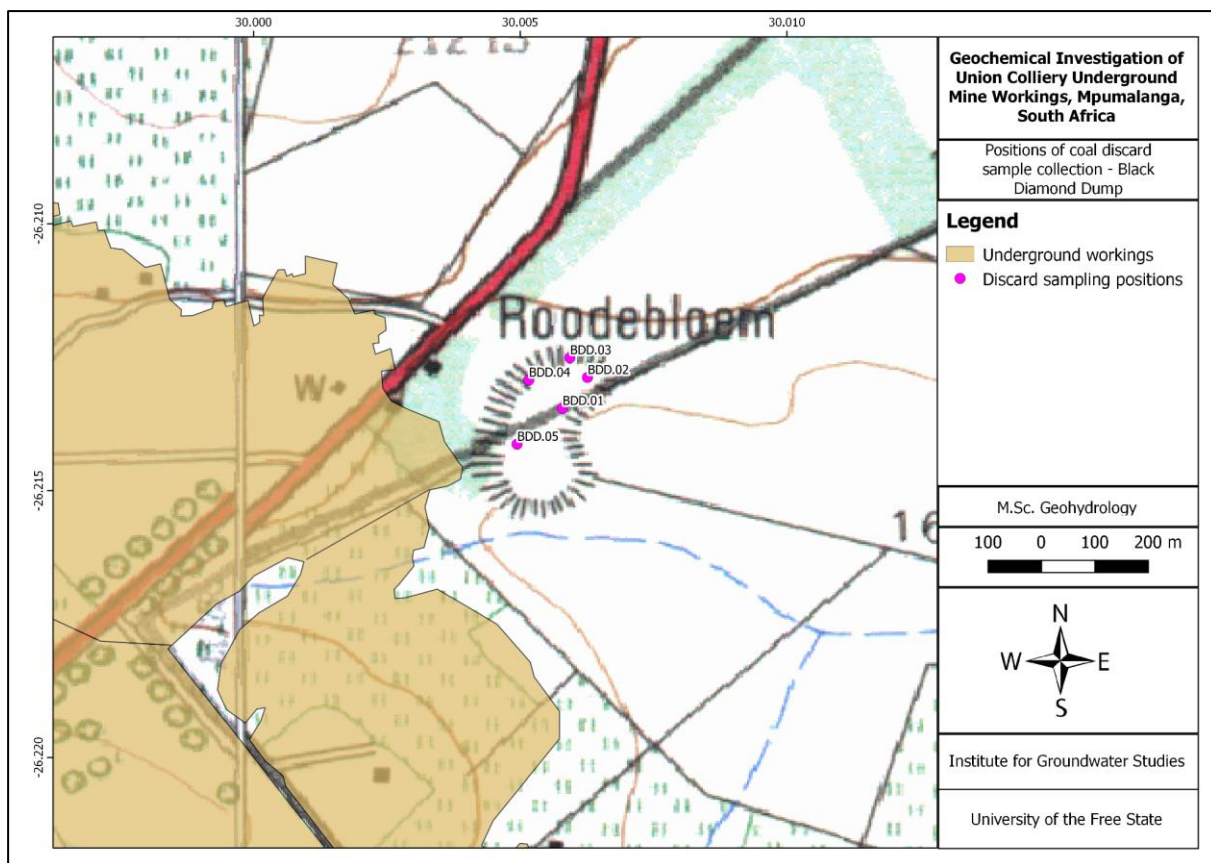
Figure 4-4: Black Diamond coal discard dump sampling positions together with the underground workings displayed on a topographic map.

Table 4-3: Coal and coal discard sampling descriptions.

Sample name	Site	Date	Latitude	Longitude	Altitude (mamsl)	Top soil (m)	Sampling depth (m)	Sample description
					Coal discard samples			
UD1.01	Union Dump 1	7-Feb-17	-26.23915	30.00532	1692	0.0-0.50	0.60-0.90	Coal discard
UD1.02	Union Dump 1	7-Feb-17	-26.23935	30.00494	1694	0.0-0.50	0.60-0.90	Coal discard
UD1.03	Union Dump 1	7-Feb-17	-26.23934	30.00463	1696	0.0-0.60	0.70-0.90	Coal discard
UD1.04	Union Dump 1	7-Feb-17	-26.23912	30.00388	1699	0.0-0.55	0.65-0.80	Soil and coal mixture (hard rock was reached at 0.8 m)
UD1.05	Union Dump 1	7-Feb-17	-26.23861	30.00394	1698	0.0-0.50	0.60-0.80	Coal discard
UD2.01	Union Dump 2	7-Feb-17	-26.23816	30.00858	1681	0.0-0.55	0.65-0.90	Coal discard
UD2.02	Union Dump 2	7-Feb-17	-26.23906	30.00888	1691	0.0-0.55	0.65-0.90	Coal discard
UD2.03	Union Dump 2	7-Feb-17	-26.23937	30.00864	1691	0.0-0.60	0.70-0.90	Coal discard
UD2.04	Union Dump 2	7-Feb-17	-26.23988	30.00825	1695	0.0-0.55	0.65-0.90	Coal discard
UD2.05	Union Dump 2	7-Feb-17	-26.24020	30.00704	1695	0.0-0.55	0.65-0.90	Coal discard
UD3.01	Union Dump 3	8-Feb-17	-26.23942	30.01052	1683	0.0-0.80	0.80-0.90	Grey loamy soil mixed with coal discard material (hard rock layer was reached at 0.9 m; refusal at 0.9 m)
UD3.02	Union Dump 3	8-Feb-17	-26.23938	30.01109	1675	0.0-0.40	0.50-0.60	Coal discard
UD3.01N	Union Dump 3	15-Mar-17	-26.23953	30.01070	1669	0.0-1.00	1.10-1.30	Coal discard
UD3.03	Union Dump 3	15-Mar-17	-26.23827	30.01074	1671	0.0-0.70	0.75-0.90	Coal discard
UD3.04	Union Dump 3	15-Mar-17	-26.23797	30.01180	1678	0.0-0.65	0.70-0.90	Coal discard
UD3.05	Union Dump 3	15-Mar-17	-26.23868	30.01102	1671	0.0-0.70	0.75-0.90	Coal discard
BDD.01	Black Diamond Dump	9-Feb-17	-26.21346	30.00579	1705	0.0-0.60	0.70-0.90	Coal discard
BDD.02	Black Diamond Dump	9-Feb-17	-26.21288	30.00626	1709	0.0-0.60	0.70-0.90	Coal discard
BDD.03	Black Diamond Dump	9-Feb-17	-26.21251	30.00593	1710	0.0-0.60	0.70-0.90	Coal discard
BDD.04	Black Diamond Dump	9-Feb-17	-26.21293	30.00516	1709	0.0-0.60	0.70-0.90	Coal discard
BDD.05	Black Diamond Dump	9-Feb-17	-26.21413	30.00494	1705	0.0-0.60	0.70-0.90	Coal discard
					Compartment coal sample			
Sus Coal	Susanna compartment	2-Jun-17	-26.24910	30.02561	1721	n/a	28-29	Coal sampled from the hanging wall

4.2.3 Acid-base accounting procedure and interpretation

The ABA procedure was formerly developed by Sobek *et al.* (1978) as a laboratory protocol for determining the acid-generation potential of mine overburden containing sulphide mineralisation (Magombedze, 2006). It is based on the principle that the likelihood for a site to produce AMD can be predicted by quantitatively determining the amount of acidity (AP) and the alkalinity (NP) of the sample material.

4.2.3.1 Considerations, advantages and limitations of ABA

It is very important to recognise that although ABA has been used fruitfully in determining mine drainage chemistry and classifying samples into acid generation potentials, the advantages, and more importantly the limitations of ABA need to be considered.

The main advantages of ABA include the following:

- ABA tests are inexpensive.

- The interpretation of the results is based on decades of international research and experience.

- The methods of interpretation are clear and well established.

- Results can be obtained within a period of a few weeks.

- Correlation to field conditions has been shown by local and international case studies.

As mentioned before, static tests can be considered and applied as an initial screening method for mine drainage prediction and provides a very good indication of the likelihood of sample material to produce acid. Acid-base accounting tests can be considered rapid and inexpensive as the tests involve single analyses and the test methodology are simple. Therefore, although the amount of information yielded by kinetic tests exceeds that of static tests, the latter are applied more widely in terms of the number of tests conducted.

During static tests the collected sample material are pulverised and implies that all the constituents can react relatively easy and the reactions are considered to occur nearly instantaneous. In field situations, however, the kinetics and the dynamics of the system will determine how the reactions of the minerals occur. Laboratory predictions may therefore be very different from actual field conditions. Usher (2003) conjectured that these tests can be described as analogous to that of an equilibrium approach since the test reflect the likely end-point of the system with no consideration of the reaction rates of the different minerals.

The limitations of ABA can therefore include the following:

- Only a probability of occurrence is provided.

- Reaction rates of minerals are not considered. It can be inferred that ABA methodology tests the fast reacting species as slow reacting species will usually not prevent acidification (Jambor *et al.*, 2000a).

- An instant availability of reactive species is assumed.

- Simple reaction stoichiometry is assumed.

- Size effects are ignored.

- Extrapolation to field conditions is not true as volumetric calculations cannot be made since the results are obtained from pulverised samples (Usher, 2003).

It was concluded by Usher (2003) that despite these limitations, ABA has successfully been applied nationally and internationally and the well-established interpretation and screening methods provide for easy interpretation and classification of samples. Although static tests only provide a first order assessment of the AMD potential of mine waste, the methods were used to reflect the overall potential of AMD generation for the specific site components.

4.2.3.2 Overview of ABA methodology

The following procedures and principles were applied to evaluate the geochemical characteristics of the sample material collected at the Union Colliery:

- Actual acidity
- NAG test
- Neutralisation/base potential ($CaCO_3$ kg/t)

Each method used alone has its own limitations as to how reliably it can predict acid-generating potential. The modification and approach used in this study was to apply these test methods in combination to get a better indication of the acid-generating potential of mine waste materials (Magombedze, 2006). The test methodology followed was that prescribed by Usher *et al.* (2003) and the more comprehensive protocol is presented in Appendix A: ABA and NAG Methodology. Each of the abovementioned test concepts will be discussed in more detail in the following sections.

4.2.3.2.1 *Actual acidity method*

This method is also referred to by Usher *et al.* (2003) and Zhao *et al.* (2010) as the initial pH method and was performed with the addition of distilled water to the samples. After a 24-hour period, samples were filtered and submitted for ICP-AES analysis for major element concentration. The results obtained from this method reflect the current state of the sample and the pH recording revealed whether the sample is already acidic or not. The pH measurements following this method are generally recorded as either initial or paste pH.

4.2.3.2.2 *Net acid-generation (NAG) or acid potential method*

According to Usher (2003) a direct determination of the acid-generating potential of sample material is the rapid pyrite oxidation technique where 30% hydrogen peroxide [H_2O_2] was utilised. This method is also often referred to as the acid potential method.

The NAG method is based on methodology proposed by Miller *et al.* (1997) and evaluates and determine the potential acidity and the net acid remaining, if any, after complete oxidation of the materials with hydrogen peroxide. It further allows complete reaction of the acid formed with the neutralising component of the material. This test therefore subjected the samples to hydrogen peroxide digestion and subsequent ICP-

AES analysis for major element concentration. The NAG test provides a direct assessment of the potential for a material to produce acid after a period of exposure and weathering and is used to refine the results of ABA prediction (Magombedze, 2006).

Samples with higher sulphur content will react more violently upon contact with the hydrogen peroxide. Samples that are darker in colour are also known to have higher sulphate content and a smaller mass sample is often subjected to hydrogen peroxide to avoid loss of sample during the peroxide reaction (Usher *et al*., 2003).

The NAG test was continued by measuring the pH (often referred to as final or NAG pH) after the samples were subjected to hydrogen peroxide and allowed to completely oxidise. The final pH values are categorised into three groups to reflect on the samples' acid-generation potential and is presented in Table 4-4.

The acid potential (AP) can be calculated by multiplying the percentage of sulphide-sulphur (Sulphide-S), determined through sulphur speciation laboratory analyses, with 31.25 (Usher, 2003). As sulphur speciation data was available for the Union Colliery samples (refer to section 4.3.3), this method was employed in the calculation of the AP.

4.2.3.2.3 *Neutralisation/base potential (CaCO$_3$ kg/t) method*

The neutralisation capacity of a sample, also referred to as the base potential of the sample, is reflected by the neutralisation potential method. During this method the net neutralisation potential (NNP) of sample material is calculated. Sulphuric acid [H$_2$SO$_4$] was used to acidify the samples to a pH value of ≤2.5 which is expected to occur in AMD environments. The sample was then titrated back to a pH of 7.0 with sodium hydroxide [NaOH]. This was done to test the ability of the sample to consume acid. The higher volume of sodium hydroxide required to reach a pH of 7.0, the less neutralisation potential it will have should the sample acidify in the field. To attain a result that is equivalent to kg/t of CaCO$_3$, the normality of the acid [H$_2$SO$_4$] and base [NaOH] along with the volumes used and the mass of the sample were considered and is reflected in Equation 4-1.

CaCO$_3$ kg/t = (N H$_2$SO$_4$ x mL acid) – (N NaOH x mL alkali/mass (g) x 50)   Equation 4-1

NNP open system = Base (NP) – acid open system (AP)   Equation 4-2

NNP closed system = Base (NP) – acid open system (AP x 2)   Equation 4-3

When interpreting the results, it is important to differentiate between open and closed systems. The difference between the two systems can be ascribed to the transfer processes of carbon between solid, liquid and gas phases. The open system is based on 1 mole of pyrite [FeS$_2$] (64 g sulphur) neutralised by 2 moles of calcium carbonate/calcite [CaCO$_3$] (200 g), and in the closed system 1 mole of pyrite is neutralised by 4 moles of calcium carbonate (this explains why the AP is multiplied by 2). Open systems (Equation 4-2) in the field may include waste rock piles while tailings vary from open and closed systems (Equation 4-3) (Usher, 2003).

4.2.3.3　　Screening criteria

As mentioned earlier, one of the major advantages of static tests is that well-defined sets of screening criteria have been developed to interpret the acquired results. Usher (2003) conjectured that although these criteria can sometimes provide slightly contradictory interpretations, their combined use can lead to a good classification of test samples into classes of non-acid-generating and potential acid-generating, with an uncertain range in-between. It was pointed out by Morin and Hutt (1994b) that ABA criteria should be determined on a site-specific basis that reflects reaction rates of the acid-generating and acid-neutralising minerals at the particular study area. However, according to Usher (2003), until there is a large enough comparable ABA database in South Africa, the international criteria should be used to classify samples.

The criteria used to classify the samples as potential acid-generating or non-acid-generating are as follows:

- Net neutralisation potential (NNP)

- Neutralisation potential ratio (NPR)

- %S and NPR

4.2.3.3.1　　*Net Neutralisation Potential (NNP)*

As mentioned before, the NNP of a sample is calculated from the difference between the neutralisation/base potential and the acid potential of a sample (Equation 4-4).

Net neutralisation potential (NNP) = Neutralisation potential (kg/t $CaCO_3$) – Acid-generating potential (kg/t $CaCO_3$)   Equation 4-4

The criteria are described by Usher *et al.* (2003) as follows:

NNP <0　　The sample has the potential to generate acid

NNP >0　　The sample has the potential to neutralise acid

Usher *et al.* (2003) stated that worldwide research and specialist experience have shown that there is an NNP range between -20 to 20 kg/t $CaCO_3$ where the sample may either become acidic or remain neutral. This uncertainty can however be reduced and completely resolved when these criteria are used in conjunction with other criteria. Therefore, the criteria are more specifically explained as any sample with NNP <20 is potentially acid generating and any sample with an NNP value >-20 might not generate acid (Usher *et al.*, 2003).

The results are typically graphically presented in combination with the NAG pH, displaying the paste pH and final pH of the sample as indicated in Figure 4-5. Samples that display values greater than zero on the x-axis are considered to potentially neutralise acid, while samples with values smaller than zero are considered to have insufficient neutralisation potential. The relationship between the final pH, which suggests the potential acidity, and the NNP is that when a negative NNP value is calculated it is typically associated with a low final pH value.
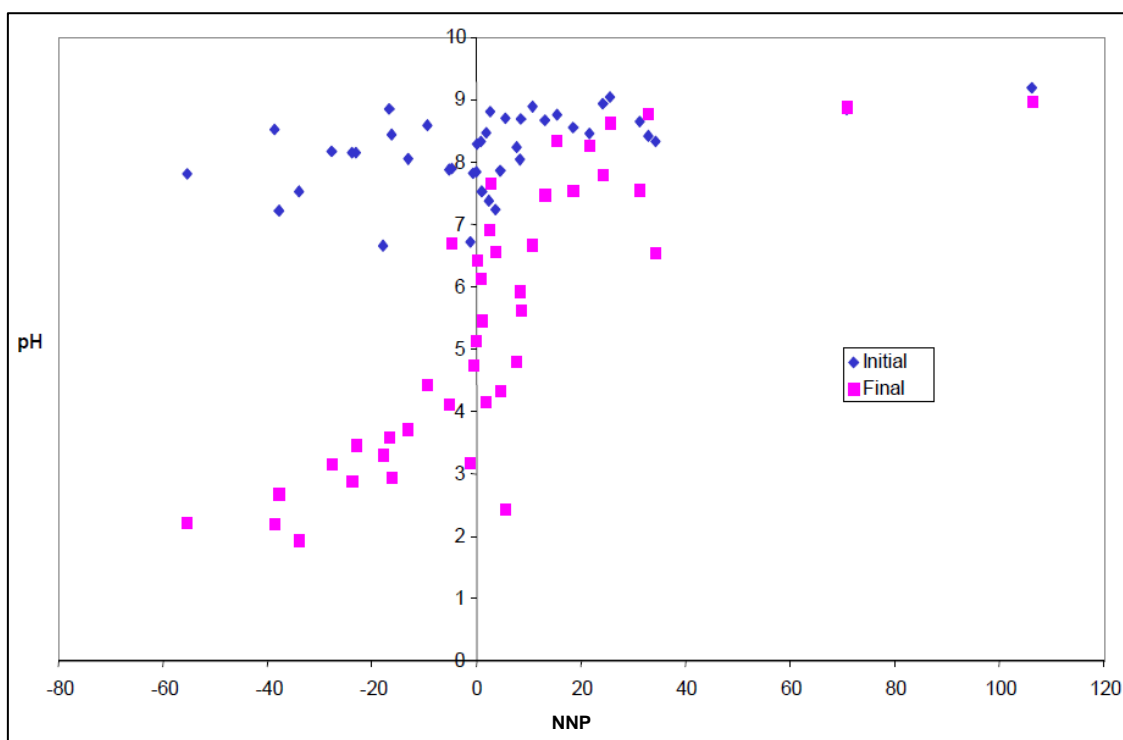
Figure 4-5: Initial and oxidised (final) pH versus NNP.

4.2.3.3.2   *Neutralisation Potential Ratio (NPR)*

The NPR can be used as a screening level assessment criterium as suggested by Price *et al.* (1997a), and Price *et al.* (1997b) and is presented in Table 4-5. By employing the IGS methodology (Usher *et al.*, 2003), the NAG pH criteria can also be applied to obtain a preliminary indication of acid generation (Table 4-4). As mentioned previously, the set of criteria is based on the final oxidised pH measured after the NAG method. According to Zhao *et al.* (2010) these criteria subdivisions are somewhat arbitrary; however, it may serve as a rough guideline of acid generation potential. It should under no circumstance be used as stand-alone criteria for classifying samples.

Table 4-4: NAG guidelines for categorising samples.

Final pH	Acid generating potential
>5.5	Non-acid-generating
3.5 to 5.5	Low risk acid-generating
<3.5	High risk acid-generating

(Price, 1997)

The reason for a pH value higher than 5.5 not being acidic is due to an average pH value of 5.9 of deionised water in equilibrium with carbon dioxide [CO_2] (Usher, 2003).

Predetermined guidelines as displayed in Table 4-5 are typically used to categorise different samples as likely, possible and with low acid potential based on the calculated ratio of NP and AP. The criteria serve as a general guide of the acid generation probability of samples. The likelihood of acid generation can also be visually

represented in the form of a graph displaying the NPR ratios where the AP is plotted against the NP. ABACUS output results are displayed in Figure 4-6 to serve as an example.

Table 4-5: Guidelines for ABA screening criteria.

NPR ratio (NP/AP)	AMD potential	Comment
<1:1	Likely	Likely AMD generating
1:1 – 2:1	Possibly	Possibly AMD generating if NP is insufficiently reactive or is depleted at a faster rate that sulphides
2:1 – 4:1	Low	Not potentially AMD generating unless significant preferential exposure of sulphides along fracture planes, or extremely reactive sulphides in combination with insufficiently reactive NP
>4.1	None	No further AMD testing required unless materials are to be used as a source of alkalinity

(Price, 1997)
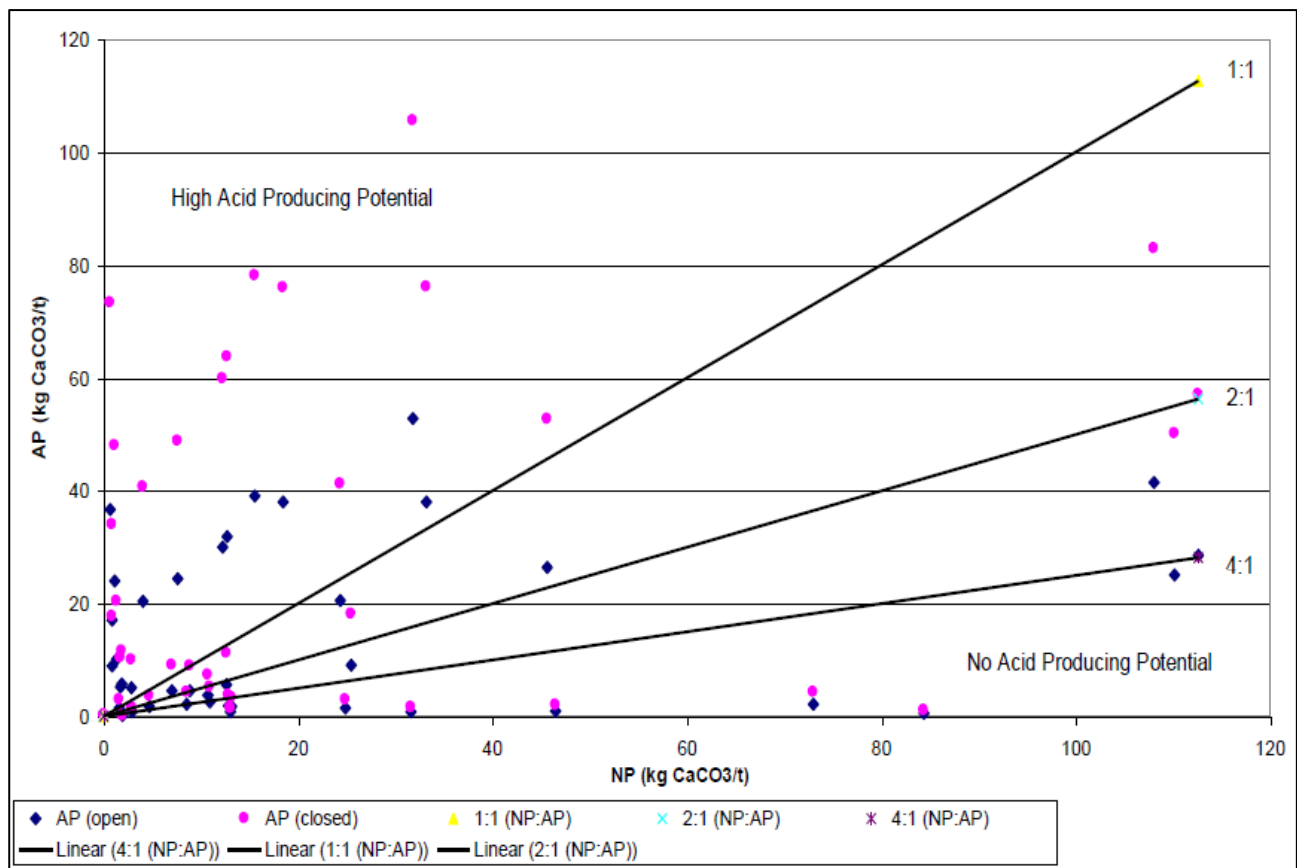
(Usher *et al.*, 2003)

Figure 4-6: Plot showing different categories of acid-generation potential based on the NPR.

4.2.3.3.3 *%S and NPR*

Soregaroli and Lawrence (1998) reported on a set of rules derived based on several factors calculated during ABA. Usher *et al.* (2003) stated that through experience it has been observed that at least 0.3% sulphide-sulphur (Sulphide-S) is required for long-term acid generation. Samples with sulphide-sulphur values below 0.3% can still yield acidity that may only pose short term concerns. Considering the NPR ratios in combination with this guideline, another set of criteria can be derived:

1. Samples with less than 0.3% Sulphide-S are regarded as having insufficient oxidizable Sulphide-S to sustain acid generation.

2. NPR ratios of >4:1 are considered to have enough neutralisation potential.

3. NPR ratios of 3:1 to 1:1 are considered inconclusive.

4. NPR ratios below 1:1 with Sulphide-S above 0.3% are potentially acid-generating.

4.3   ADDITIONAL DATA

4.3.1   External water quality database

As mentioned, a monitoring programme at the Union Colliery was initiated in the year 2000. The monitoring network started with the drilling of 16 boreholes that intersect the underground mine voids to monitor water levels and water quality. Drilling of nine monitoring boreholes positioned upstream and downstream of the coal discard dumps with the goal to monitor pollution plumes followed shortly afterwards in the year 2002. Groundwater, surface water within the Vaalwaterspruit and Boesmanspruit, as well as mine void and decant water have been monitored since. Several boreholes have in the meantime failed or were destroyed so that very little or almost no data is available. The data sets compiled by South 32 personnel were made available for this study (refer to section 4.1).

The water quality database combining historical as well as more recent water chemistry data of the Union Colliery was compiled from two separate data sets. The database contains irregular and continuous monthly monitoring of surface waters and quarterly monitoring of groundwater and mine void water from 2000 to 2007. Moreover, it contains more continuous monthly and quarterly data from 2012 to 2017. Missing data in the event of droughts, seasonal changes and borehole destruction frequently occur. Information regarding the acquired data sets used in this study was already referred to under section 4.1, where Table 4-6 merely indicates the monitoring frequency and the number of monitoring stations present in each external water quality data set. Note that monitoring stations may overlap between the monitoring data sets. Figure 4-7 shows the spatial distribution of the external monitoring stations. Information regarding the geographic location as well as monitoring period for each monitoring station is presented in Table 4-7.

Table 4-6: Information of the external water quality databases used in this study.

Data source	Year	Monitoring frequency	No. of monitoring stations
South 32	2000-2007	Monthly/Quarterly	37
South 32	2012-2017	Monthly/Quarterly	39
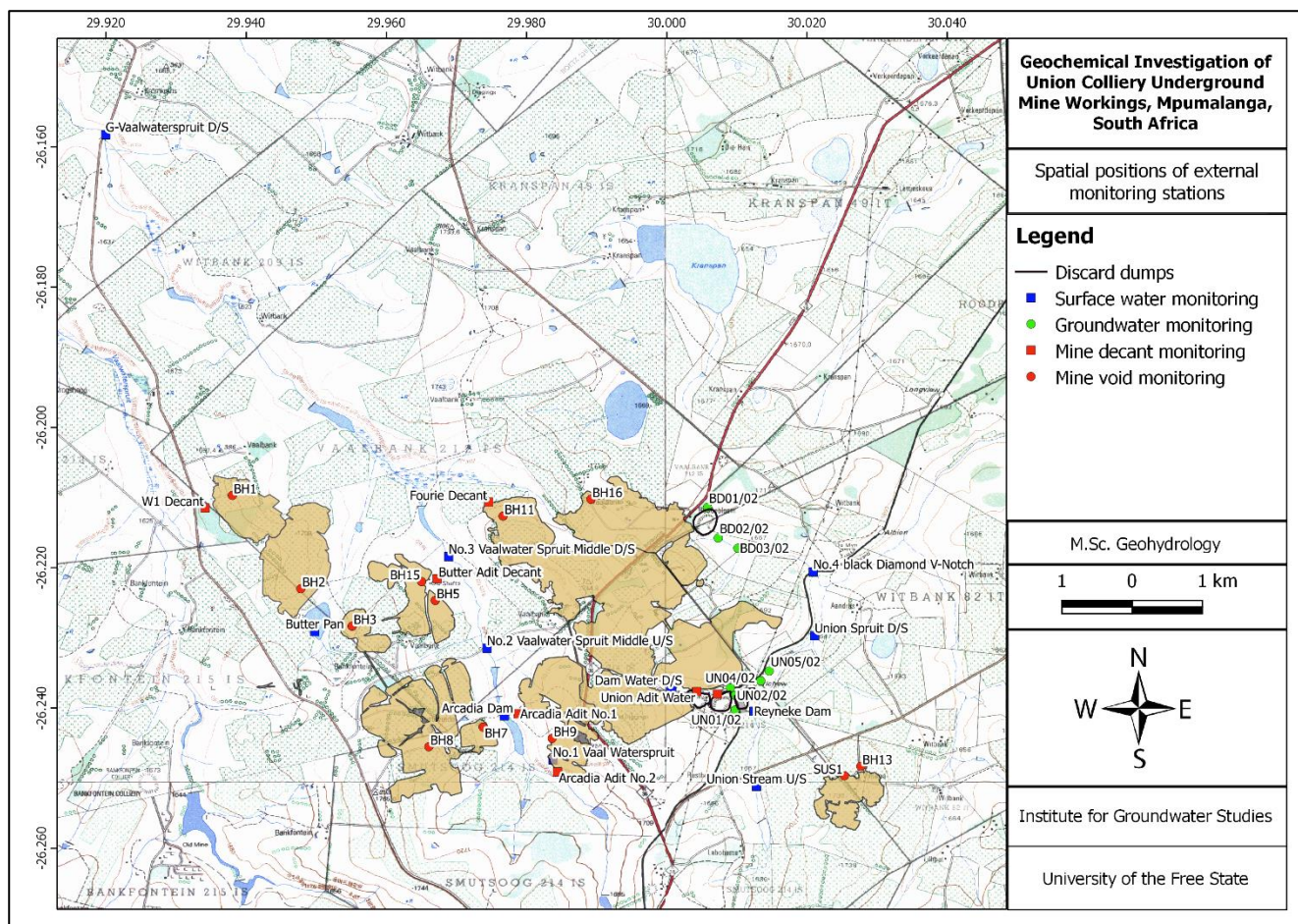
Figure 4-7: Spatial distribution of external monitoring stations displayed on a topographic map.

Table 4-7: The Union Colliery monitoring stations for which historic monitoring data exists.

Site Name	Latitude	Longitude	Location description	First sampling date	Most recent sample date
			Groundwater monitoring		
UN01/02	-26.23973	30.01001	Downstream of Union Dump 1 and 2	15-Aug-02	21-Jun-17
UN02/02	-26.23764	30.00998	Downstream of Union Dump 1 and 2	15-Aug-02	21-Jun-17
UN04/02	-26.23656	30.00933	Upstream of Union Dump 1, 2, and 3	15-Aug-02	21-Jun-17
UN05/02	-26.23416	30.01488	Further downstream of Union Dump 3	22-Jul-02	21-Jun-17
UN06/02	-26.23556	30.01367	Downstream of Union Dump 3	15-Aug-02	21-Jun-17
BD01/02	-26.21085	30.00607	Upstream of Black Diamond discard dump	15-Aug-02	21-Jun-17
BD02/02	-26.21519	30.00760	Directly downstream of Black Diamond coal discard dump	15-Aug-02	21-Jun-17
BD03/02	-26.21666	30.01041	Further downstream of Black Diamond coal discard dump (Artesian)	22-Jul-02	21-Jun-17
			Mine water monitoring		
BH1	-26.20914	29.93827	W1 compartment	13-Jul-00	1-Jun-17
BH2	-26.22243	29.94806	W1 compartment	13-Jul-00	21-Jun-17
BH3	-26.22777	29.95537	W2 compartment	8-Aug-00	21-Jun-17
BH5	-26.22410	29.96723	W3 compartment	13-Jul-00	21-Jun-17
BH7	-26.24217	29.97407	W4 compartment	13-Jul-00	21-Jun-17
BH8	-26.24497	29.96632	W4 compartment	13-Jul-00	21-Jun-17
BH9	-26.24377	29.98391	E4 west compartment	19-Jul-00	21-Jun-17
BH11	-26.21208	29.97690	E1 compartment western lobe	13-Jul-00	21-Jun-17
BH13	-26.24775	30.02796	Susanna compartment	13-Jul-00	21-Jun-17
SUS1	-26.24910	30.02561	Susanna compartment (newly drilled)	2-Jun-17	2-Jun-17
BH15	-26.22142	29.96530	W3 compartment	20-Oct-00	21-Jun-17
BH16	-26.20968	29.98944	E1 compartment eastern lobe	11-April-02	2-Jun-17
Arcadia Adit No.1	-26.24028	29.97907	E4 compartment decant	25-Sept-02	21-Jun-17
Arcadia Adit No. 2	-26.24856	29.98467	E4 compartment decant	19-Oct-07	21-Jun-17
Butter Adit Decant	-26.22100	29.96751	W3 compartment decant	1-Jan-00	21-Jun-17
Duck Pond Decant	-26.23746	30.00750	E3 compartment decant	25-Sept-02	21-Jun-17
Fourie Decant	-26.21007	29.97485	E1 compartment decant	25-Sept-02	21-Jun-17
Union Adit Water	-26.23711	30.00454	E3 compartment decant	22-Jul-02	21-Jun-17
W1 Decant	-26.21091	29.93440	W1 compartment decant	8-Feb-17	8-Feb-17
			Surface water monitoring		
Arcadia Dam	-26.24056	29.97709	Dam between W4 and E4 compartments within the Vaalwaterspruit (middle)	14-Feb-00	21-Jun-17
Butter Pan	-26.22856	29.95004	Salt pan between W1 and W2 compartments	25-Sept-02	22-Mar-17
Dam Water D/S	-26.23659	30.00090	Dam between E4 and E3 compartments	25-Sept-02	21-Jun-17
G-Vaalwaterspruit D/S	-26.15769	29.92023	Further downstream within the Vaalwaterspruit (middle)	21-Nov-03	21-Jun-17
No.1 Vaal Waterspruit	-26.24684	29.98403	Upstream in the Vaalwaterspruit (middle)	24-Jan-03	21-Jun-17
No.2 Vaalwater Spruit Middle U/S	-26.23092	29.97462	Downstream within the Vaalwaterspruit (middle)	1-Jan-00	21-Jun-17
No.3 Vaalwater Spruit Middle D/S	-26.21786	29.96915	Downstream within the Vaalwaterspruit (middle)	1-Jan-00	21-Jun-17
No.4 black Diamond V-Notch	-26.22003	30.02117	Downstream within the Boesmanspruit tributary	1-Jan-00	21-Jun-17
Reyneke Dam	-26.23991	30.01271	Dam south-east of the Union discard dumps	15-Aug-02	21-Jun-17
Union Spruit D/S	-26.22914	30.02137	Downstream within the Boesmanspruit tributary	10-Jul-03	21-Jun-17
Union V-notch	-26.23699	30.00961	Stream flowing past Union coal discard dumps	1-Jan-00	21-Jun-17
Union Stream U/S	-26.25063	30.01307	Upstream within the Boesmanspruit tributary	25-Sept-02	25-Sept-02

During the data processing of the water quality chemical data, parameter values at concentrations below the laboratory detection limit were substituted with values half of the detection limit value to complete the data set. The abovementioned assumption was made for statistical and modelling purposes since the chemical species below detection can still be present in very low concentrations which can still cause reactions to occur. Data handling will further be addressed in Chapter 5.

4.3.1.1 Quality Assurance and Quality Control analysis (QA/QC)

This section presents the reliability assessment of the external data sets. As mentioned earlier, the main objective of the QA/QC was to identify possible sampling and laboratory errors and to provide the basis for future validation and use of the analytical data in order to interpret the results correctly.

4.3.1.1.1 *Charge balance*

Charge balance was used to assess the analytical quality of the external data sets. Chemical analysis of all water samples was evaluated for charge balance using the GWB software package. Of all the samples (n=1663) 92.36% displayed an ion balance error of <10%.; furthermore, 79.25% of these samples displayed an ion balance error <5%.

4.3.2 Mineralogy properties and whole-rock and near-total solid phase elemental analysis (XRD and XRF)

As mentioned under section 4.2.2, mineralogical and geochemical information is an essential component of mine drainage chemistry prediction because mineralogical properties determine the physical and geochemical stability and relative weathering rates of geologic materials under different weathering conditions (Price, 2009). This information serves an important input to the geochemical models and for the interpretation of the ABA results.

The same samples that were used for ABA and NAG tests were submitted to the University of the Free State's Department of Geology, with the request that it be investigated mineralogically and chemically. X-ray fluorescent spectrometry (XRF) and X-ray diffractometry (XRD) analyses were performed. The results are presented and discussed in Chapter 6 of this dissertation.

4.3.3 Sulphur speciation data

As stated before, the collected solid samples were used to mix representative composite samples for each of the coal discard dumps. Five samples (four composite samples representing the four coal discard dumps, and the coal material sampled from the Susanna hanging wall) were submitted to Metron Loboratory with the request that it be investigated for sulphur species. The Elemental Analyser: Eltra technique was used during the %C and %S analyses. The objective in sulphur analysis was to identify and measure the concentration and composition of different sulphur species with sufficient accuracy and precision which is important for the

calculation of AP. The results are presented and discussed in Chapter 6 (Table 6-5) of this dissertation and was used to aid in the interpretation of the ABA results.

4.4 DATA ANALYSIS

4.4.1 Application of statistics during water quality data evaluation

According to Zhang and Selinus (1998) questions regarding the probability distribution, mean calculation, correlation, outlier detection and differentiation between anthropogenic influenced and natural background values may be asked when evaluating environmental geochemical data. Statistical assessments do not necessarily establish cause-and-effect relationships but do present the information in a condensed format as an initial step in complete data analysis. Statistical associations may further assist in generating hypothesis for the interpretation of hydro-chemical processes (Guler *et al*., 2002).

The application of statistics in this study was limited to evaluating the distribution characteristics of individual variables measured or analysed. The physical and chemical properties were evaluated using central tendency (mean, median, and standard deviation) assuming the data were normally distributed or lognormally distributed. Supplementary descriptive statistics applied to selected variables included calculations for the minimum, maximum, 5th percentile, 95th percentile and coefficient of variance (COV%) to evaluate the variability of a certain variable. Statistical and graphical analyses were done using Microsoft Excel 2016 (Microsoft Corporation, 1985). Microsoft Excel 2016 was further used to show graphical displays of the data as line graphs (time series analysis) and box-and-whisker plots. The application of statistics on the acquired and external data sets are further discussed in Chapter 5.

4.4.2 Hydrogeochemical characterisation

The acquired and external data sets were analysed by means of standard hydro-chemical descriptive plots (Piper -and Durov plots) to depict the major ion chemistry and to classify the water into set water types. The GWB student software package was used to show graphical displays of the major ion chemistry by means of Piper -and Durov plots and Stiff diagrams.

The data sets included parameters that do not match the input values needed for GWB and thus ortho-PO_4 (P) was converted to the pure ion form HPO_4^-. Laboratory results further reported As, B and Si concentrations that were converted to $As(OH)_4$, $B(OH)_3$ and SiO_2, respectively, for aqueous geochemical modelling and analysis reasons.

4.5 GEOCHEMICAL MODELLING

Equilibrium thermodynamic applications in the form of kinetic numerical geochemical models were used to quantify the identified risks posed by the mine waste components and evaluate long-term mine waste drainage

stability. The specific assumptions and information regarding the development and setup of the forward reaction path models are comprehensively discussed in Chapter 8 of this dissertation. The GWB commercial software package developed by Bethke (1996) was used for all modelling purposes.

4.6   CONCLUDING SUMMARY

In summary, Chapter 4 describes the main data sets used and test methods performed during this study. Data sets and methods described in this chapter contributed to the hydrogeochemical characterisation of the study area and the geochemical characterisation of the mine waste, which were the main objectives during data acquisition and tests performed.

Various data sets, which include external water quality data sets were made available during this study. Detailed water monitoring -and sampling programmes were undertaken during hydrocensus surveys and additional field campaigns. Focus areas included the underground compartments, coal discard dump monitoring boreholes and farms situated in the area of interest. Sampling mainly included:

- Stratified sampling from underground stored water;

- sampling from underground compartment discharge points (decants);

- sampling from water monitoring boreholes;

- sampling from boreholes and surface water sources situated on farms in the Union Colliery area.

Results obtained from water chemical analyses following the sampling exercises augmented the existing water quality database.

Sampling of solid materials for geochemical assessment during this study included:

- Coal discard sampling from surface coal discard dumps;

- Coal roof sampling during drilling.

Collected solid samples were submitted to several accredited laboratories for mineralogical, chemical and sulphur speciation analyses. Static ABA and NAG tests were performed on the waste samples to evaluate the acid-generation potential of the coal discard dump material and the coal roof sample with the aim to contribute to the geochemical characterisation of the mine waste. Sulphur speciation data serve a complementary role in terms of the interpretation of the ABA and NAG results. Mineralogical data (XRD and XRF) will be used to specify mineral phases to be used as input mineralogical data in the forward reaction path models.

Data analysis included statistical applications that were limited to evaluate the distribution characteristics of individual variables measured or analysed. Therefore, central tendency and additional descriptive statistical variables were used to summarise the water quality data. The dominant hydro-chemical facies of the water were investigated by means of Piper -and Durov plots. The final tier of methodology performed during the study included kinetic geochemical modelling.

The main limitations identified from the specific methodology applied during this study include the following:

- Roof -and floor material of the different underground compartments (with the exception of the Susanna compartment) were not sampled due to the inaccessibility of adits and shafts.

- Seepage water from the coal discard dumps were not collected and analysed.

- Geochemical assessments to characterise the waste material were limited to static tests. Kinetic tests fell outside the scope of the study due to the associated long time-scales.

It can be concluded that field surveys together with laboratory geochemical assessment and characterisation are important to understand the processes dominant in the study area. This would serve as a constant guide during the development of the conceptual models and further provides crucial inputs to the geochemical models.

CHAPTER 5:

BASELINE HYDROGEOCHEMCAL CONDITIONS

This chapter presents hydrogeochemical characterisation of the groundwater, stream water and mine waters of the study area which comprises a critical part of the research framework. Methods for data analyses mainly included standard descriptive plots and univariate statistical tools. Chapter 5 focuses on the identification of baseline hydrogeochemical conditions for the groundwater, surface water and mine water regimes as well as the identification of spatial and temporal trends of the water physico-chemical parameters. Furthermore, the identification of non-compliant parameters and the possible underlying geochemical processes, which will be used as basis in developing the site conceptual models in Chapter 7, are also presented. Collectively, this information serves as an important baseline of environmental conditions at the Union Colliery for use in future environmental impact assessments and studies investigating anthropogenic development on and in the surrounding catchment region.

5.1   BACKGROUND

Reinmann and Garrett (2005) defines the term 'baseline' or often referred to as 'ambient background' in the context of measuring levels now so that future change can be quantified. It is further made clear that the term 'baseline' gives the impression that there is a single value, where in fact there are a range of values characterising any particular area or region. A range of values better reflects the heterogeneity of the environment. This is also supported by Darnley *et al*. (1995) who claimed that the 'baseline' should account for the inherent variability within a dynamic system, therefore reporting the baseline as a range rather than a single value is recommended.

Reinmann and Garrett (2005) established that to estimate baseline conditions the presence of, or complete absence of, anomalous samples or outliers, spatial scale, location, the kind of sample material, and why and for what purpose the 'baseline' is needed all must be considered. This fundamentally supports that no single background range exist for any one parameter in any sample material except for specific, often spatially local, instances. According to Reinmann *et al*. (2005) geochemical data are imprecise as it is associated with uncertainty that is unavoidably introduced at the time of sampling, during sample preparation and analyses. At each sample site a multitude of different processes will have an influence on the measured analytical value. These processes, to name a few, may include differences in parent material, topography, vegetation, climate, iron or/and manganese oxyhydroxides, content of organic material, grain size distribution, pH, mineralogy, and the presence of mineralisation or contamination.

Whilst the mining industry has traditionally used hydrogeochemical baselines for exploration, this study used baseline in the context of measuring and evaluating water quality now so that future change can be quantified (Reinmann & Garrett, 2005). The study area is too heterogeneous for a single baseline range to be scientifically

supportable, therefore baseline ranges were deduced for the respective groundwater, surface water and mine waters within the study area.

The external data sets as well as the supplementary data collected provide useful input to the baseline information required. However, the surveys undertaken at the Union Colliery often include analysis of only the major ions and/or samples prove to be poorly and inconsistently collected, so that incomplete and/or contradictory information was provided.

5.2 METHODS USED IN THIS RESEARCH

As mentioned in Chapter 4, two external data sets which contains macro -and micro water chemistry data from July 2012 to June 2017 and irregular and continuous monitoring of selected monitoring sites from 2000 to 2007 were provided and were used in this assessment. Additional sampling was carried out during the hydrocensus and additional field campaigns to augment the existing database, especially since the external data sets lacked certain trace elements.

The data collected during the hydrocensus and field campaigns as well as the data presented in the two external data sets were combined to make data handling and further analyses thereof easier. The combined database is presented in Appendix B: Water Quality Data and is provided on request. The final database contained 51 variables and 1 868 observations. However, not all observations have values for the same variable since the external data sets were compiled from different sources.

To estimate baseline conditions the location and the kind of sample and sample material need to be considered (Reinmann & Garrett, 2005). For this reason, the database was organised into four primary groups namely, groundwater in unmined areas, groundwater upstream and downstream of the coal discard dumps, surface water, and mine water. These groups inherently represent different hydrogeochemical areas or components within the study area and will be discussed separately in terms of water type characterisation, basic statistical analysis and time series analysis. The discussions are aimed to determine hydrogeochemical baseline ranges for each respective component within the study area.

5.2.1 Treatment of censored data and missing values

Environmental samples usually present concentrations below the detection limit (DL) of the analytical methods, yielding left-censored data sets, meaning that concentrations of some elements are reported as non-detected, less than or greater than values. Since metal(loid)s can pose environmental and human health threats even at trace level concentrations, the censored data should not be ignored or deleted from the data set. Censored data are however not appropriate for statistical analysis and must therefore be replaced with unqualified values (Farnham *et al*., 2002). In this case, concentrations reported as below the detection limit were replaced by half of the value of the lower detection limit (Lee *et al*., 2001).

The external data sets reported numerous zero concentration values, especially for alkalinity, iron and manganese, which were replaced by half of the detection limit values to avoid confusion.

5.2.2 Statistical data treatment

Basic descriptive statistical analyses were conducted to assess the distribution of the data for each specified area from which a baseline range water quality conditions could be inferred. As mentioned, the descriptive statistical assessment included calculations for the minimum, maximum, arithmetic mean, median, percentiles (5% and 95%), standard deviation and coefficient of variance (COV%) for selected variables. Note that not all 51 variables were included in this assessment. The inclusion of variables was based on the number of observations and the relevance to the current study. The descriptive statistical analyses were performed separately for each defined hydrogeochemical area and for the relevant variables to define baseline conditions.

According to Reinmann *et al*. (2005) the most important task in a geochemical study should always be to identify anomalous data points or outliers for the specific variables and to first understand the processes involved which may cause the high or low values. Apart from mineralisation and contamination, several quite different processes can cause outlier values. The recommended method by Hawkes and Webb (1962) to identify and isolate the uppermost outlier values of a variable is to determine the uppermost 2%, 2.5% or 5% of the data. The same method can be used to represent the lowermost outlier values. This approach is however not necessarily valid as the real percentage of outliers could be very different in reality. Nevertheless, in practice the percentile approach delivers a number of samples for further inspection that can easily be handled (Reinmann *et al.,* 2005). According to Reinmann *et al*. (2005) the 98th percentile of background data has been applied as a more sensible inspection threshold level by environmental legislators. However, the detection of data outliers and unusual data behaviour was not one of the main tasks during the statistical analysis of the hydro-chemical data in this study. Therefore, the 5th and 95th percentiles were used to define a baseline range that is resilient to extreme outlier values for selected variables for the different components.

As there was no background or pre-mining baseline values available for the specific site, the water quality data were compared to the SANS (241: 2015) drinking water guideline values to identify non-compliant parameters. Parameter concentrations of the mine void -and decant water were also compared to the groundwater quality baseline ranges observed in unmined areas (section 5.3.1.1) to indicate mineralisation or contamination

The box-and-whisker plot graphical method is presented in section 5.4. This method was used to graphically compare the variable parameter distribution for the different hydrogeochemical areas thereby gaining insight into the spatial data structure of the data sets. Box-and-whisker plots provide a graphical data summary relying solely on the inherent data structure and not on any assumptions about the distribution of the data. Besides outliers, it presents the median, inter-quartile range and non-outlier maximum and minimum values of a given data set (Azzie, 2002; Reinmann *et al*., 2005). Observations that were considered outliers, were excluded from the initial plots as the range shown was meant to be representative of typical concentrations for each hydrogeochemical area, so that comparisons can be made. Furthermore, where a particular hydrogeochemical area or component appeared to be an outlier, they were excluded from the inclusive box-and-whisker plots and plotted separately.

5.2.3 Geochemical evaluation

Water quality data of each hydro-chemical area were studied using the Piper diagram in order to determine the water type according with the major cations and anions present. Additionally, water quality data were studied using Durov diagrams to evaluate the distribution and degree of association between observations based on their pH and Total Dissolved Solids (TDS) concentrations.

5.2.4 Time series analysis

Time series water quality data are frequently used to monitor and assess changes in the quality of drainage from selected sites. To assess the seasonal fluctuations of selected variables (pH, sulphate [SO_4^{2-}], iron [Fe] and manganese [Mn]) within the specified hydrogeochemical areas, time series graphs for the reported monitoring periods were utilised. Although more local rainfall data was not available for the study area, daily rainfall data collected from the DWS Nooitgedacht Dam station (X1E003) from January 2000 to July 2017 (refer to section 3.5.2) were included in the time series graphs to augment visualisation of the seasonal fluctuation of the selected variables.

5.3 HYDROGEOCHEMICAL DESCRIPTION

According to Pitkanen *et al*. (2004) baseline hydrogeochemistry provide conditions for long-term geochemical stability, which is a requirement for safe long-term management strategies of the mine waste. The concept of hydrogeochemical evolution forms the basis to evaluate changes resulted from the underground mining activities, and finally, in evaluating hydrogeochemical conditions post closure. The establishment of reliable post-mining baseline conditions for the current mine water, groundwater and surface water is crucial for rigorous environmental assessments, comprehensive monitoring initiatives and well-informed stewardship of the region in the future.

Although generating hydrogeochemical baseline information, a major limitation of the current monitoring protocol implemented at the Union Colliery is that measurements and specific parameters analysed for were often singular. Only a few sampling positions provide a continuous time series of measurements and report seasonal and inter-annual variation in water quality. Furthermore, these momentary and sporadic observations have traditionally been water samples analysed to reveal traditional physical and chemical parameters, thus not incorporating certain trace element concentrations important during geochemical risk assessments at mines. Not only are these observations often limited in their temporal scope, but they also fail to reflect and integrate other relevant physical and chemical conditions of the mine water, groundwater and surface water crucial to defining its current state. The combination of these challenges has resulted in sparse baseline data, especially for several trace elements, available for assessment and comparison.

Additionally, the spatial positions of the monitoring stations, especially within the underground mine voids, are very limited in its distribution. There is a lack of monitoring stations located around the mine voids which

makes it almost impossible to determine and verify the impact of mine void water on the surrounding groundwater regime. Nevertheless, to aid in the assessment of baseline conditions for the groundwater, surface water, and mine water components, available groundwater, surface water and mine water monitoring data were analysed. Mine water monitoring refers to the monitoring of boreholes that were drilled to intersect the underground voids, and the specific decant points.

The following sub-sections aim to characterise each defined hydrogeochemical area based on observed water quality. Summaries for each defined hydrogeochemical area can be found under section 5.4.

5.3.1 Groundwater characterisation

In this section water quality data collected during the hydrocensus and additional field surveys together with acquired water quality monitoring data, that formed part of the pollution plume monitoring protocol implemented at the coal discard dumps, are evaluated.

5.3.1.1 Groundwater in unmined areas

The direction and extent of contaminant transport from the underground voids and coal discard dumps (refer to section 3.7) were considered during the selection of boreholes located around the mined areas that were assumed to be minimally affected by the mine water. The hydrocensus data thus include water quality of boreholes that is specifically located some distance away from the mined areas. Only four boreholes representative of groundwater conditions minimally affected by contamination were considered and include VIN1, BACK1, VA-H2, and PP.H1 (refer to Table 4-2).
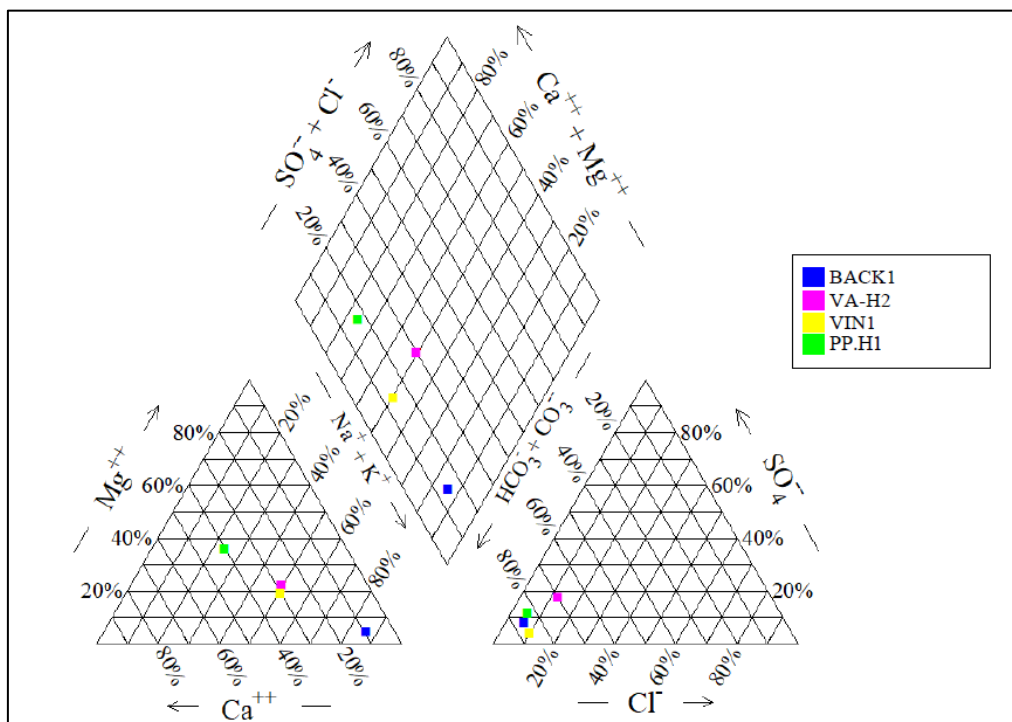
Figure 5-1: Piper diagram showing the hydro-chemical groundwater types in the unmined areas.

The order of abundance of the major ions in most collected groundwater samples are $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $HCO_3^- > SO_4^{2-} > Cl^-$ (Figure 5-1). Therefore, the principal water facie of the groundwater sampled in areas located some distance away from the underground operations is Na-HCO_3 (75% of the samples). This type of water is typical for shallower portions of regional confined aquifers and waters deduced to have been affected by ion exchange (Younger, 2007). The major cations in the borehole samples are sodium [Na^+] and calcium [Ca^{2+}] with predominant bicarbonate [HCO_3^-] anions. As mentioned, the former is typical of ambient groundwater in Karoo sediments which have been affected by ion exchange.
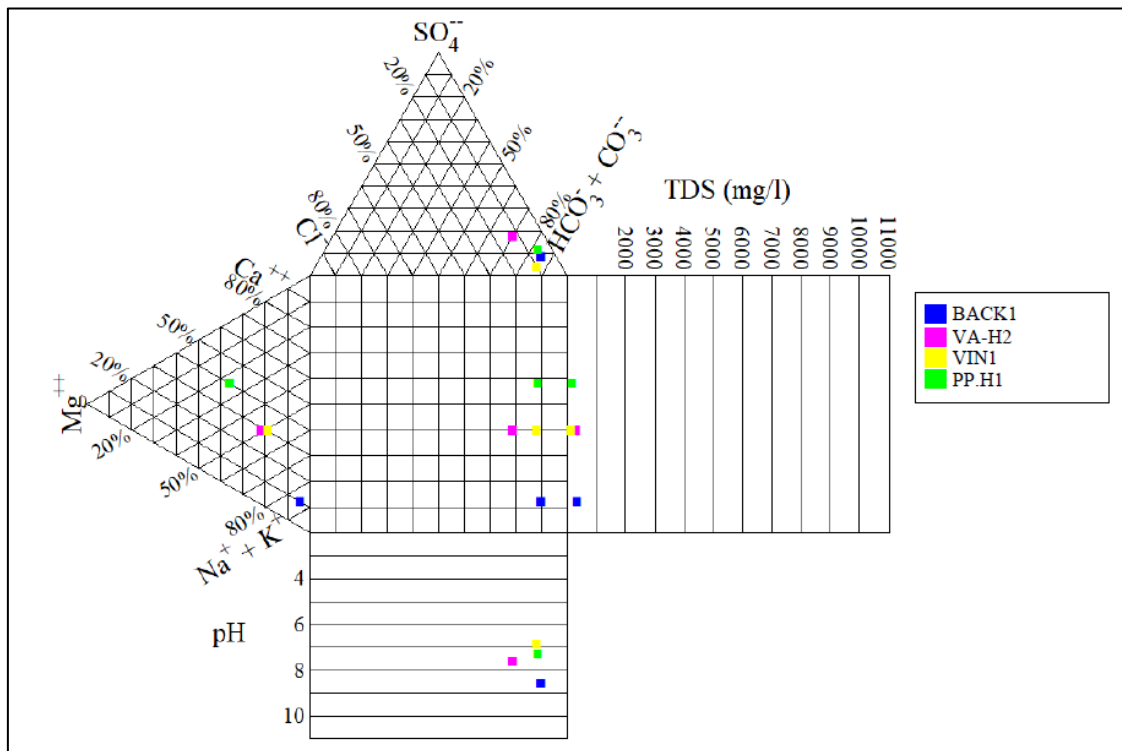
Figure 5-2: Durov diagram showing the pH and TDS distribution for groundwater in the unmined areas.

The Durov diagram of the sampled groundwater (Figure 5-2) shows that the TDS is <1 000 mg/L for all samples and the pH is >6.0 for all samples.

Table 5-1 reports summary statistics of the hydrocensus groundwater data in comparison to the SANS (2015) drinking water quality guidelines.

The pH measured in the groundwater samples ranges between 6.87 to 8.59 (can also be depicted from Figure 5-2) which characterises circum-neutral to alkaline groundwaters. Due to the circum-neutral to alkaline nature of all observations, associated metal concentrations are very low. The data presented in Table 5-1 shows that the salinity is dominated by alkalinity [CO_3^{2-}/HCO_3^-], sodium [Na^+], sulphate [SO_4^{2-}], calcium [Ca^{2+}], and magnesium [Mg^{2+}]. All variables are within the accepted guideline values.

Table 5-1: Summary descriptive statistics of the major and trace ions detected in hydrocensus boreholes, VIN1, PP.H1, VA-H2 and BACK 1; also shown in the table is the SANS (2015) drinking water quality guidelines (pH is in pH units, TDS and ion concentrations are in mg/L).

Parameter	n^e	n^c	Min	Max	Arithmetic mean	Median	5th Percentile	95th Percentile	Standard deviation	COV %	SANS guideline	% Above guideline
pH	4	0	6.870	8.590	7.598	7.465	6.936	8.445	0.632	8.318	≥5 and ≤9.70	0
TDS	4	0	145.000	354.000	242.216	234.932	146.828	347.801	92.386	38.142	≤1200	0
Ca	4	0	9.200	25.432	16.181	15.046	9.635	24.316	6.210	38.378	-b	0
Mg	4	0	2.500	11.810	7.164	7.174	2.815	11.500	3.761	52.498	-b	0
Na	4	0	10.916	90.400	41.982	33.306	12.174	83.937	31.033	73.920	≤200	0
K	4	0	2.539	6.700	5.171	5.722	2.930	6.640	1.623	31.391	-b	0
Total Alkalinity	4	0	90.700	213.000	140.725	129.600	91.525	205.500	50.509	35.892	-b	0
F	4	0	0.025	0.590	0.232	0.156	0.037	0.532	0.216	93.349	≤1.50	0
Cl	4	0	4.579	20.637	10.812	9.015	4.984	19.154	6.080	56.235	≤300	0
$NO_3(N)$	4	1	0.025	0.495	0.265	0.270	0.041	0.482	0.193	73.010	≤11	0
$NH_3(N)$	4	2	0.025	0.970	0.381	0.265	0.047	0.879	0.360	94.446	≤1.50	0
SO_4	4	0	3.800	38.149	18.433	15.892	5.118	35.307	12.626	68.494	≤250*	0
Al	4	0	0.029	0.191	0.074	0.039	0.029	0.169	0.068	91.104	≤0.30	0
Fe	4	2	0.010	0.246	0.098	0.069	0.010	0.228	0.098	99.507	≤0.30*	0
Mn	4	3	0.010	0.024	0.014	0.010	0.010	0.022	0.006	45.848	≤0.10*	0
As	4	4	0.005	0.005	0.005	0.005	0.005	0.005	0.000	0.000	≤0.01	0
Ba	4	0	0.022	0.183	0.108	0.113	0.026	0.182	0.073	67.450	≤0.70	0
Cr	4	4	0.010	0.010	0.010	0.010	0.010	0.010	0.000	0.000	≤0.05	0
Co	4	4	0.010	0.010	0.010	0.010	0.010	0.010	0.000	0.000	≤0.05	0
Cu	4	4	0.005	0.009	0.007	0.007	0.005	0.009	0.002	21.510	≤2	0
Ni	4	4	0.010	0.010	0.010	0.010	0.010	0.010	0.000	0.000	≤0.07	0
Pb	4	4	0.004	0.008	0.007	0.008	0.005	0.008	0.002	22.876	≤0.01	0
Se	4	4	0.010	0.010	0.010	0.010	0.010	0.010	0.000	0.000	≤0.01	0
Zn	4	2	0.010	0.045	0.022	0.017	0.011	0.041	0.013	60.236	≤5	0
Si	4	0	11.679	21.676	15.210	13.743	11.913	20.562	3.844	25.269	-b	0

e – Number of observations; c – Number of observations below detection; b – No established guideline value; * - Aesthetic guideline value

5.3.1.2   Coal discard dump monitoring boreholes

Monitoring boreholes located upstream (BD01/02 and UN04/02) and downstream (BD02/02, BD03/02, UN01/02, UN02/02, UN05/02, and UN06/02) of the coal discard dumps (shown spatially in Figure 4-1) were hydrogeochemically assessed. The assessment was aimed to deduce baseline conditions for upstream (U/S) and downstream (D/S) groundwater conditions thereby also reflecting the possible influence of contaminant leaching from the coal discard material on the downstream groundwater regime. Note that BD03/02 and UN05/02 are located further downstream of the coal discard dumps and were grouped accordingly in Figure 5-3 and Figure 5-4. The reader is referred to Table 4-7 for the description and location of the monitoring boreholes.
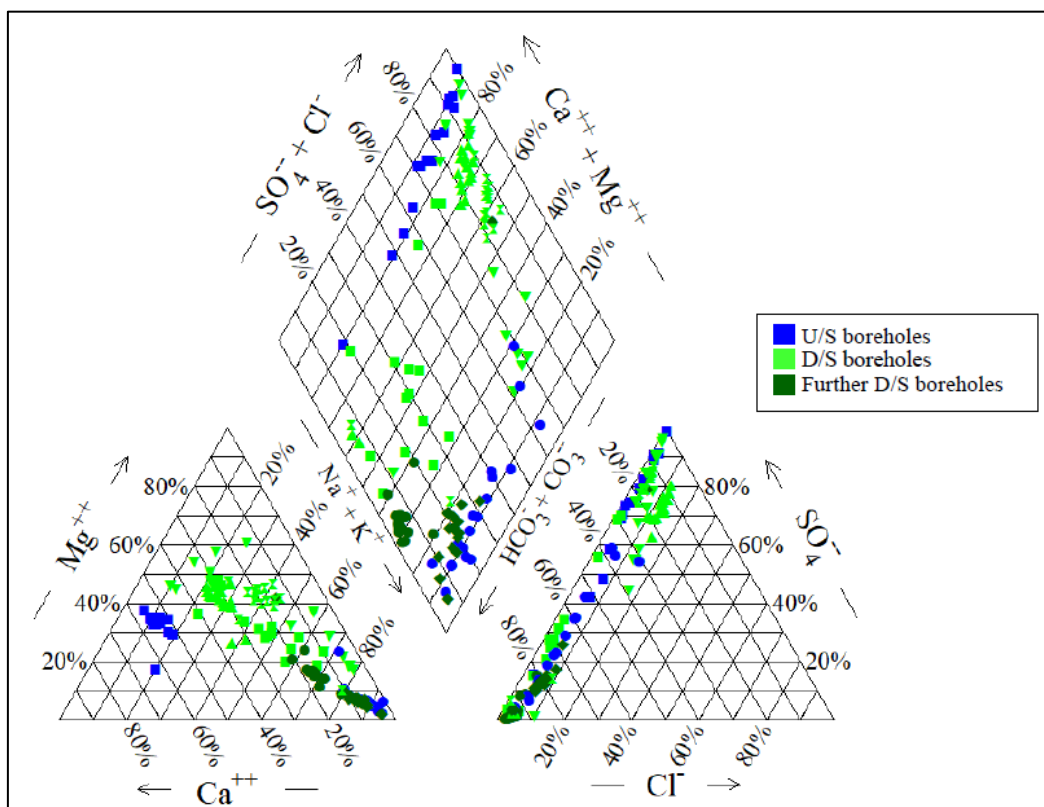
Figure 5-3: Piper diagram showing the hydro-chemical groundwater types for the coal discard dump monitoring boreholes.

The order of abundance of the major ions in most collected upstream groundwater samples are $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $HCO_3^- > SO_4^{2-} > Cl^-$ (Figure 5-3). The principal water facies of the upstream groundwater samples are therefore Na-HCO$_3$ (45% of the upstream samples) and Ca-SO$_4$ (36% of the upstream samples). The major cations in the upstream borehole samples are sodium and calcium with either predominant bicarbonate or sulphate ions. The dominance of bicarbonate in the water originates from the dissolution of carbonate minerals from the host rocks. As mentioned earlier, Na-HCO$_3$ type is the typical water type for shallower portions of regional confined aquifers and waters deduced to have been affected by ion exchange, whereas a Ca-SO$_4$ water type is representative of groundwaters affected by the oxidation of pyrite (Younger, 2007). The sulphate dominant waters thus reflect the influence of mining. It is evident that BD01/02, which is located upstream of the Black Diamond coal discard dump, display enrichment of sulphate ions, therefore

displaying predominant Ca-SO$_4$ type of water. When considering the location of BD01/02 relative to the underground mine voids, it is possible that subsurface seepage from the eastern compartments may contribute to the elevated sulphate concentrations analysed for (refer to section 3.7). A few of the samples plot as Na-SO$_4$ (9% of the upstream samples) and Ca-HCO$_3$ (9% of the upstream samples) minor hydro-chemical types. Minor hydro-chemical groundwater types are probably a reflection of the mixing processes that occur as the groundwater evolves to the main Na-HCO$_3$ and Ca-SO$_4$ type (Gomo & Vermeulen, 2014).

The order of abundance of the major ions in most collected downstream groundwater samples are Na$^+$ > Mg^{2+} > Ca^{2+} > K$^+$ and HCO$_3^-$ > SO$_4^{2-}$ > Cl$^-$ (Figure 5-3). The principal water facies of the downstream groundwater samples are Na-HCO$_3$ (48% of all downstream samples) and Mg-SO$_4$ (34% of all downstream samples). The major cations in these borehole samples are sodium and magnesium with either predominant bicarbonate or sulphate anions. The increase of magnesium along the flow path may indicate dissolution of dolomite and clay minerals. The increase of sulphate ions in the directly downstream samples (indicated in light green in Figure 5-3) may be the consequence of sulphide mineral oxidation within the coal discard dumps. As will be discussed in Chapter 6 of this dissertation, the mineral pyrite constitutes the dominant sulphide bearing mineral in the mine waste. The products of sulphide oxidation are transported by infiltrating rainwater which then leach to the groundwater table and thus contributes sulphate along the flow path (Younger, 2007). The movement towards more sulphate dominating waters, especially in boreholes directly downstream of the coal discard dumps as shown by the Piper and Durov plots, are thus expected. The further downstream boreholes (indicated as dark green in Figure 5-3) seem to be less influenced and reflect a dominant Na-HCO$_3$ water type. Donovan *et al*. (1999), and Perry (2001) have reported that sodium increases substantially along mine affected water flow paths. Evolution from Ca^{2+}/Mg^{2+} dominated to Na$^+$ dominated water types along flow paths are very common. The latter may result from exchange of Ca^{2+} and Mg^{2+} for adsorbed Na$^+$ or it may be derived from weathering (Azzie, 2002). A few of the samples plot as Na-SO$_4$ (15% of all downstream samples) and Ca-HCO$_3$ (2% of all downstream samples) minor hydro-chemical types.
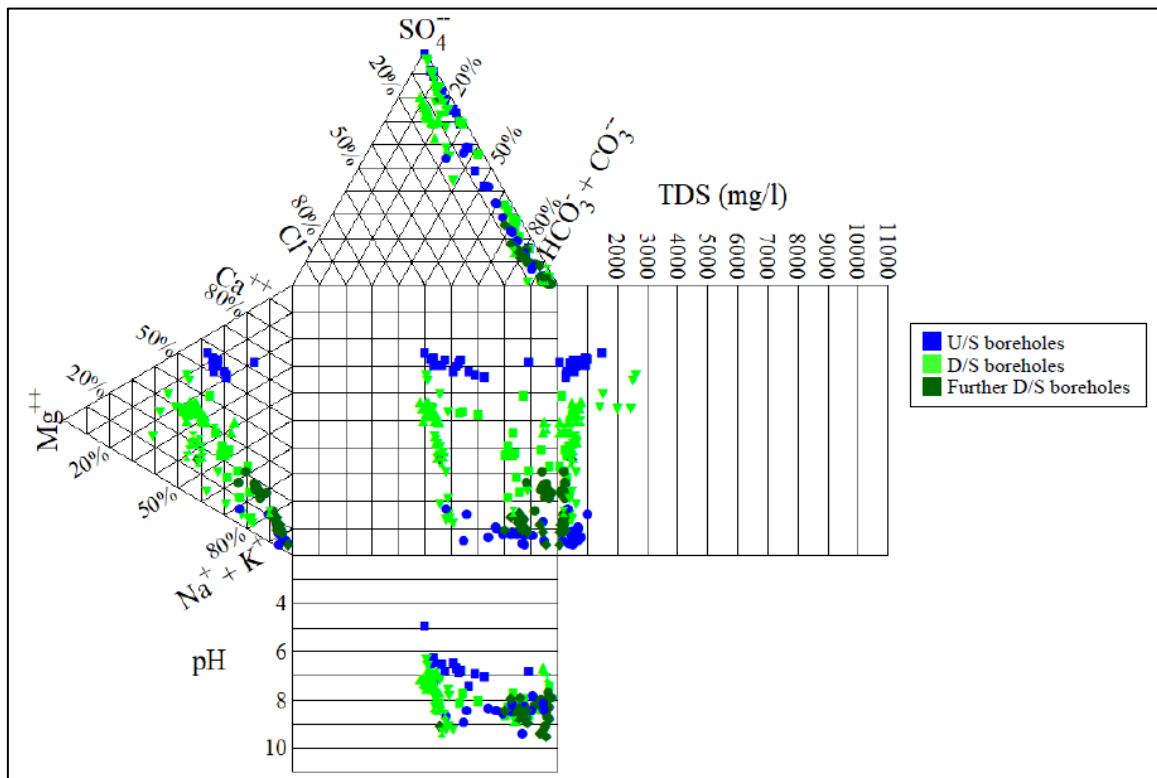
Figure 5-4: Durov diagram showing the pH and TDS distribution for the coal discard dump monitoring boreholes.

The Durov diagram of the groundwater samples (Figure 5-4) shows that the TDS is <1 000 mg/L for most samples and the pH is >6.0 for most samples.

Table 5-2 and Table 5-3 show summaries of the statistical assessments for the respective upstream and downstream groundwater data in comparison to the SANS (2015) drinking water quality guidelines.

The percentile pH range of the upstream groundwater samples is 6.38 to 8.82 which portrays circum-neutral to alkaline groundwaters. The percentile pH range of the downstream groundwater samples is 6.87 to 9.20 which indicate more alkaline groundwater conditions downstream of the coal discard dumps. As mentioned before, the dominance of bicarbonate in the water may originate from the dissolution of carbonate minerals present in the coal discard material and host rock sediments. This explains the circum-neutral to alkaline nature of the groundwater.

Almost all variables show significant variation as depicted by the coefficient of variation in percent (COV%). The only exceptions are the pH (13.24 and 8.77%, respectively for U/S and D/S conditions) and lead [Pb] (0%) which show very low variability to no variability at all. As explained by Horowitz and Elrick (1988) cation exchange capacity, surface charge, the presence of iron -and manganese oxides and hydroxides, as well as the concentrations of organic matter and clay minerals significantly influence the variability of trace element concentrations in sediments and groundwater.

Of the 25 variables included in the statistical assessment, 11 parameters exceed regulation limits for drinking water. These parameters are the major constituents of concern to human health and the environment as a direct or indirect consequence of mining activites and related leaching of acid (AMD) or neutral mine drainage

products to the groundwater regime, and include pH (only U/S), TDS, sodium (only U/S), fluoride [F^-] (only U/S), nitrate [NO_3^-] (only D/S), ammonia [NH_3], sulphate, aluminium (only U/S), iron, manganese, and selenium.

Table 5-2: Summary descriptive statistics of the major and trace ions detected in upstream monitoring boreholes, UN04/02 (Union dumps) and BD01/02 (Black Diamond dump) the monitoring period; also shown in the table is the SANS (2015) drinking water quality guidelines (pH is in pH units and TDS and ion concentrations are in mg/L).

Parameter	n^e	n^c	Min	Max	Arithmetic mean	Median	5th Percentile	95th Percentile	Standard deviation	COV%	SANS guideline	% Above guideline
pH	33	0	4.970	9.450	7.664	8.140	6.378	8.816	1.015	13.241	≥5 and ≤9.70	3
TDS	30	0	280.000	1492.000	642.002	576.000	308.500	1001.500	257.084	40.044	≤1200	3
Ca	33	0	1.100	252.000	54.889	16.000	5.056	158.000	62.184	113.290	-^{b}	0
Mg	33	0	1.500	101.000	22.288	9.250	3.630	62.180	23.329	104.671	-^{b}	0
Na	33	0	12.183	266.000	108.518	128.598	16.720	237.200	84.057	77.459	≤200	18
K	33	0	3.302	11.900	6.243	6.070	4.339	10.840	1.962	31.423	-^{b}	0
Total Alkalinity	33	0	2.500	351.000	200.409	183.000	52.400	342.000	119.493	59.625	-^{b}	0
F	33	0	0.090	2.000	0.424	0.300	0.100	0.738	0.340	80.301	≤1.50	3
Cl	33	0	3.300	28.900	13.866	12.000	5.470	25.400	6.774	48.850	≤300	0
NO$_3$(N)	33	2	0.025	1.720	0.284	0.110	0.040	1.314	0.428	150.666	≤11	0
NH$_3$(N)	30	10	0.010	1.620	0.547	0.360	0.010	1.506	0.543	99.276	≤1.50	7
SO$_4$	33	0	10.200	969.000	233.021	141.000	18.098	616.000	224.739	96.446	≤250*	36
Al	33	5	0.005	0.160	0.060	0.060	0.008	0.134	0.039	65.587	≤0.30	0
Fe	33	8	0.005	9.700	0.587	0.080	0.005	2.600	1.728	294.349	≤0.30*	21
Mn	33	12	0.005	2.550	0.423	0.020	0.005	1.662	0.639	151.066	≤0.10*	42
As	5	5	0.005	0.010	0.007	0.005	0.005	0.010	0.002	34.993	≤0.01	0
Ba	5	0	0.034	0.201	0.127	0.124	0.051	0.192	0.055	43.323	≤0.70	0
Cr	5	5	0.003	0.010	0.006	0.003	0.003	0.010	0.003	59.126	≤0.05	0
Co	4	3	0.003	0.025	0.008	0.003	0.003	0.022	0.010	119.911	≤0.05	0
Cu	5	4	0.002	0.010	0.004	0.003	0.002	0.009	0.003	70.556	≤2	0
Ni	5	4	0.004	0.052	0.014	0.005	0.004	0.043	0.019	133.127	≤0.07	0
Pb	5	5	0.008	0.008	0.008	0.008	0.008	0.008	0.000	0.000	≤0.01	0
Se	5	4	0.003	0.030	0.010	0.003	0.003	0.026	0.010	106.710	≤0.01	20
Zn	5	5	0.004	0.018	0.010	0.009	0.004	0.017	0.005	51.114	≤5	0
Si	30	0	0.580	17.300	7.301	3.415	0.658	16.220	5.811	79.584	-^{b}	0

^{e} – Number of observations; ^{c} – Number of observations below detection; ^{b} – No established guideline value; * - Aesthetic guideline values

Table 5-3: Summary descriptive statistics of the major and trace ions detected in downstream monitoring boreholes, UN01/02, UN02/02, UN05/02, UN06/02 (Union dumps), BD02/02, and BD03/02 (Black Diamond dump) the monitoring period; also shown in the table is the SANS (2015) drinking water quality guidelines (pH is in pH units and TDS and ion concentrations are in mg/L).

Parameter	n^e	n^c	Min	Max	Arithmetic mean	Median	5th Percentile	95th Percentile	Standard deviation	COV%	SANS guideline	% Above guideline
pH	97	0	6.290	9.580	8.128	8.160	6.870	9.196	0.713	8.775	≥5 and ≤9.70	0
TDS	86	0	148.000	2448.000	475.579	422.000	214.291	805.500	355.148	74.677	≤1200	5
Ca	97	0	2.203	353.676	37.310	20.500	4.664	131.839	56.740	152.076	-^{b}	0
Mg	97	0	0.820	225.977	33.942	19.300	2.438	136.135	43.941	129.461	-^{b}	0
Na	97	0	12.000	165.000	65.409	64.600	36.426	107.600	23.671	36.189	≤200	0
K	97	0	1.182	38.024	8.308	5.653	2.509	19.680	6.876	82.763	-^{b}	0
Total Alkalinity	97	0	44.000	444.000	129.133	135.000	49.600	219.400	69.153	53.552	-^{b}	0
F	97	1	0.008	0.590	0.239	0.250	0.094	0.410	0.118	49.242	≤1.50	0
Cl	97	0	1.780	47.500	14.874	9.990	3.530	41.860	12.107	81.398	≤300	0
NO$_3$(N)	97	4	0.025	11.240	0.416	0.080	0.050	0.916	1.508	362.586	≤11	1
NH$_3$(N)	86	23	0.090	43.200	1.021	0.390	0.100	1.500	4.605	450.822	≤1.50	6
SO$_4$	97	0	0.100	1848.000	219.697	99.700	1.478	912.580	339.593	154.574	≤250*	36
Al	97	15	0.005	0.510	0.070	0.050	0.010	0.210	0.081	115.953	≤0.30	3
Fe	97	22	0.005	7.554	0.288	0.073	0.005	1.237	0.869	301.928	≤0.30*	14
Mn	97	42	0.004	0.710	0.127	0.020	0.005	0.562	0.193	151.539	≤0.10*	31
As	17	17	0.005	0.010	0.007	0.005	0.005	0.010	0.002	35.322	≤0.01	0
Ba	17	1	0.010	0.494	0.110	0.054	0.020	0.342	0.124	112.851	≤0.7	0
Cr	17	15	0.003	0.050	0.011	0.003	0.003	0.050	0.015	132.732	≤0.05	0
Co	17	17	0.003	0.010	0.005	0.003	0.003	0.010	0.004	69.635	≤0.05	0
Cu	17	15	0.002	0.010	0.004	0.003	0.002	0.010	0.003	63.673	≤2	0
Ni	17	17	0.005	0.015	0.007	0.005	0.005	0.013	0.003	44.381	≤0.07	0
Pb	17	17	0.008	0.008	0.008	0.008	0.008	0.008	0.000	0.000	≤0.01	0
Se	17	13	0.003	0.030	0.009	0.003	0.003	0.028	0.009	103.415	≤0.01	24
Zn	17	9	0.005	0.072	0.023	0.019	0.007	0.051	0.017	71.660	≤5	0
Si	86	0	0.340	23.500	6.861	4.550	0.423	17.750	6.784	98.878	-^{b}	0

^{e} – Number of observations; ^{c} – Number of observations below detection; ^{b} – No established guideline value; * - Aesthetic guideline values

The ranges of pH, sulphate, iron and manganese fluctuation throughout the monitoring period from 2012 to 2017 for the upstream and downstream boreholes are illustrated in Figure 5-5. As referred to before, groundwater upstream and downstream of the discard dumps shows a general pH range between 6.38 to 9.20. Upstream borehole, BD01/02, shows an outlier minimum pH value of 4.97 in the wetter months of 2014. Occasional releases of high metal concentration above the regulation limit, especially for iron and manganese, are observed in specifically upstream boreholes, BD01/02 and UN04/02, and downstream boreholes, BD02/02, UN01/02 and UN02/02. The occasional occurrence of high metal concentrations in the upstream boreholes might suggest influence from the underground operations through subsurface seepage, as mentioned earlier. According to Magombedze (2006), acidity, metal(loid) concentration, and levels of other contaminants generally tend to increase in the dry season with lower values and concentrations observed in the wetter months from October to March. Lower concentrations during the wetter months may be due to increased percolation of infiltrated rainwater to the groundwater table. Therefore, increased mixing and dilution along the flow path may occur. This is evident from the water quality data which displays elevated concentrations of sulphate, iron and manganese in the drier months, however higher concentrations are also observed in the wetter months. This may be indicative of the flushing out of built up oxidation products within the coal discard dumps after the first precipitation event, where after concentrations decrease due to mixing and dilution processes driven by further precipitation events and the circulation of shallow groundwater.
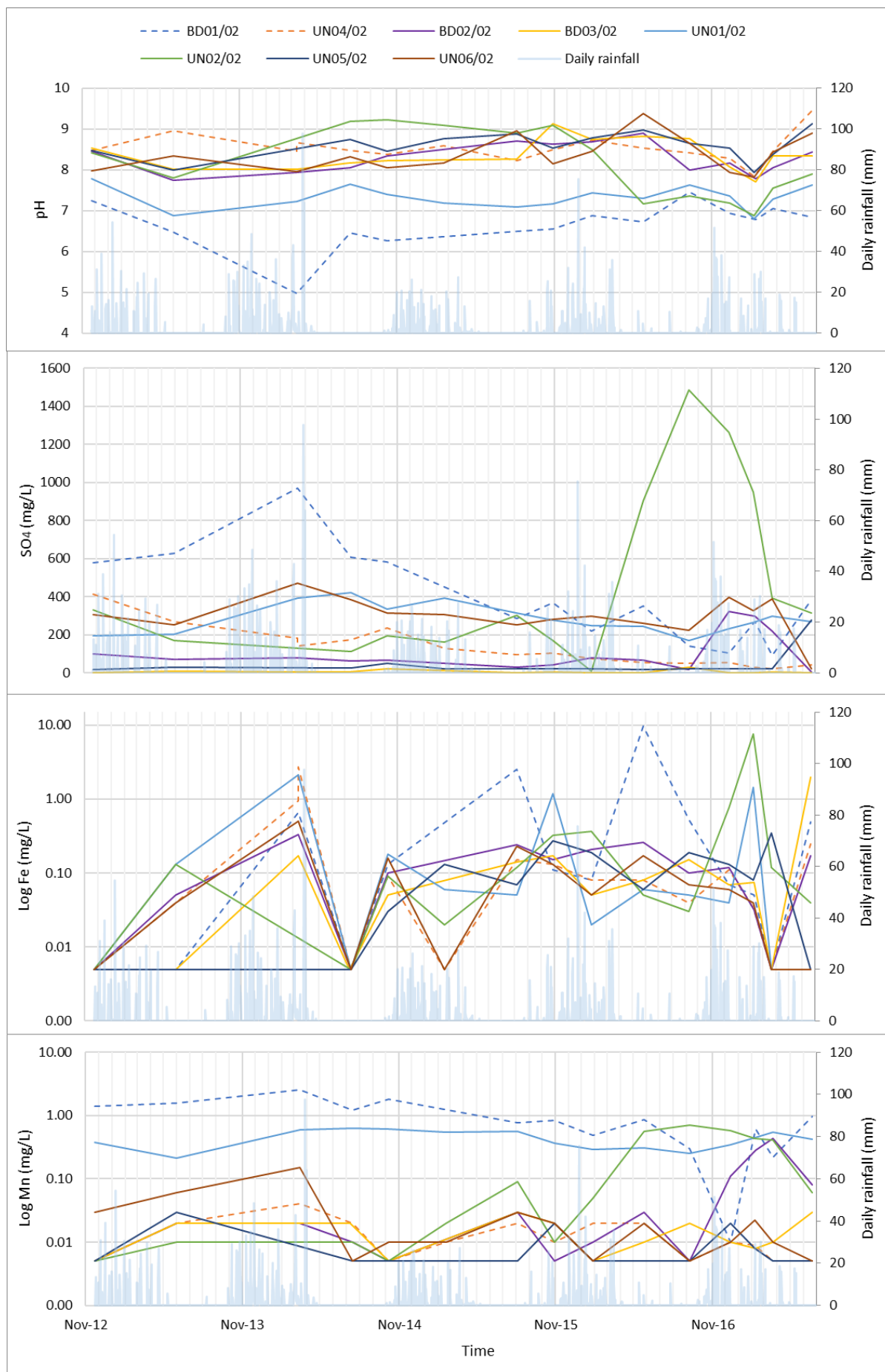
Figure 5-5: Measured groundwater quality upstream (dashed lines) and downstream (solid lines) of the coal discard dumps the monitoring period (2012 to 2017) together with the daily rainfall.

5.3.2   Surface water characterisation

In this section stream water quality data collected as part of the mine's monthly surface water monitoring protocol were assessed. The stream water quality data primarily includes chemical analyses of the surface water streams draining the area. Five sampling locations along the middle Vaalwaterspruit tributary and six sampling locations along the Boesmanspruit tributary were identified (refer to Table 4-7). These sampling locations include one upstream (No.1 Vaalwaterspruit), -and four downstream (Arcadia Dam, No.2 Vaalwater Spruit Middle U/S, No.3 Vaalwater Spruit Middle D/S, and G-Vaalwaterspruit D/S) sampling stations within the middle Vaalwaterspruit tributary. Note that G-Vaalwaterspruit D/S is located further downstream within the Vaalwaterspruit tributary and was grouped accordingly in Figure 5-6 and Figure 5-7. Two upstream (Reyeneke Dam and Union Stream U/S), -and four downstream (Union Spruit D/S, Dam Water D/S, Union V-notch and No.4 black Diamond V-Notch) sampling stations were grouped within the Boesmanspruit tributary. Sampling stations located downstream of an adit outflow (decant) were considered as downstream samples. The locations of the sampling points are spatially shown in Figure 4-7.

The water chemistry characterisation for the Vaalwaterspruit and Boesmanspruit tributaries are presented and discussed separately as to deduce the effects of the decant water and subsurface seepages from the underground voids on the respective stream quality.

5.3.2.1   Vaalwaterspruit
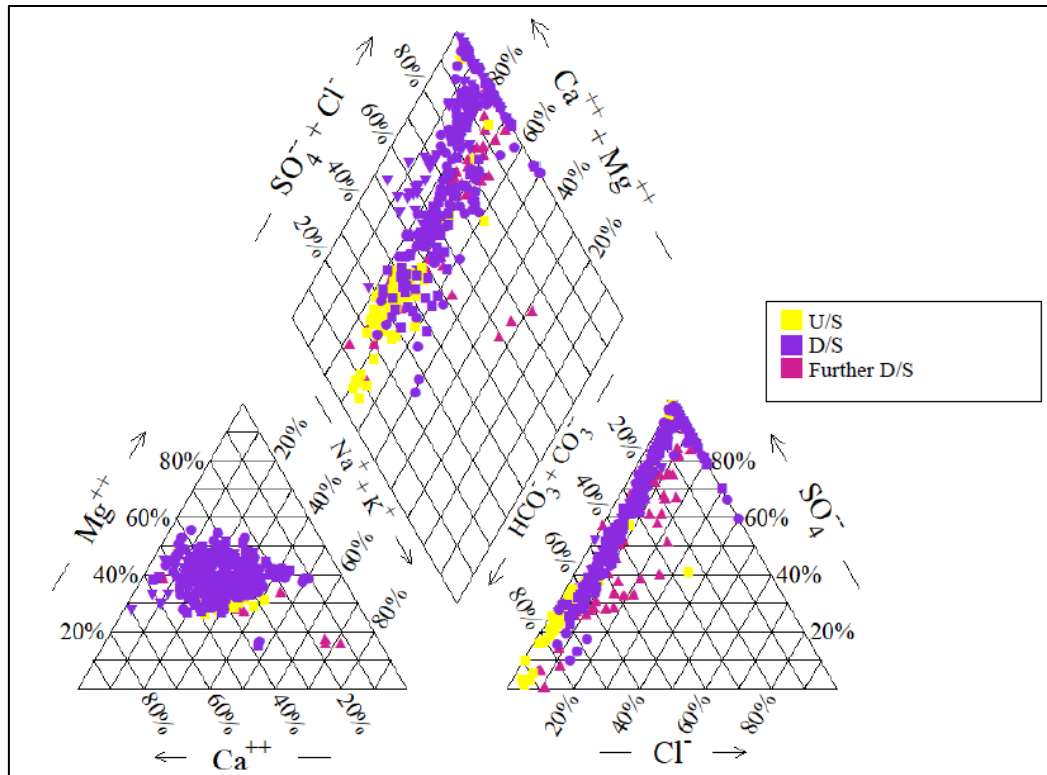
Figure 5-6: Piper diagram showing the hydro-chemical water types for the Vaalwaterspruit tributary.

The order of abundance of the major ions in most collected upstream surface water samples within the Vaalwaterspruit are $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ and $HCO_3^- > SO_4^{2-} > Cl^-$ (Figure 5-6). The major cations in the

surface water samples are calcium and sodium with predominant bicarbonate anions. Therefore, the principal water facie of the upstream water samples is Ca-HCO$_3$ (72% of the upstream samples). A few of the samples plot as Na-HCO$_3$ (11% of the upstream samples), Mg-HCO$_3$ (7% of the upstream samples), Ca-SO$_4$ (4% of the upstream samples), Mg-SO$_4$ (4% of the upstream samples), and Na-Cl (1% of the upstream samples) minor hydro-chemical types.

As the stream passes along the topographic depression between the eastern -and western underground operations, it is subjected to four adit outflows or decants (three originating from the eastern compartments and one from the western compartments). As expected, the water composition changes from a dominantly Ca-HCO$_3$ type to dominantly Mg-SO$_4$ (37% of all downstream samples) and Ca-SO$_4$ (34% of all downstream samples) types. A few of the downstream samples plot as Na-HCO$_3$ (5% of all downstream samples), Ca-HCO$_3$ (14% of all downstream samples), Mg-HCO$_3$ (7% of all downstream samples), and Na-SO$_4$ (4% of all downstream samples) water types. The closed, partially flooded mine workings on either side of the stream are expected to contribute sulphate and bicarbonate to the stream.
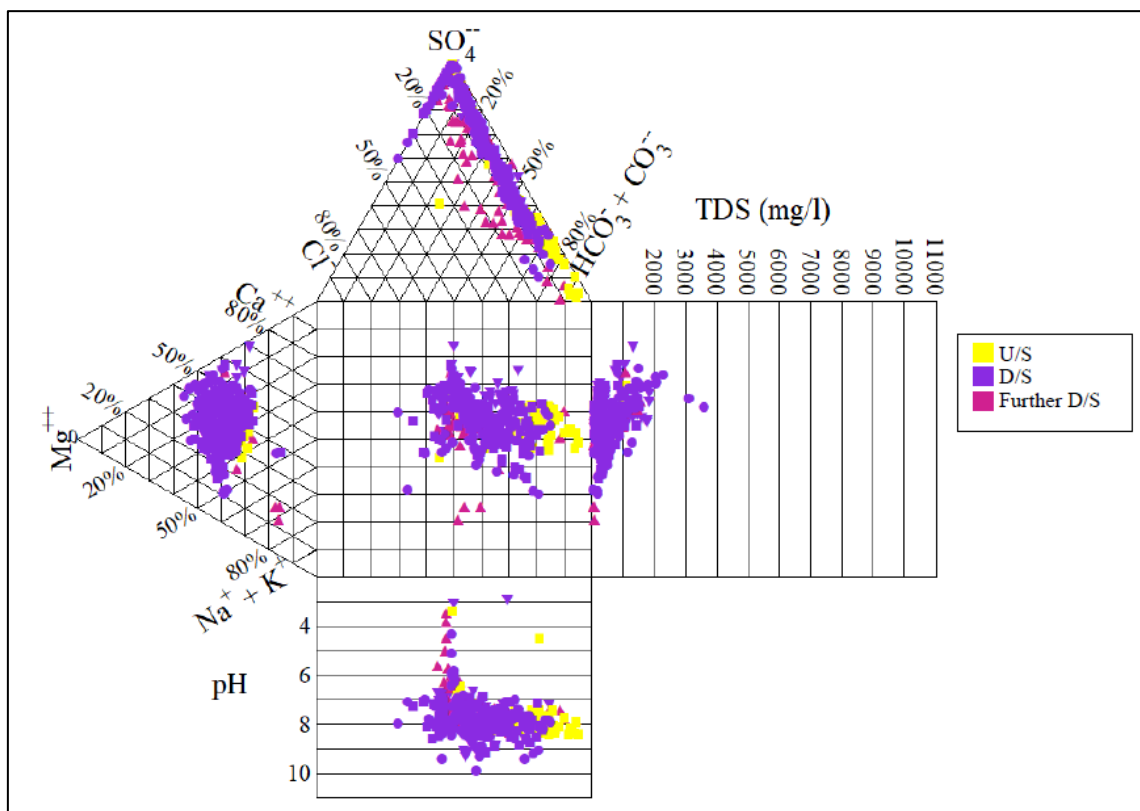
Figure 5-7: Durov diagram showing the pH and TDS distribution for the Vaalwaterspruit tributary sampling stations.

The Durov diagram of the surface water (Figure 5-7) shows that the TDS is <1 000 mg/L for all upstream samples and <2 000 mg/L for most downstream samples and the pH is >6.0 for most samples.

Table 5-4 and Table 5-5 show statistical summaries of the respective upstream and downstream surface water chemical analyses data. Also shown in the tables are the SANS (2015) drinking water quality guidelines to give an indication of non-compliant parameters.

The percentile pH range of the upstream conditions is 6.99 to 8.39 which portrays circum-neutral to alkaline stream waters, whereas the percentile pH range of the downstream samples is between 6.29 to 8.78. It is prevalent that the TDS increases downstream of the mine outflows and is reflected in the increased sulphate, calcium and magnesium concentrations.

Almost all variables show significant variation, as depicted by the COV%, except for the pH that shows very low variability for the respective upstream (9.75%) and downstream (11%) conditions. Of the 16 variables included in the statistical assessment, seven variables exceed regulation limits for drinking water. These parameters are the major constituents of concern in terms of risk and may occur as a direct or indirect consequence of the mining activities and related acidic and neutral mine drainage seepages and inflows. These include pH, TDS (only D/S), ammonia (only D/S), sulphate, aluminium, iron, and manganese.

Table 5-4: Summary descriptive statistics of the major and trace ions detected in an upstream monitoring station, No.1 Vaalwaterspruit the monitoring period; also shown in the table is the SANS (2015) drinking water quality guidelines (pH is in pH units and TDS and ion concentrations are in mg/L).

Parameter	n^e	n^c	Min	Max	Arithmetic mean	Median	5th Percentile	95th Percentile	Standard deviation	COV%	SANS guideline	% Above guideline
pH	71	0	3.400	8.440	7.934	8.160	6.990	8.390	0.773	9.748	≥5 and ≤9.70	3
TDS	49	0	180.000	944.000	537.918	522.000	416.000	788.000	123.762	23.008	≤1200	0
Ca	71	0	21.200	159.000	71.282	72.300	40.600	96.550	19.740	27.693	$-^b$	0
Mg	71	0	9.450	105.000	35.725	34.700	22.250	52.500	11.988	33.557	$-^b$	0
Na	71	0	11.600	100.000	55.183	53.500	24.800	85.600	16.622	30.121	≤200	0
K	71	0	1.140	16.700	5.737	4.920	2.640	12.150	2.896	50.482	$-^b$	0
Total Alkalinity	71	0	2.500	604.000	293.256	318.000	65.500	465.500	111.122	37.893	$-^b$	0
F	71	0	0.100	0.980	0.493	0.520	0.215	0.780	0.163	32.969	≤1.50	0
Cl	71	0	2.880	107.397	13.641	11.500	4.900	22.300	12.544	91.955	≤300	0
$NO_3(N)$	71	12	0.005	0.928	0.101	0.050	0.009	0.295	0.162	160.182	≤11	0
$NH_3(N)$	49	45	0.100	0.360	0.113	0.100	0.100	0.206	0.047	41.953	≤1.50	0
SO_4	71	0	9.190	806.000	131.792	111.000	21.800	266.500	112.036	85.010	≤250*	6
Al	71	27	0.005	7.000	0.190	0.040	0.005	0.410	0.825	434.538	≤0.30	8
Fe	71	15	0.005	0.690	0.135	0.090	0.007	0.423	0.152	112.532	≤0.30*	13
Mn	71	50	0.005	5.300	0.167	0.005	0.005	0.710	0.719	430.583	≤0.10*	10
Si	49	0	2.730	19.300	8.654	7.870	4.084	15.460	3.346	38.657	$-^b$	0

^{e} – Number of observations; ^{c} – Number of observations below detection; ^{b} – No established guideline value; * - Aesthetic guideline values

Table 5-5: Summary descriptive statistics of the major and trace ions detected in downstream monitoring stations, Arcadia Dam, No.2 Vaalwater Spruit Middle U/S, No.3 Vaalwater Spruit Middle D/S, and G-Vaalwaterspruit D/S the monitoring period; also shown in the table is the SANS (2015) drinking water quality guidelines (pH is in pH units and TDS and ion concentrations are in mg/L).

Parameter	n^e	n^c	Min	Max	Arithmetic mean	Median	5th Percentile	95th Percentile	Standard deviation	COV%	SANS guideline	% Above guideline
pH	345	0	2.890	9.900	7.687	7.810	6.290	8.776	0.845	10.998	≥5 and ≤9.70	2
TDS	135	0	116.000	2294.000	788.404	712.000	250.400	1584.400	445.123	56.459	≤1200	19
Ca	345	0	3.300	525.000	78.361	55.000	20.420	197.800	66.720	85.145	$-^b$	0
Mg	345	0	2.580	233.000	48.923	35.100	11.383	126.200	37.966	77.605	$-^b$	0
Na	345	0	4.010	267.000	41.466	39.300	11.060	82.460	27.286	65.805	≤200	0.29
K	345	0	0.009	45.400	8.145	6.740	2.386	18.665	5.749	70.590	$-^b$	0
Total Alkalinity	296	0	2.500	411.390	117.005	110.000	9.950	245.550	67.633	57.803	$-^b$	0
F	345	4	0.009	1.589	0.398	0.370	0.100	0.806	0.209	52.490	≤1.50	0.29
Cl	345	0	1.000	93.744	16.828	14.100	5.824	34.080	10.961	65.136	≤300	0
$NO_3(N)$	345	86	0.001	2.120	0.112	0.050	0.009	0.327	0.217	194.028	≤11	0
$NH_3(N)$	135	108	0.100	3.170	0.186	0.100	0.100	0.429	0.328	176.778	≤1.50	1
SO_4	345	0	0.970	2440.000	337.045	200.000	44.018	967.600	337.902	100.254	≤250*	43
Al	345	123	0.005	16.000	0.190	0.050	0.006	0.684	0.910	478.933	≤0.30	10
Fe	345	81	0.004	25.200	0.332	0.090	0.005	0.930	1.450	436.720	≤0.30*	21
Mn	344	220	0.005	33.000	0.711	0.005	0.005	3.900	2.603	365.898	≤0.10*	23
Si	135	0	0.100	13.500	3.536	3.000	0.489	8.288	2.717	76.833	$-^b$	0

^{e} – Number of observations; ^{c} – Number of observations below detection; ^{b} – No established guideline value; * - Aesthetic guideline values

The ranges of pH, sulphate, iron and manganese fluctuation throughout the monitoring period from 2000 to 2017 for upstream and downstream surface water conditions are presented in Figure 5-8. Note that the straight, dashed lines represent interpolated values.Several pH values below 5.0 are evident in especially downstream stations (Arcadia Dam, No.3 Vaalwater Spruit Middle D/S, and G-Vaalwaterspruit D/S) mostly in the wetter months between October and March and corresponds to elevated metal concentration. The increased concentration fluxes of especially sulphate, iron and manganese in the wetter months may be indicative of the flushing out of accumulated oxidation products from the mine voids with infiltrated rainfall water and shallow groundwater which subsequently enters the stream water. When dry conditions are re-established, contaminant loads are generally lower when compared to wet conditions due to reduced flow (Magombedze, 2006). However, when longer dry periods are permitted there is a continual build-up of pyrite oxidation products which may cause higher acidity in the leachates during a following precipitation event (Nordstrom, 1982). No.1 Vaalwaterspruit (upstream sampling station) also displays an outlier minimum pH of 3.4 in January 2017 that is further associated with increased sulphate and manganese concentrations. This may indicate the influence of mine sites located further upstream. Occasional releases of high metal concentration above the regulation limit, especially iron and manganese, are observed in specifically the downstream sampling locations.
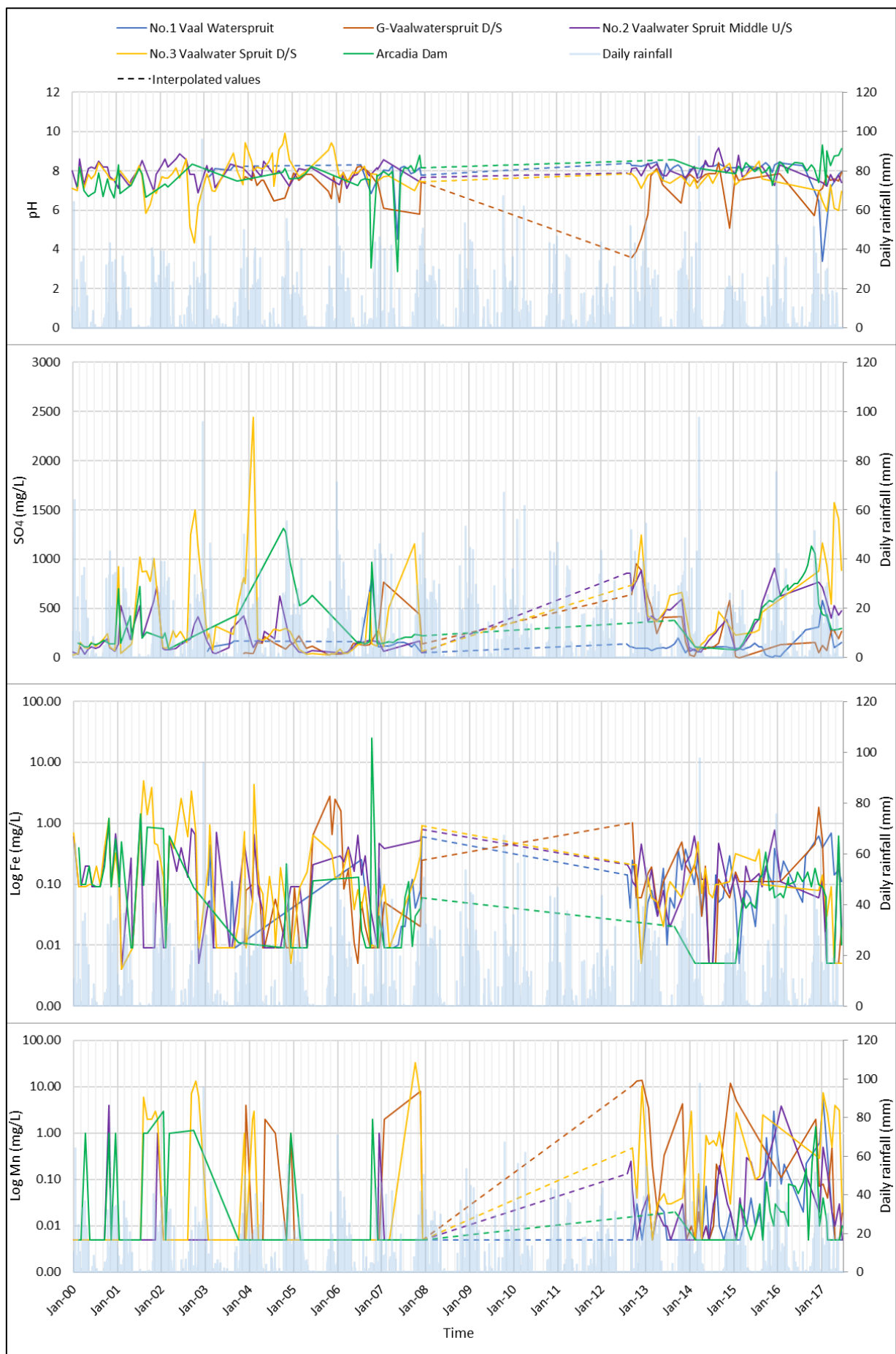
Figure 5-8: Measured surface water quality from the Vaalwaterspruit monitoring stations the monitoring period (2000 to 2017) together with the daily rainfall.

5.3.2.2   Boesmanspruit
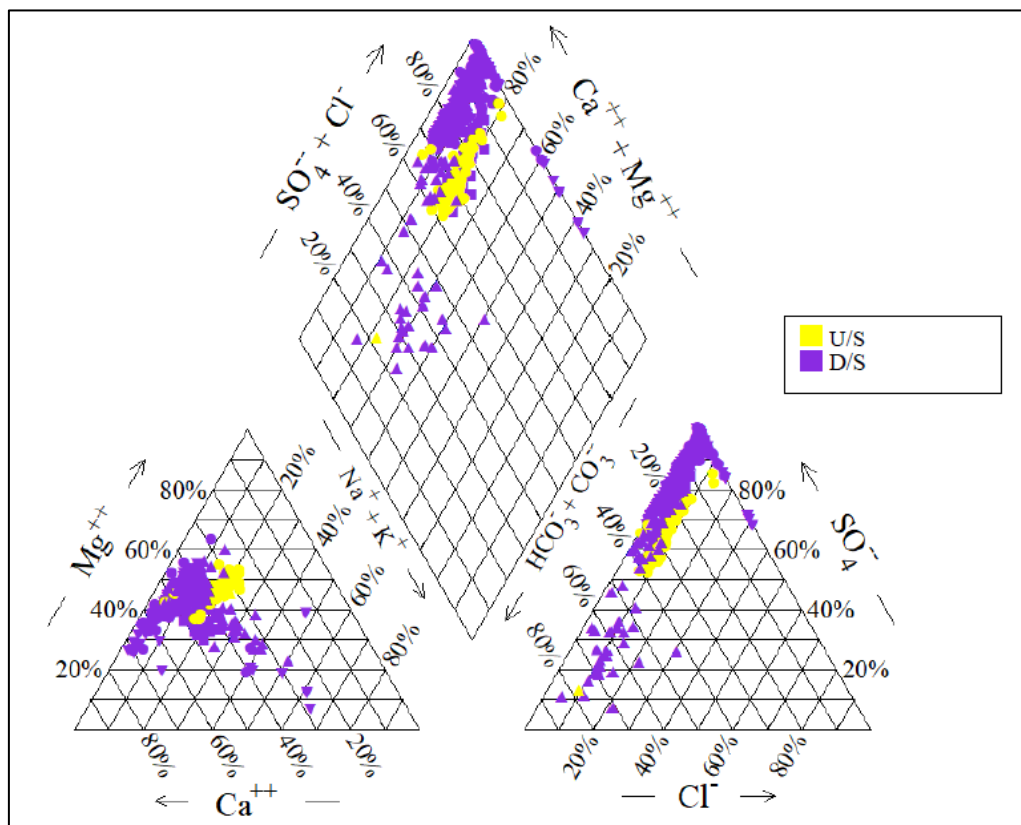
Figure 5-9: Piper diagram showing the hydro-chemical water types for the Boesmanspruit tributary.

The order of abundance of the major ions in most collected upstream surface water samples within the Boesmanspruit tributary are $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ and $SO_4^{2-} > HCO_3^- > Cl^-$ (Figure 5-9). The major cations in the surface water samples are calcium and magnesium with predominant sulphate anions. Therefore, the principal water facies of the upstream water samples are $Ca-Mg-SO_4$ (73% of the upstream samples) type. A few of the samples plot as $Mg-SO_4$ (17% of upstream samples), $Ca-SO_4$ (8% of the upstream samples) and $Mg-HCO_3$ (2% of the upstream samples) minor hydro-chemical types.

As the stream flows past the eastern underground operations it confluences with a smaller stream that contains water from two adit outflows (decants). As a result of this, the water composition changes to dominantly $Ca-SO_4$ (57% of the downstream samples) and $Mg-SO_4$ (36% of the downstream samples) water types. A few of the downstream samples plot as minor $Na-HCO_3$ (1% of the downstream samples), $Ca-HCO_3$ (3% of the downstream samples) and $Mg-HCO_3$ (2% of the downstream samples) types (Figure 5-9). The closed, partially flooded mine workings on the western side of the stream are expected to contribute sulphate and bicarbonate to the stream.
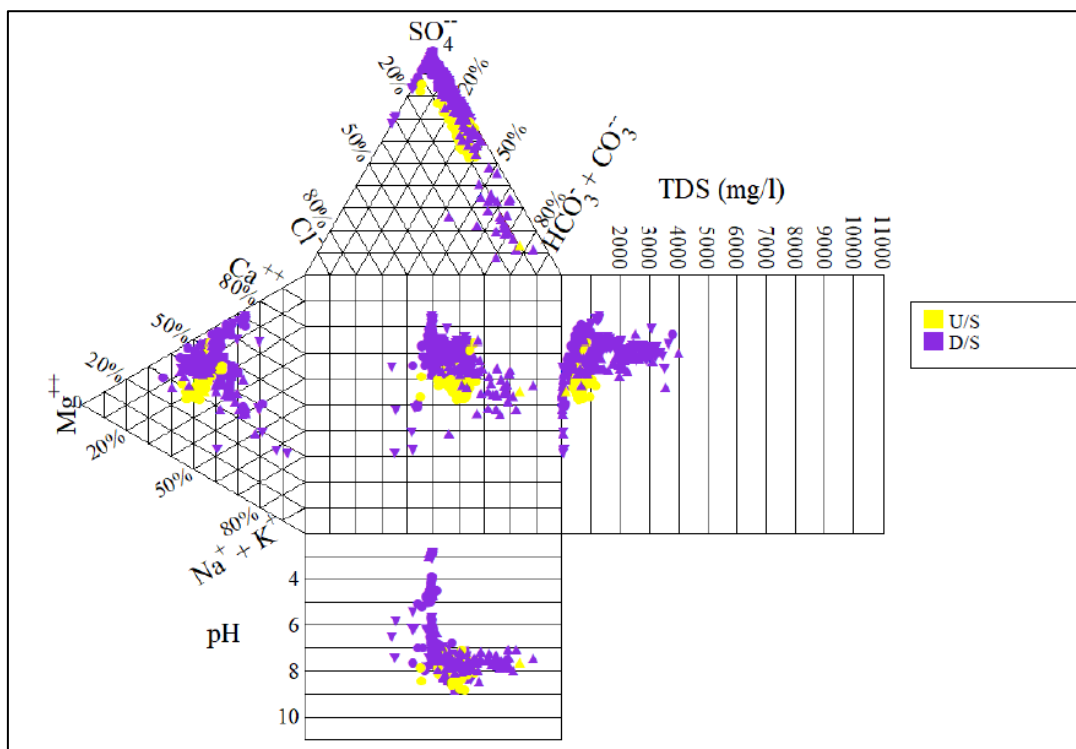
Figure 5-10: Durov diagram showing the pH and TDS distribution for the Boesmanspruit tributary sampling stations.

The Durov diagram of the surface water (Figure 5-10) shows that the TDS is <2 000 mg/L for all upstream samples and <3 000 mg/L for most downstream samples. The pH is >6.0 for all upstream samples. The pH distribution for the downstream samples ranges from acidic to alkaline, however most of the samples display a pH higher than 6.0.

Table 5-6 and Table 5-7 present summary statistics of the respective upstream and downstream surface water chemical analyses data in comparison to the SANS (2015) drinking water quality guidelines.

The percentile pH range of the upstream samples is between 7.54 to 8.63 which indicate circum-neutral to slightly alkaline stream waters. The downstream samples reflect a percentile pH range of 4.46 to 8.26. Surface water upstream within the Boesmanspruit tributary display a very small pH range, whereas the pH distribution in downstream conditions are much broader. Similar to the Vaalwaterspruit conditions, it is clear that the TDS increases downstream of the mine inflows and is mirrored in the increased sulphate, calcium and magnesium concentrations.

Almost all variables show significant variation, as depicted by the COV%. The only exception is the pH for the respective upstream (4.38%) and downstream (16.46%) conditions, that shows very small variabilities.

Of the 16 variables included in the statistical assessment, eight variables exceed regulation limits for drinking water. These parameters may indicate elevated concentrations as a direct or indirect consequence of AMD and related mining activities and present risks to the surrounding environment and threats to human health. These parameters include pH (only D/S), TDS, fluoride (only D/S), ammonia, sulphate, aluminium (only D/S), iron, and manganese.

Table 5-6: Summary descriptive statistics of the major and trace ions detected in upstream monitoring stations, Reyneke Dam and Union Stream U/S the monitoring period; also shown in the table is the SANS (2015) drinking water quality guidelines (pH is in pH units and TDS and ion concentrations are in mg/L).

Parameter	n^e	n^c	Min	Max	Arithmetic mean	Median	5th Percentile	95th Percentile	Standard deviation	COV%	SANS guideline	% Above guideline
pH	60	0	7.120	8.880	8.019	7.985	7.539	8.633	0.351	4.375	≥5 and ≤9.70	0
TDS	57	0	402.000	1206.000	637.263	596.000	472.800	986.800	160.204	25.139	≤1200	2
Ca	60	0	39.432	190.583	69.687	61.950	49.580	122.250	26.314	37.760	$-^b$	0
Mg	60	0	32.400	100.000	58.739	56.300	36.395	93.503	16.856	28.697	$-^b$	0
Na	60	0	12.000	70.100	37.734	35.900	24.006	59.285	11.549	30.607	≤200	0
K	60	0	4.985	37.800	11.689	11.150	7.460	18.100	4.464	38.191	$-^b$	0
Total Alkalinity	60	0	10.000	294.000	138.024	135.500	92.950	212.123	42.656	30.904	$-^b$	0
F	60	0	0.170	0.730	0.467	0.470	0.278	0.622	0.107	23.002	≤1.50	0
Cl	60	0	5.700	59.300	29.073	28.000	19.970	47.115	9.215	31.698	≤300	0
$NO_3(N)$	60	3	0.005	0.650	0.092	0.050	0.049	0.230	0.093	100.683	≤11	0
$NH_3(N)$	57	42	0.100	2.380	0.194	0.100	0.100	0.378	0.320	165.076	≤1.50	2
SO_4	60	0	36.000	675.000	300.800	263.000	180.700	523.150	111.978	37.227	≤250*	63
Al	60	10	0.005	0.290	0.079	0.075	0.005	0.151	0.056	71.115	≤0.30	0
Fe	60	10	0.005	1.140	0.098	0.065	0.005	0.234	0.150	153.411	≤0.30*	5
Mn	60	21	0.005	0.468	0.058	0.020	0.005	0.301	0.091	157.261	≤0.10*	13
Si	57	0	0.320	13.400	2.901	2.720	0.726	4.986	1.927	66.429	$-^b$	0

[e] – Number of observations; [c] – Number of observations below detection; [b] – No established guideline value; * - Aesthetic guideline values

Table 5-7: Summary descriptive statistics of the major and trace ions detected in downstream monitoring stations, Union V-notch, Dam Water D/S, Union Spruit D/S, and No.4 black Diamond V-Notch the monitoring period; also shown in the table is the SANS (2015) drinking water quality guidelines (pH is in pH units and TDS and ion concentrations are in mg/L).

Parameter	n^e	n^c	Min	Max	Arithmetic mean	Median	5th Percentile	95th Percentile	Standard deviation	COV%	SANS guideline	% Above guideline
pH	419	0	2.790	8.840	7.268	7.610	4.456	8.260	1.197	16.464	≥5 and ≤9.70	9
TDS	218	0	262.000	4016.000	1130.069	861.000	380.000	2414.400	692.056	61.240	≤1200	41
Ca	419	0	3.600	646.000	173.480	131.000	8.265	473.095	135.759	78.257	$-^b$	0
Mg	419	0	0.900	410.000	94.794	71.500	4.508	261.081	78.472	82.782	$-^b$	0
Na	419	0	1.000	158.000	27.678	22.502	5.935	65.299	18.701	67.566	≤200	0
K	419	0	0.178	65.000	10.452	6.010	1.654	37.530	10.930	104.565	$-^b$	0
Total Alkalinity	387	0	1.430	799.000	138.055	93.000	2.500	309.352	118.998	86.196	$-^b$	0
F	419	15	0.001	4.876	0.354	0.270	0.051	0.894	0.385	108.797	≤1.50	2
Cl	418	0	0.240	59.500	11.986	10.000	3.489	26.321	7.970	66.491	≤300	0
$NO_3(N)$	418	54	0.050	10.026	0.248	0.050	0.009	1.106	0.664	268.121	≤11	0
$NH_3(N)$	218	161	0.100	3.990	0.191	0.100	0.100	0.519	0.314	164.395	≤1.50	0.46
SO_4	419	0	3.070	2780.000	710.540	556.000	19.700	2081.000	596.412	83.938	≤250*	78
Al	419	118	0.005	62.730	0.990	0.082	0.005	6.168	4.203	424.730	≤0.30	15
Fe	419	96	0.004	47.500	1.058	0.090	0.005	1.775	4.979	470.666	≤0.30*	16
Mn	419	183	0.004	71.000	0.727	0.020	0.005	2.643	3.794	522.092	≤0.10*	34
Si	218	0	0.110	659.000	10.238	7.240	0.508	14.500	44.303	432.724	$-^b$	0

^{e} – Number of observations; ^{c} – Number of observations below detection; ^{b} – No established guideline value; * - Aesthetic guideline values

The ranges of pH, sulphate, iron and manganese fluctuation throughout the monitoring period from 2000 to 2017 for upstream and downstream surface water conditions are graphically shown in Figure 5-11. Several pH values below 5.0 is evident in especially downstream sampling stations (Union Spruit D/S, Union V-notch, and No.4 black Diamond V-Notch) mostly in the wetter months between October and March and corresponds to elevated metal concentration. Similar trends were observed in the Vaalwaterspruit. As mentioned before, the increased concentration fluxes of especially sulphate, iron and manganese in the wetter months may be indicative of the flushing out of accumulated oxidation products from the mine voids after precipitation events. The streams thus receive inflows enriched in oxidation products. As expected, when dry conditions are re-established, contaminant loads are lower when compared to the wet season conditions due to reduced flow.
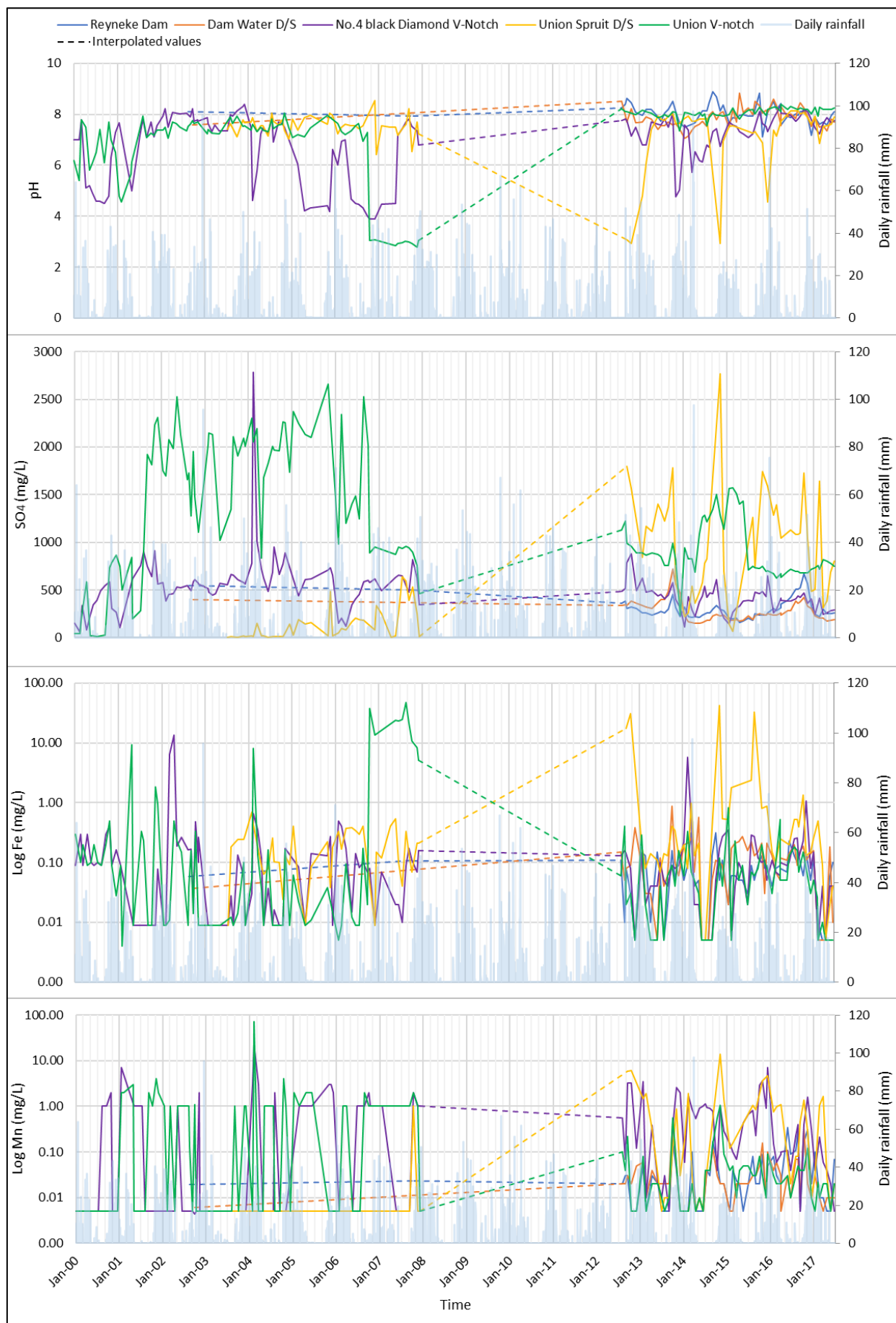
Figure 5-11: Measured surface water quality from the Boesmanspruit monitoring stations the monitoring period (2000 to 2017) together with the daily rainfall.

5.3.3 Mine water characterisation

In this section, water quality assessment for the underground mine void water and mine decant water are presented and briefly discussed. As mentioned in Chapter 3 of this dissertation, the mined area primarily comprises eastern and western operations. The eastern operations include two compartments, whereas the western operations include four compartments. For the purpose of this study water quality data from the different compartments in the respective eastern and western operations, was evaluated and discussed collectively. As mentioned before, the monitoring protocol implemented at the Union Colliery dictates monthly mine decant sampling and quarterly mine void sampling. Water chemical analyses data the whole monitoring period, from 2000 to 2017, were included in the assessments.

5.3.3.1 Eastern underground operations
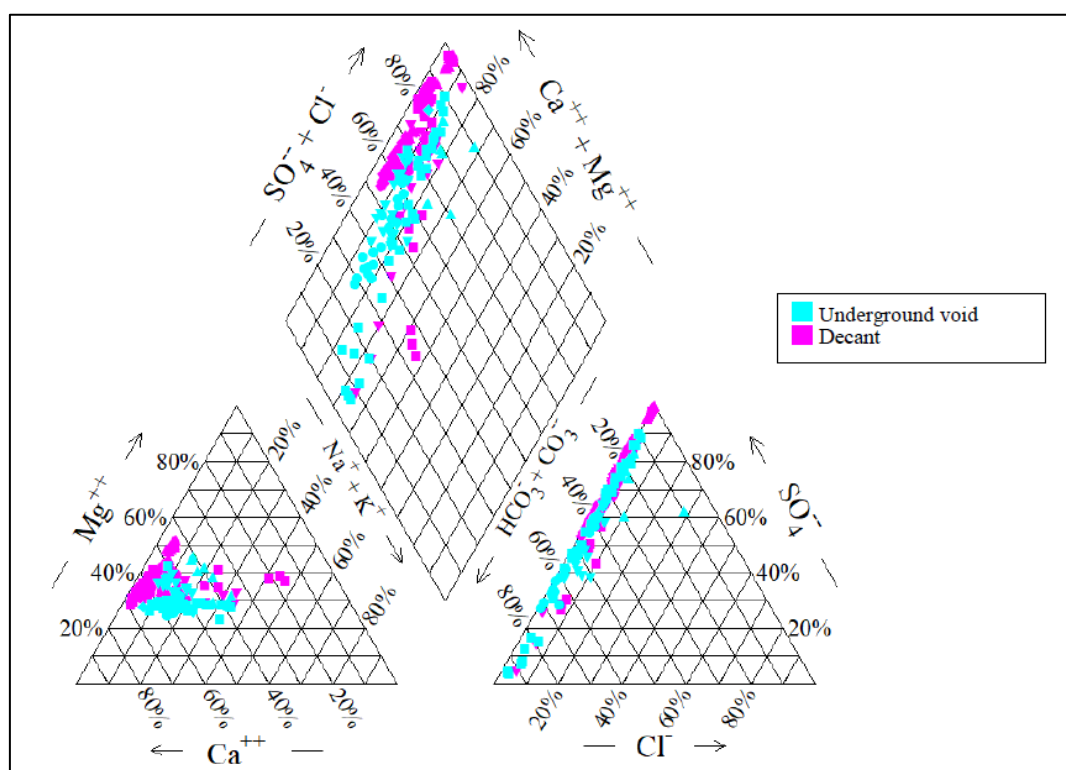
Figure 5-12: Piper diagram showing the hydro-chemical water types for the eastern underground operations.

The order of abundance of the major ions in most collected underground void water samples are $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ and $SO_4^{2-} > HCO_3^- > Cl^-$ (Figure 5-12). The major cations in the mine void water samples are thus calcium and magnesium, with either predominant bicarbonate or sulphate anions. Therefore, the principal water facies of the mine void water samples are $Ca-HCO_3$ (49% of the void samples) and $Ca-SO_4$ (44% of the void samples). A few of the samples plot as $Na-SO_4$ (1% of the void samples), $Mg-SO_4$ (5% of the void samples) and $Fe-SO_4$ (1% of the void samples) minor hydro-chemical types. Although iron is not included as a macro cation in the Piper diagram, the GWB software includes Fe^{2+} during the calculation of the ion balance error due to its significant concentration in certain samples (refer to section 4.3.1.1.1). This explains why 1% of the samples are associated with a $Fe-SO_4$ water type.

As the water progresses or evolves along the flow paths towards the decant outflows, the water composition changes to a dominantly Ca-SO$_4$ (87% of the decant samples) water type (Figure 5-12). A few of the decant samples plot as minor Ca-HCO$_3$ (6% of the decant samples), Mg-SO$_4$ (5% of the decant samples) and Na-HCO$_3$ (1% of the decant samples) water types.
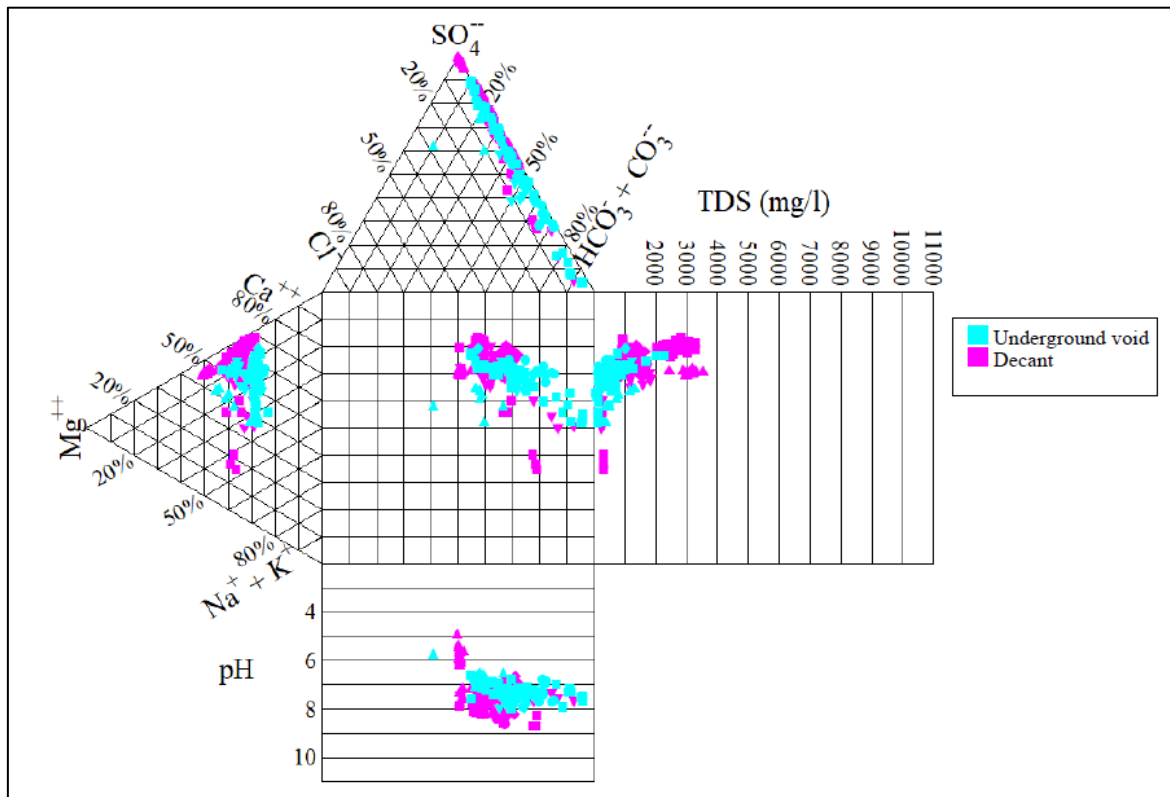
Figure 5-13: Durov diagram showing the pH and TDS distribution within the eastern operations.

The Durov diagram of the mine water (Figure 5-13) shows that the TDS is <2 000 mg/L for most mine void samples, whereas the TDS is <3 000 mg/L for most mine decant samples. The mine void -and decant water display a pH distribution primarily above a pH of 6.0, where a few pH observations below 6.0 were made within the mine decant water.

Table 5-8 and Table 5-9 present statistical summaries of the respective mine void and mine decant water chemical analyses data. The SANS (2015) drinking water guidelines are also presented in the tables as no pre-mining baseline exists. However, as it is very likely that the mine void -and decant water will not be used for domestic use, the parameter concentrations were also compared to the groundwater quality baseline ranges observed in unmined areas (refer to section 5.3.1.1) to indicate mineralisation or contamination.

The percentile pH range of the mine void observations is between 6.60 to 7.86 and indicate circum-neutral waters. Moreover, the percentile pH range of the mine decant observations is 6.33 to 8.30. When considering the median values, it is evident that the TDS increases along the flow path until final discharge and is mirrored in the increased sulphate, calcium and magnesium concentrations observed in the mine decant water.

Almost all variables show significant variation, as reflected by the COV%. The exception is the pH that shows very little variability in the mine void water (5.56%) as well as in the mine decant water (7.80%). Of the 25 variables included in the statistical assessment, 11 parameters do not comply with the drinking water regulation

limits. These constituents may reach concentrations that pose severe risks to the surrounding environment and potential users as a direct consequence of the mining activities that took place. These include pH (only decant water), TDS, ammonia, sulphate, aluminium, iron, manganese, lead, selenium, cobalt and nickel (only decant water). Most parameters, with only a few exceptions, exceed the groundwater baseline range as observed in unmined areas.

Table 5-8: Summary descriptive statistics of the major and trace ions detected in the eastern operations' underground void water (BH9, BH11, BH13, SUS1, BH16) the monitoring period; also shown in the table is the SANS (2015) drinking water quality guidelines and the unmined groundwater baseline ranges (pH is in pH units and TDS and ion concentrations are in mg/L).

Parameter	n^e	n^c	Min	Max	Arithmetic mean	Median	5th Percentile	95th Percentile	Standard deviation	COV%	SANS guideline	% Above guideline	Baseline range	% Above baseline
pH	79	0	5.770	8.000	7.258	7.300	6.599	7.860	0.403	5.558	≥5 and ≤9.70	0	6.87-8.59	16
TDS	35	0	244.000	1688.000	707.966	670.000	381.800	1267.800	301.021	42.519	≤1200	9	145.00-354.00	97
Ca	79	0	17.700	469.345	104.565	82.800	36.340	214.020	78.519	75.092	-^{b}	0	9.20-25.43	97
Mg	79	0	6.670	130.655	36.898	28.500	11.993	88.140	26.571	72.013	-^{b}	0	2.50-11.81	94
Na	79	0	5.700	81.268	29.652	24.100	9.090	63.340	17.793	60.007	≤200	0	10.92-90.40	0
K	79	0	1.842	13.600	5.682	4.420	2.308	11.320	2.913	51.263	-^{b}	0	2.54-6.70	28
Total Alkalinity	79	0	30.600	357.000	171.060	158.610	81.200	252.651	57.766	33.770	-^{b}	0	90.70-213.00	24
F	79	0	0.030	0.730	0.266	0.250	0.100	0.531	0.123	46.438	≤1.50	0	0.02-0.59	3
Cl	79	0	0.800	60.310	8.317	6.200	2.360	20.686	7.855	94.450	≤300	0	4.58-20.64	5
NO₃(N)	79	3	0.025	3.260	0.487	0.320	0.050	1.732	0.564	115.755	≤11	0	0.03-0.49	33
NH₃(N)	35	14	0.025	16.800	1.040	0.300	0.078	2.295	2.789	268.069	≤1.50	11	0.03-0.97	26
SO₄	79	0	7.000	1588.045	286.166	195.000	14.473	809.449	287.009	100.294	≤250*	42	3.80-38.15	92
Al	79	24	0.005	0.900	0.125	0.060	0.010	0.520	0.191	153.161	≤0.30	13	0.03-0.19	16
Fe	79	19	0.005	12.100	0.735	0.140	0.005	2.370	1.989	270.487	≤0.30*	28	0.01-0.25	34
Mn	79	8	0.005	12.900	1.363	0.660	0.010	6.758	2.257	165.570	≤0.10*	78	0.01-0.02	89
As	12	12	0.001	0.005	0.004	0.005	0.001	0.005	0.002	51.426	≤0.01	0	0.005	0
Ba	12	0	0.040	0.441	0.150	0.081	0.045	0.399	0.134	89.382	≤0.70	0	0.02-0.18	25
Cr	12	12	0.003	0.010	0.005	0.003	0.003	0.010	0.003	61.872	≤0.05	0	0.01	0
Co	12	11	0.003	0.033	0.007	0.004	0.003	0.020	0.008	111.897	≤0.05	0	0.01	8
Cu	11	8	0.002	0.013	0.006	0.003	0.002	0.013	0.004	67.870	≤2	0	0.005-0.01	0
Ni	12	10	0.005	0.043	0.013	0.008	0.005	0.031	0.011	84.480	≤0.07	0	0.01	42
Pb	12	11	0.008	0.027	0.009	0.008	0.008	0.016	0.005	59.264	≤0.01	8	0.0075	8
Se	12	11	0.003	0.023	0.006	0.003	0.003	0.016	0.006	90.751	≤0.01	8	0.01	8
Zn	12	6	0.008	0.052	0.023	0.020	0.010	0.047	0.013	55.585	≤5	0	0.01-0.045	8
Si	35	0	6.580	18.900	11.201	11.000	7.193	16.604	2.842	25.378	-^{b}	0	11.68-21.68	0

^{e} – Number of observations; ^{c} – Number of observations below detection; ^{b} – No established guideline value; * - Aesthetic guideline values

Table 5-9: Summary descriptive statistics of the major and trace ions detected in the eastern operations' decant water (Arcadia Adit No.1, Arcadia Adit No.2, Fourie Decant, Union Adit Water, Duck Pond Decant) the monitoring period; also shown in the table is the SANS (2015) drinking water quality guidelines and the unmined groundwater baseline ranges (pH is in pH units and TDS and ion concentrations are in mg/L).

Parameter	n^e	n^c	Min	Max	Arithmetic mean	Median	5th Percentile	95th Percentile	Standard deviation	COV%	SANS guideline	% Above guideline	Baseline range	% Above baseline
pH	286	0	4.960	8.740	7.550	7.540	6.325	8.300	0.589	7.804	≥5 and ≤9.70	0.35	6.87-8.59	6
TDS	230	0	152.000	3314.000	1749.660	1476.000	767.450	3087.300	791.702	45.249	≤1200	75	145.00-354.00	100
Ca	286	0	17.700	686.000	286.098	247.328	119.500	544.000	138.819	48.522	$-^b$	0	9.20-25.43	100
Mg	286	0	9.560	319.025	109.660	87.950	53.275	259.750	59.450	54.213	$-^b$	0	2.50-11.81	100
Na	286	0	5.610	98.100	36.776	26.500	19.100	71.296	19.422	52.812	≤200	0	10.92-90.40	1
K	286	0	2.330	35.600	5.538	5.280	2.990	9.369	2.789	50.370	$-^b$	0	2.54-6.70	9
Total Alkalinity	286	0	5.000	562.000	268.439	272.000	42.500	410.750	100.758	37.535	$-^b$	0	90.70-213.00	79
F	286	0	0.037	1.064	0.262	0.260	0.100	0.512	0.147	56.322	≤1.50	0	0.02-0.59	3
Cl	286	0	1.670	24.000	7.160	6.925	3.533	10.875	3.073	42.923	≤300	0	4.58-20.64	1
$NO_3(N)$	286	27	0.009	2.080	0.097	0.050	0.009	0.250	0.152	156.151	≤11	0	0.03-0.49	1
$NH_3(N)$	230	113	0.100	3.020	0.324	0.200	0.100	0.936	0.374	115.191	≤1.50	2	0.03-0.97	5
SO_4	286	0	24.649	2620.354	904.966	740.000	328.250	2063.500	552.147	61.013	≤250*	96	3.80-38.15	100
Al	286	87	0.005	1.970	0.107	0.060	0.005	0.410	0.185	172.308	≤0.30	7	0.03-0.19	11
Fe	286	67	0.004	15.000	0.565	0.070	0.005	2.413	2.015	356.369	≤0.30*	13	0.01-0.25	16
Mn	286	70	0.005	6.280	0.719	0.450	0.005	4.925	1.270	176.674	≤0.10*	62	0.01-0.02	71
As	14	9	0.001	0.010	0.006	0.005	0.001	0.010	0.004	62.245	≤0.01	0	0.005	36
Ba	14	3	0.012	0.050	0.030	0.028	0.014	0.046	0.012	38.245	≤0.70	0	0.02-0.18	0
Cr	14	13	0.003	0.050	0.009	0.003	0.003	0.024	0.012	134.055	≤0.05	0	0.01	0
Co	14	13	0.003	0.126	0.013	0.003	0.003	0.051	0.031	233.132	≤0.05	7	0.01	7
Cu	14	9	0.001	0.024	0.008	0.007	0.002	0.019	0.006	77.459	≤2	0	0.005-0.01	0
Ni	14	9	0.005	0.423	0.044	0.015	0.005	0.171	0.106	239.954	≤0.07	7	0.01	64
Pb	14	10	0.008	0.029	0.012	0.008	0.008	0.026	0.008	62.441	≤0.01	29	0.0075	29
Se	14	9	0.003	0.043	0.015	0.003	0.003	0.041	0.016	107.387	≤0.01	36	0.01	36
Zn	14	8	0.009	0.361	0.045	0.014	0.009	0.159	0.089	197.424	≤5	0	0.01-0.045	14
Si	230	0	3.350	87.310	9.048	8.780	6.355	10.965	5.420	59.904	$-^b$	0	11.68-21.68	0

^{e} – Number of observations; ^{c} – Number of observations below detection; ^{b} – No established guideline value; * - Aesthetic guideline values

The ranges of pH, sulphate, iron and manganese fluctuation throughout the monitoring period from 2000 to 2017 for the mine void -and mine decant water are illustrated in Figure 5-14 and Figure 5-15, respectively. It is apparent that the pH of the mine void water displays minor fluctuations between pH of 6.0 and 8.0. Occasional releases of very high sulphate and metal concentration, far above the regulation limit, are observed in specifically BH9, BH11, and BH16. Relatively lower sulphate, iron -and manganese concentrations are shown by BH13. BH13 is located in the Susanna compartment which is isolated from the rest of the eastern operations; it may be possible that the geochemical processes within the Susanna compartment have not progressed as it has in the rest of the eastern operations.

The pH of the mine decant water displays slight fluctuations between a pH of 6.0 and 9.0, with Duck Pond Decant displaying a minimum pH of 4.96 in April 2015 (Figure 5-15). This lower pH value is accompanied by very high sulphate, iron, and manganese concentration fluxes. Occasional releases of very high sulphate and metal concentration, far above the regulation limit, are observed in especially Union Adit Water, Fourie Decant, Arcadia Adit No.1 and Duck Pond Decant. The pH, however, remains circum-neutral. Increased sulphate, iron, and manganese concentration fluxes are evident for the wetter months (October to March) and may indicate flushing processes of built-up oxidation products within the mine voids with increased infiltrated water volumes. When dry conditions are re-established, contaminant loads are generally lower in comparison to wet conditions due to reduced flow within the compartments. Iribar (2004) explained that temporal changes observed in mine drainage can be caused by various factors relating to changes in mineral availability within the sulphide ores or in the host rocks, and with hydrologic changes. Changes in mineral availability may be related to mineral depletion, surface coatings or kinetic processes. Furthermore, dynamic factors that include variations in recharge and solute transport may also result in temporal variability in water chemistry (Zhao *et al.,* 2010).

The most acidic drainage is expected to originate in areas rich in pyrite. Waters circulating near well buffered host country rocks are expected to have near neutral pH, but high metal concentrations (Azzie, 2002). Nevertheless, this might suggest an underlying problem with AMD at its still early stages. The presence of calcium carbonates [$CaCO_3$] in the mine waste could effectively buffer any acidity produced during pyrite oxidation, however, as the buffering capacity is depleted over time, the acid problem may become more pronounced with time.

Figure 5-14: Measured mine void water quality from the eastern operations the monitoring period (2000 to 2017) together with the daily rainfall.

Figure 5-15: Measured groundwater quality from the eastern operation's decant locations the monitoring period (2002 to 2017) together with the daily rainfall.

5.3.3.2   Western underground operations
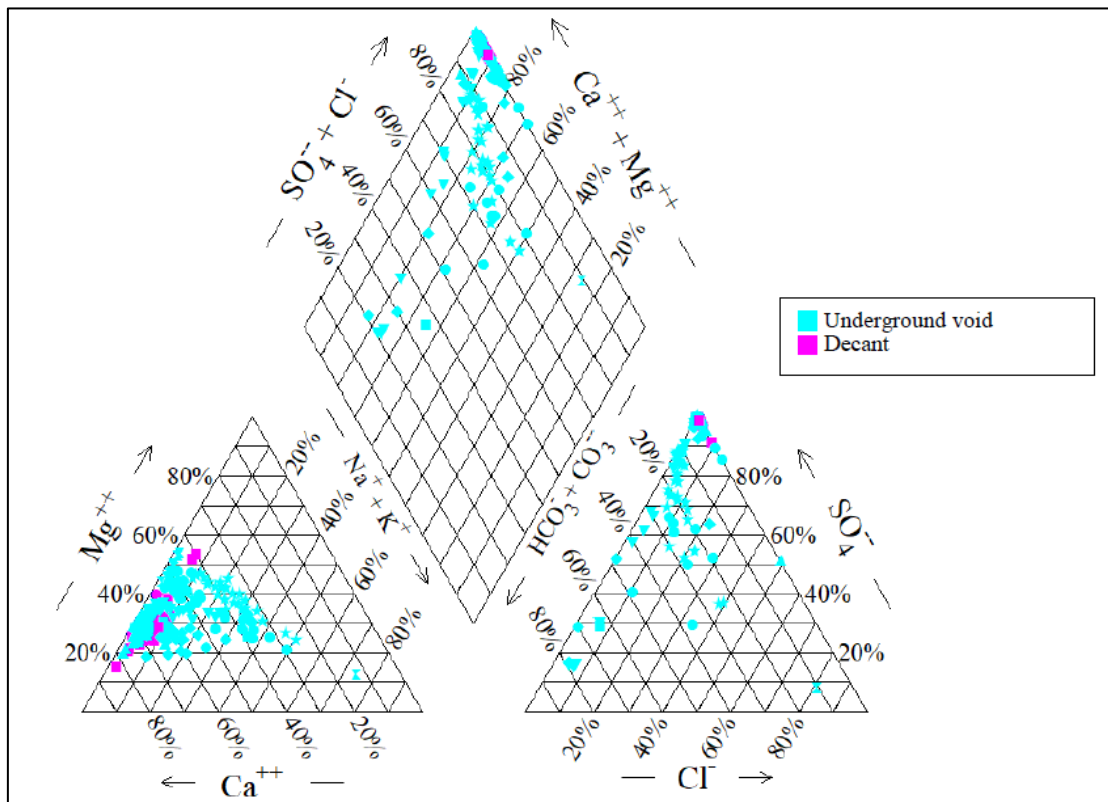
Figure 5-16: Piper diagram showing the hydro-chemical water types for the western underground operations.

The order of abundance of the major ions in most collected underground void water samples are $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ and $SO_4^{2-} > HCO_3^- > Cl^-$ (Figure 5-16). The major cations in the mine water are therefore calcium and magnesium with predominant sulphate and bicarbonate anions. The principal water facies of the mine void water samples are thus Ca-SO$_4$ (65% of the void samples) type. A few of the samples plot as Mg-SO$_4$ (16% of the void samples), Fe-SO$_4$ (11% of the void samples), Ca-HCO$_3$ (4% of the void samples), Na-SO$_4$ (1% of the void samples) and Na-Cl (1% of the void samples) minor hydro-chemical water types.

As the water progresses or evolves along the flow paths towards the final discharge points, the water composition changes to a dominantly Ca-SO$_4$ (97% of the decant samples) water type (Figure 5-16). A few of the decant samples plot as Mg-SO$_4$ (2% of the decant samples) type.
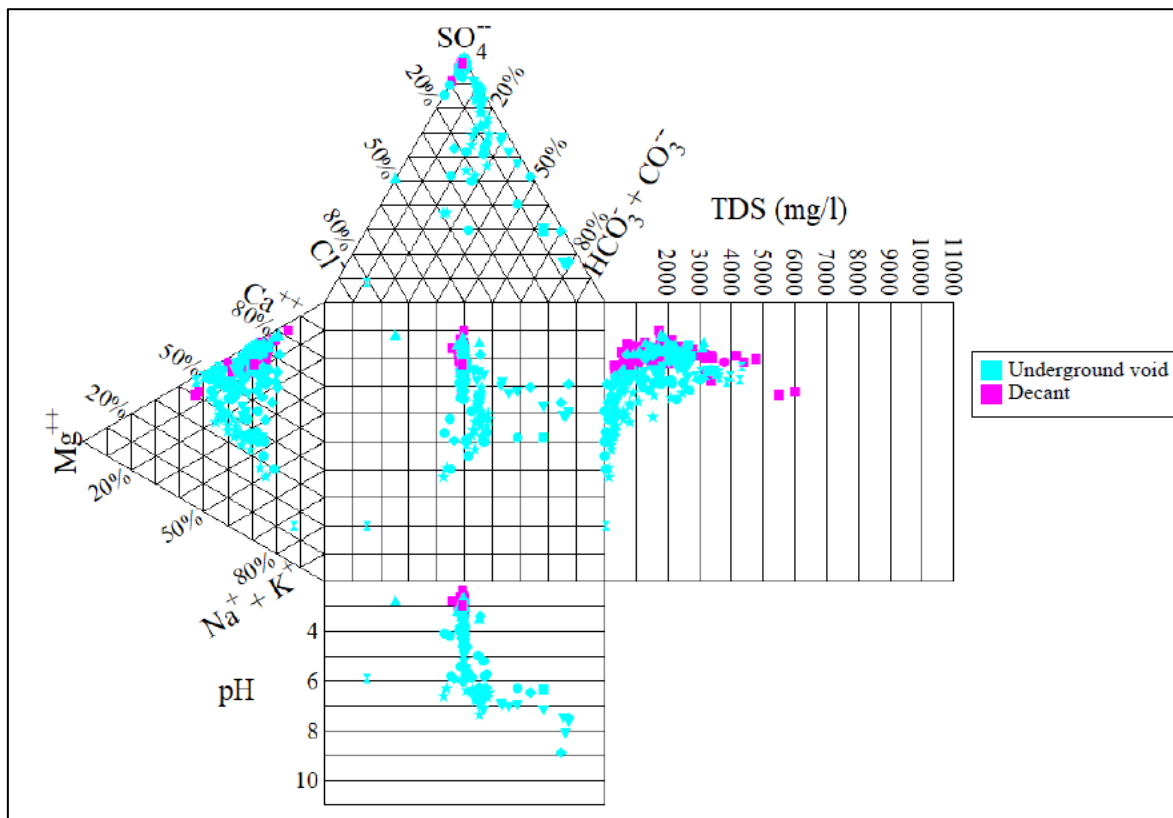
Figure 5-17: Durov diagram showing the pH and TDS distribution within the western operations.

The Durov diagram of the mine water (Figure 5-17) shows that the TDS is <4 000 mg/L for most samples. It is clear that the mine void water is characterised by a wider pH range, whereas acidic pH prevails (<4.0) within the decant water.

Table 5-10 and Table 5-11 present statistical summaries of the respective mine void -and mine decant water chemical analyses data. The SANS (2015) drinking water quality guidelines as well as the groundwater baseline ranges observed in unmined areas in the Union Colliery area, are also included in the tables to facilitate comparison and to indicate mineralisation in the mining-influenced waters (MIW).

The percentile pH range of the mine void water observations is between 2.87 and 7.07. The mine void water is therefore characterised by acidic to circum-neutral waters. The percentile pH range of the mine decant water is 2.67 to 3.16 which dictates predominant acidic conditions. Measurements in especially BH8, indicate generally higher alkalinity when compared to the rest of the monitoring stations. BH8 intersect the mine voids at a much greater depth (>55 mbgl) than the other monitoring boreholes. It is possible that circulating groundwater has not yet leached all alkalinity from the country rocks and mine waste material, which may explain the higher bicarbonate measurements in this specific borehole. Nevertheless, it is clear that the mine decant has completely progressed to AMD conditions, where all neutralisation capacity have been depleted along the flow paths to final discharge. Similar to the eastern operations, it is evident that the TDS increases along the flow paths towards the decant points and is reflected in the increased sulphate and calcium concentrations.

Almost all variables show significant variation as depicted by the COV%. The only exceptions are the pH (7.31%) and Total Alkalinity (0%) of the mine decant water that shows very low to no variability.

Of the 25 variables included in the statistical assessment, 14 variables exceed regulation limits for drinking water. These parameters pose high level risks to the surrounding environment and potential water users as a direct consequence of the mining activities that took place, and AMD. These parameters include the pH, TDS, fluoride, chloride [Cl⁻] and nitrate (only mine void water), ammonia, sulphate, aluminium, iron, manganese, arsenic, cobalt, nickel, and lead. Furthermore, almost all parameters exceed the upper limit of the groundwater baseline range, with the only exceptions of copper [Cu] (only mine void water), sodium, Total Alkalinity, barium [Ba], selenium (only mine decant water), and chromium [Cr].

Table 5-10: Descriptive statistics of the major and trace ions detected in the western operations' underground void water (BH1, BH2, BH3, BH5, BH7, BH8, BH15) the monitoring period; also shown in the table is the SANS (2015) drinking water quality guidelines and the unmined groundwater baseline ranges (pH is in pH units and TDS and ion concentrations are in mg/L).

Parameter	n^e	n^c	Min	Max	Arithmetic mean	Median	5th Percentile	95th Percentile	Standard deviation	COV%	SANS guideline	% Above guideline	Baseline range	% Above baseline
pH	174	0	2.700	9.940	4.797	4.230	2.873	7.065	1.521	31.699	≥5 and ≤9.70	61	6.87-8.59	91
TDS	74	0	48.000	3620.000	1117.592	832.000	152.000	3190.000	920.729	82.385	≤1200	39	145.00-354.00	73
Ca	174	0	2.030	606.000	219.534	149.936	8.606	501.800	177.159	80.697	-^{b}	0	9.20-25.43	90
Mg	174	0	1.170	337.000	81.273	57.150	4.822	249.750	75.709	93.153	-^{b}	0	2.50-11.81	88
Na	174	0	2.000	118.000	22.623	19.050	5.602	48.390	16.425	72.602	≤200	0	10.92-90.40	1
K	174	0	1.010	56.800	6.615	5.895	2.527	11.375	4.622	69.867	-^{b}	0	2.54-6.70	30
Total Alkalinity	150	0	1.840	272.000	36.351	2.500	2.500	180.650	58.249	160.242	-^{b}	0	90.70-213.00	2
F	174	0	0.010	2.840	0.399	0.220	0.050	1.300	0.479	120.247	≤1.50	4	0.02-0.59	21
Cl	172	0	0.010	513.000	11.257	7.455	1.110	16.057	38.810	344.762	≤300	1	4.58-20.64	1
NO$_3$(N)	136	5	0.010	14.500	2.076	0.300	0.050	11.450	3.734	179.896	≤11	7	0.03-0.49	38
NH$_3$(N)	74	26	0.090	9.600	0.801	0.430	0.100	2.140	1.354	169.060	≤1.50	11	0.03-0.97	22
SO$_4$	174	0	2.810	3240.000	1008.273	947.000	22.300	2331.155	770.170	76.385	≤250*	76	3.80-38.15	93
Al	174	12	0.005	82.000	16.119	5.235	0.010	61.335	21.047	130.573	≤0.30	70	0.03-0.19	72
Fe	174	12	0.005	819.000	65.275	4.565	0.010	403.200	137.068	209.985	≤0.30*	78	0.01-0.25	80
Mn	174	3	0.005	11.000	2.401	1.420	0.030	7.070	2.439	101.584	≤0.10*	89	0.01-0.02	97
As	19	10	0.001	0.040	0.009	0.005	0.002	0.019	0.008	90.278	≤0.01	16	0.005	47
Ba	19	1	0.002	0.263	0.080	0.052	0.020	0.224	0.069	86.652	≤0.70	0	0.02-0.18	16
Cr	19	19	0.003	0.010	0.005	0.003	0.003	0.010	0.003	59.760	≤0.05	0	0.01	0
Co	19	5	0.003	0.188	0.073	0.049	0.003	0.174	0.065	88.747	≤0.05	47	0.01	74
Cu	19	9	0.001	0.093	0.019	0.010	0.001	0.061	0.024	127.505	≤2	0	0.005-0.01	0
Ni	19	4	0.005	0.736	0.299	0.187	0.010	0.708	0.248	82.695	≤0.07	79	0.01	89
Pb	19	14	0.008	0.058	0.014	0.008	0.008	0.038	0.013	93.610	≤0.01	26	0.0075	26
Se	19	18	0.003	0.020	0.006	0.003	0.003	0.011	0.005	79.144	≤0.01	5	0.01	5
Zn	19	2	0.010	1.106	0.401	0.254	0.012	1.053	0.381	94.891	≤5	0	0.01-0.045	84
Si	74	0	8.610	214.000	23.401	16.200	9.899	42.200	28.907	123.527	-^{b}	0	11.68-21.68	30

^{e} – Number of observations; ^{c} – Number of observations below detection; ^{b} – No established guideline value; * - Aesthetic guideline values

Table 5-11: Descriptive statistics of the major and trace ions detected in the western operations' decant water (Butter Adit Decant, W1 Decant) the monitoring period; also shown in the table is the SANS (2015) drinking water quality guidelines and the unmined groundwater baseline ranges (pH is in pH units and TDS and ion concentrations are in mg/L).

Parameter	n^e	n^c	Min	Max	Arithmetic mean	Median	5th Percentile	95th Percentile	Standard deviation	COV%	SANS guideline	% Above guideline	Baseline range	% Above baseline
pH	141	0	2.350	4.470	2.921	2.900	2.670	3.160	0.214	7.313	≥5 and ≤9.70	100	6.87-8.59	100
TDS	57	0	644.000	3772.763	1142.823	1082.000	808.800	1496.000	410.800	35.946	≤1200	30	145.00-354.00	100
Ca	141	0	48.630	749.000	261.072	218.000	112.000	565.000	140.810	53.935	-b	0	9.20-25.43	100
Mg	141	0	16.681	471.522	72.841	52.100	26.600	188.000	65.569	90.016	-b	0	2.50-11.81	100
Na	141	0	1.600	83.970	16.810	13.400	5.210	38.566	12.687	75.477	≤200	0	10.92-90.40	0
K	141	0	2.700	51.103	10.097	7.510	4.360	23.790	7.742	76.678	-b	0	2.54-6.70	57
Total Alkalinity	125	0	2.500	2.500	2.500	2.500	2.500	2.500	0.000	0.000	-b	0	90.70-213.00	0
F	141	7	0.005	11.642	0.746	0.280	0.100	3.142	1.495	200.438	≤1.50	14	0.02-0.59	24
Cl	141	0	0.090	53.042	7.337	5.290	1.170	20.390	7.399	100.839	≤300	0	4.58-20.64	5
$NO_3(N)$	141	17	0.009	2.590	0.235	0.090	0.009	0.827	0.333	141.527	≤11	0	0.03-0.49	16
$NH_3(N)$	57	0	0.290	2.000	0.940	0.860	0.478	1.610	0.343	36.445	≤1.50	7	0.03-0.97	35
SO_4	141	0	213.000	4458.217	1122.248	899.000	473.000	2470.000	701.704	62.527	≤250*	99	3.80-38.15	100
Al	141	1	0.009	165.002	27.218	18.300	10.400	75.600	27.370	100.557	≤0.30	99	0.03-0.19	99
Fe	141	0	0.680	170.056	14.993	11.800	2.606	37.300	16.622	110.869	≤0.30*	100	0.01-0.25	100
Mn	141	1	0.005	130.000	13.348	3.160	1.090	67.000	24.665	184.784	≤0.10*	99	0.01-0.02	99
As	4	1	0.005	0.021	0.012	0.012	0.006	0.020	0.006	47.209	≤0.01	50	0.005	75
Ba	4	2	0.010	0.024	0.017	0.016	0.010	0.024	0.007	39.504	≤0.70	0	0.02-0.18	0
Cr	4	4	0.003	0.010	0.007	0.007	0.003	0.010	0.004	53.846	≤0.05	0	0.01	0
Co	4	0	0.053	0.882	0.310	0.152	0.054	0.786	0.339	109.562	≤0.05	100	0.01	100
Cu	4	2	0.003	0.043	0.017	0.011	0.003	0.039	0.016	94.917	≤2	0	0.005-0.01	50
Ni	4	0	0.198	2.591	0.807	0.220	0.199	2.238	1.030	127.624	≤0.07	100	0.01	100
Pb	4	2	0.008	0.048	0.024	0.021	0.008	0.046	0.017	71.580	≤0.01	50	0.0075	50
Se	4	4	0.003	0.010	0.007	0.007	0.003	0.010	0.004	53.846	≤0.01	0	0.01	0
Zn	4	0	0.208	3.003	0.933	0.261	0.212	2.595	1.195	128.104	≤5	0	0.01-0.045	100
Si	57	0	0.520	127.800	19.180	16.500	13.121	31.500	15.308	79.809	-b	0	11.68-21.68	12

e – Number of observations; c – Number of observations below detection; b – No established guideline value; * - Aesthetic guideline values

The ranges of pH, sulphate, iron and manganese fluctuation throughout the monitoring period from 2000 to 2017 as observed in the mine void -and mine decant water are shown in Figure 5-18 and Figure 5-19, respectively. It is clear that the pH of the mine void water displays fluctuations mainly between a pH of 2.0 and 8.0, with BH15 showing an outlier maximum pH value of 9.94. BH8 displays minor pH fluctuations the monitoring period. Occasional releases of very high sulphate and metal concentrations, far above the regulation limits, are observed in especially BH5, BH7 and BH15.

That pH of the mine decant water displays slight fluctuations between a pH of 2.5 and 3.5 the monitoring period from 2012 to 2017 (Figure 5-19). These minor fluctuations might suggest that the system has reached dynamic equilibrium conditions. The same trend can be identified from the sulphate and manganese concentrations over time. The acidic pH measurements are accompanied by especially high iron concentrations. Similar to the eastern operations, increased concentration fluxes of sulphate, iron, and manganese predominantly occur during the wetter months (October to March). When dry conditions are re-established, contaminant loads are generally lower due to reduced flow and circulation within the mine voids. Secondary minerals are also highly soluble, potentially releasing sulphate, iron, manganese, and acidity to the system during periods of increased precipitation and groundwater flow.
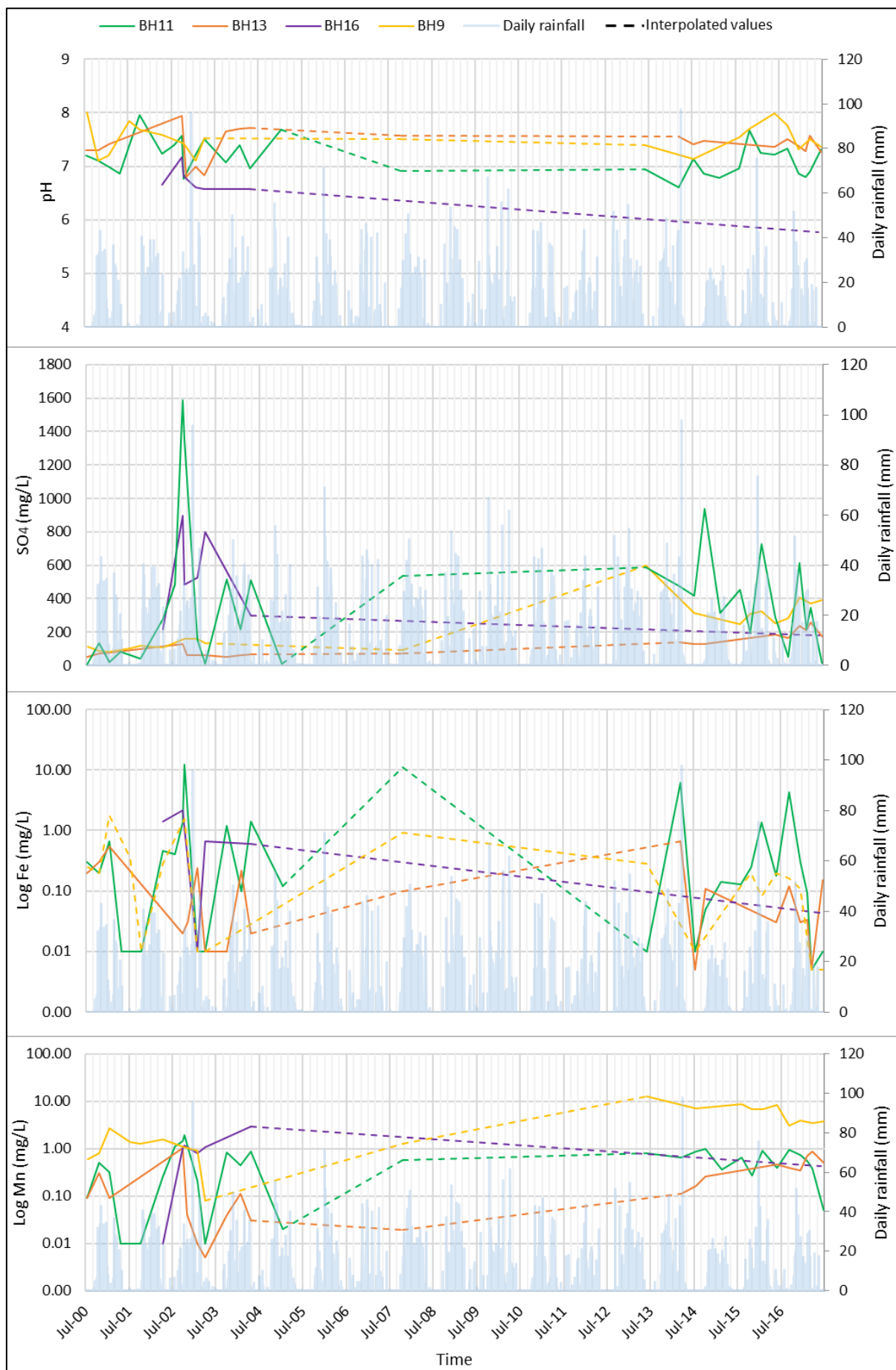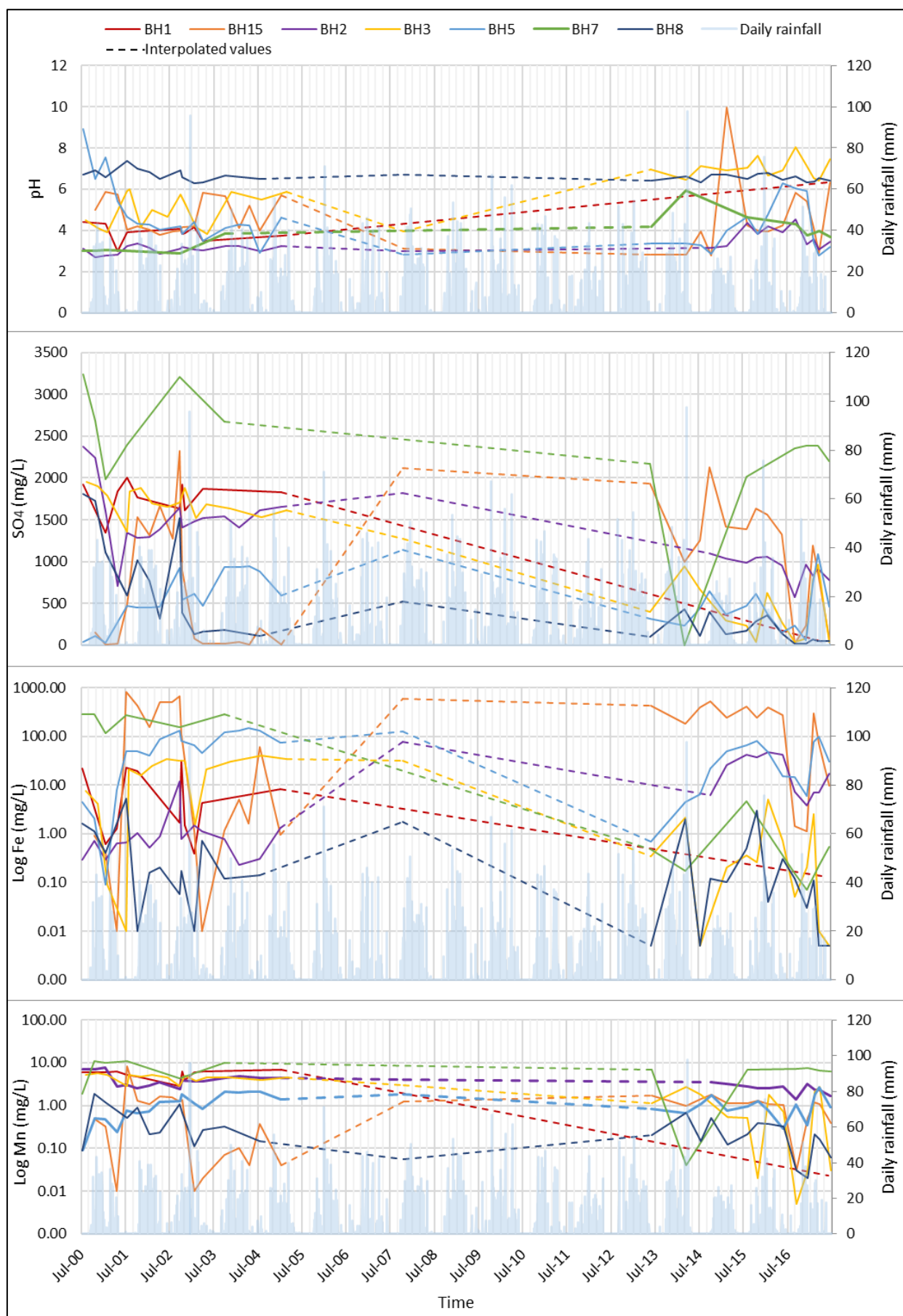
Figure 5-18: Measured mine void water quality from the western operations the monitoring period (2000 to 2017) together with the daily rainfall.
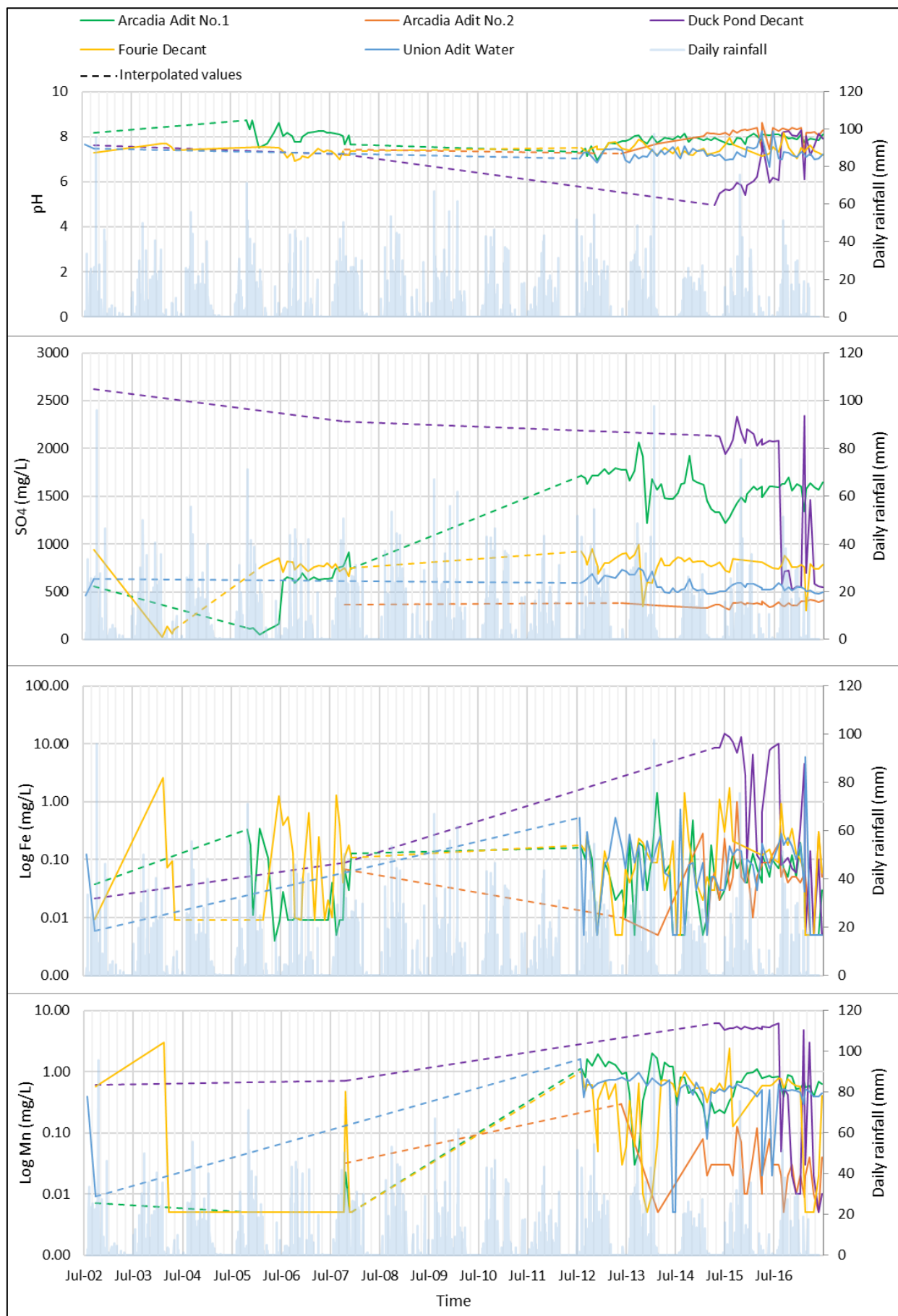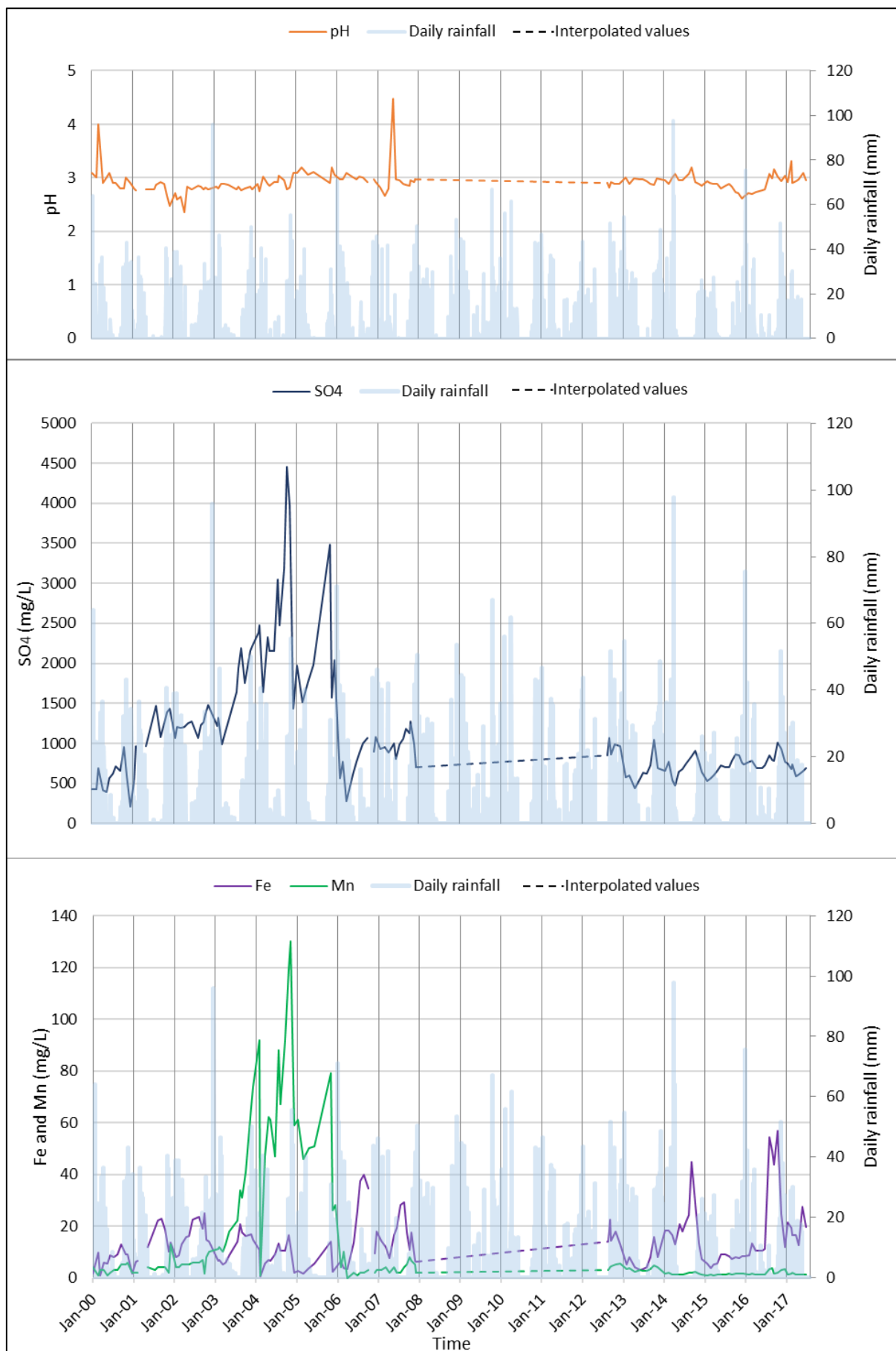
Figure 5-19: Measured groundwater quality from the Butter Adit decant the monitoring period (2000 to 2017) together with the daily rainfall.

5.4 HYDRO-CHEMICAL CHARACTERISTICS SUMMARY

Following the statistical and hydro-chemical evaluations, a summary grouping was developed based on the hydro-chemical assessment results. The summary is aimed to augment understanding of the current baseline conditions at the Union Colliery so that future changes in the geochemical systems can be measured. The dominant water types of each hydrogeochemical area as well as the parameters of concern (exceed regulatory limits), are presented in this grouping so that clearer comparison can be made between the different areas (Table 5-12). Furthermore, box-and-whisker plots are presented in Figure 5-20 to Figure 5-31 to graphically present and compare certain parameter distributions for the different hydrogeochemical areas. Statistical representation of each parameter using box-and-whisker plots provides more meaningful information in terms of the variation in each constituent in the different hydrogeochemical areas (Usher, 2003). Only significant observations to augment conceptual understanding, of especially the underground mining operations, will be addressed in this section.

Table 5-12: Grouping of the hydrogeochemical areas or components considered in this study.

Group	Abbreviated group	Dominant water type	Parameters/constituents of concern
Groundwater in unmined areas	Unmined land GW	$Na-HCO_3$	None
Groundwater upstream of the coal discard dumps	Discard D U/S GW	$Na-HCO_3$ and $Ca-SO_4$	pH, TDS, Na, F, SO_4, Fe, Mn, Se
Groundwater downstream of the coal discard dumps	Discard D D/S GW	$Na-HCO_3$ and $Mg-SO_4$	pH, TDS, NO_3, NH_3, SO_4, Al, Fe, Mn, Se
Vaalwaterspruit upstream	Vaal U/S	$Ca-HCO_3$	pH, SO_4, Al, Fe, Mn
Vaalwaterspruit downstream	Vaal D/S	$Mg-SO_4$ and $Ca-SO_4$	pH, TDS, SO_4, NH_3, Al, Fe, Mn
Boesmanspruit upstream	Boesman U/S	$Ca-Mg-SO_4$	TDS, NH_3, SO_4, Fe, Mn, Pb
Boesmanspruit downstream	Boesman D/S	$Ca-SO_4$ and $Mg-SO_4$	pH, TDS, F, SO_4, Al, Fe, Mn, Se
Eastern operations mine void water	E-void	$Ca-HCO_3$ and $Ca-SO_4$	TDS, NH_3, SO_4, Al, Fe, Mn, Pb, Se
Eastern operations mine decant water	E-decant	$Ca-SO_4$	TDS, NH_3, SO_4, Al, Fe, Mn, Co, Ni, Pb, Se
Western operations mine void water	W-void	$Ca-SO_4$	pH, TDS, F, Cl, NO_3, NH_3, SO_4, Al, Fe, Mn, As, Co, Ni, Pb
Western operations mine decant water	W-decant	$Ca-SO_4$	pH, TDS, F, NH_3, SO_4, Al, Fe, Mn, As, Co, Pb

- The broadest pH range is observed in the western operations' void water, though this may be due to the different spatial locations of the boreholes within the operations (refer to section 5.3.3.2). The monitoring boreholes also intersect the mine voids at different depths (mbgl) which may infer different hydrogeochemical influences or controls where differences in for instance mineral availability and groundwater circulation may occur.

- A bimodal pH distribution in the MIW (includes E-void, E-decant, W-void and W-decant), with modes at 2.35 to 4.47 and 5.77 to 8.0, is evident from Figure 5-20. This is especially significant between the eastern and western operations. The former can be ascribed to highly reactive pyritic and calcareous minerals within the mine waste (Azzie, 2002). According to Cravotta *et al.* (1999), who performed a

series of field and laboratory studies as well as computer simulations, the pH will be driven towards one mode or the other. The latter predominantly depends on the relative abundance and extent of pyrite weathering as well as neutralisation mediated by calcite dissolution. Thus, the pH values in the near-neutral mode result from carbonate buffering and imply the presence of sufficient carbonate minerals, and acidity produced by pyrite oxidation is successfully neutralised. The pH values in the acidic mode result from pyrite oxidation where acidity is not effectively neutralised. This implies a deficiency or depletion of carbonate minerals and thus the absence of sufficient neutralisation processes.

- Drainage leaving the eastern operations is characterised by near neutral to alkaline pH with occasional releases of high metal concentrations, especially aluminium, iron and manganese.

- The western operations are characterised by acidic drainage with highly elevated aluminium, iron, and manganese concentrations (Figure 5-28 to Figure 5-31). The immediate environmental impact of the low pH is acidification of fresh water receptors. However, this may not be significant as monitoring stations within the Vaalwaterspruit mostly indicate near neutral conditions. Nevertheless, metal contamination poses significant risks. In general, the trend of increasing soluble metal content with decreasing pH is strongly reflected in the mine drainage from the western operations. It is further prevalent that the acidic waters are characterised by very low alkalinity concentrations (Figure 5-25). It therefore appears that the western operations have insufficient carbonate minerals along the flow paths to final decant to facilitate neutralisation reactions and thus counteract acid production through pyrite weathering. The dissolution of feldspars, soluble hydroxide, and clay minerals becomes enhanced in acidic solutions which releases iron, manganese and aluminium into the water. The elevated aluminium and iron concentrations may indicate increased dissolution of soluble secondary hydroxides such as aluminium -and iron hydroxides.

- The spatial variability observed in the water chemistry, especially between the eastern and western operations, is most likely controlled locally by the geochemistry of the different underground compartments as explained by Zhao *et al*. (2010) (also refer to section 2.1.2.1.2).
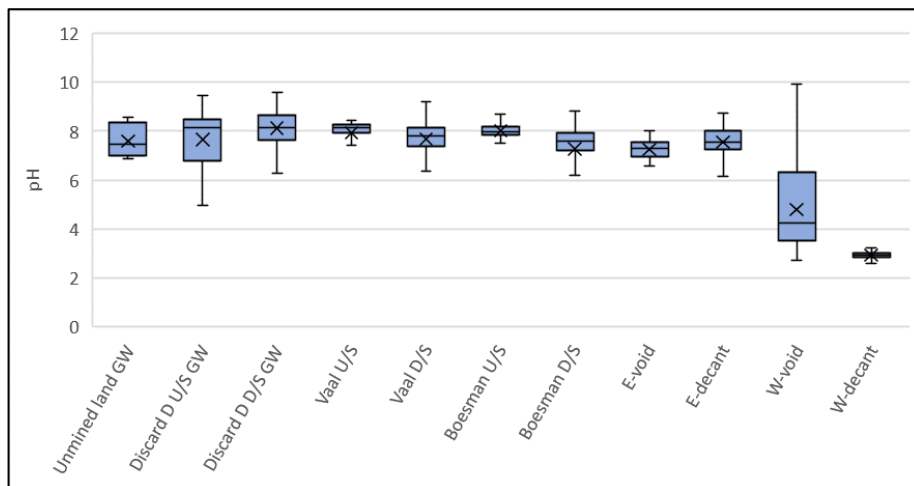
Figure 5-20: Comparison of pH distribution between hydrogeochemical areas.
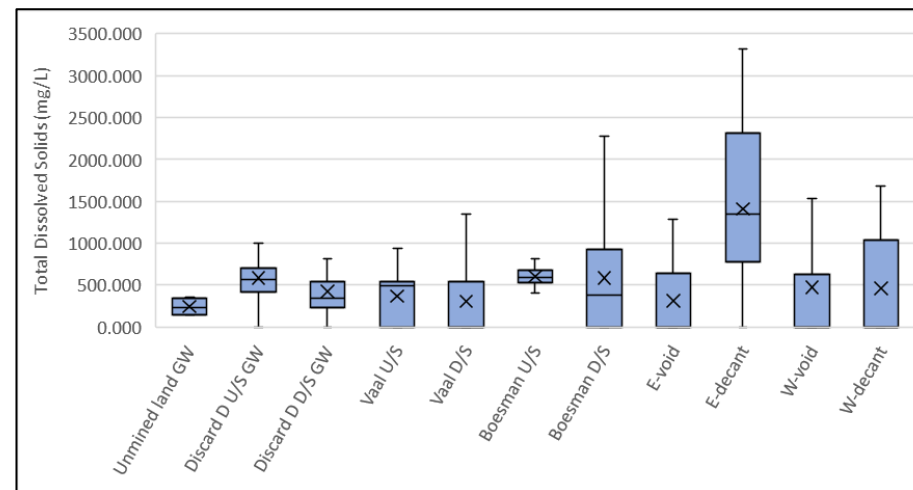
Figure 5-21: TDS distribution within the hydrogeochemical areas
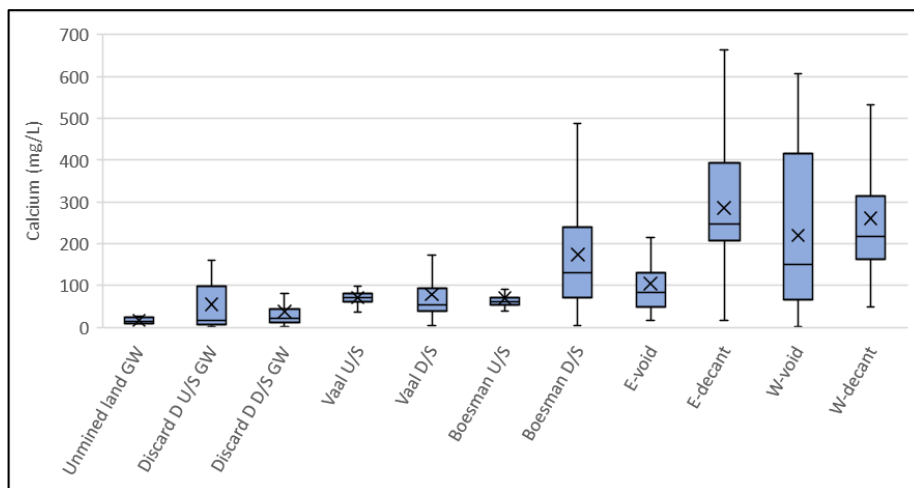
Figure 5-22: Calcium distribution within the hydrogeochemical areas.
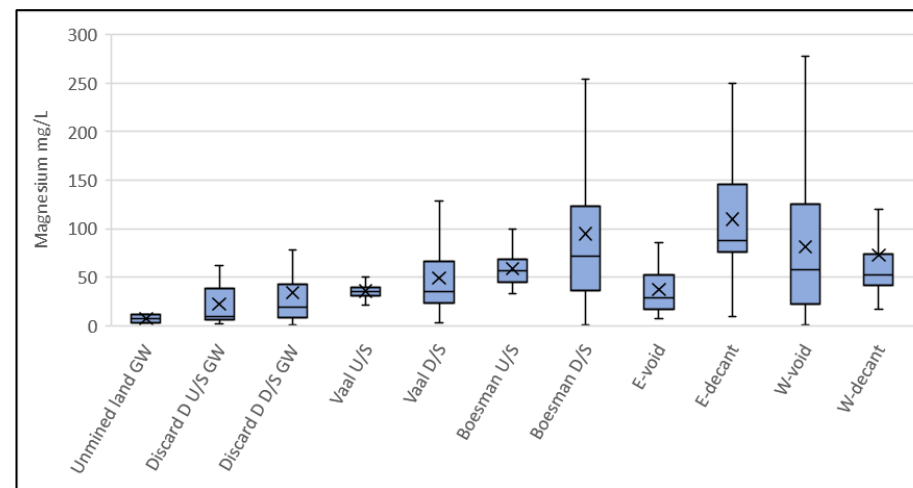
Figure 5-23: Magnesium distribution within the hydrogeochemical areas.
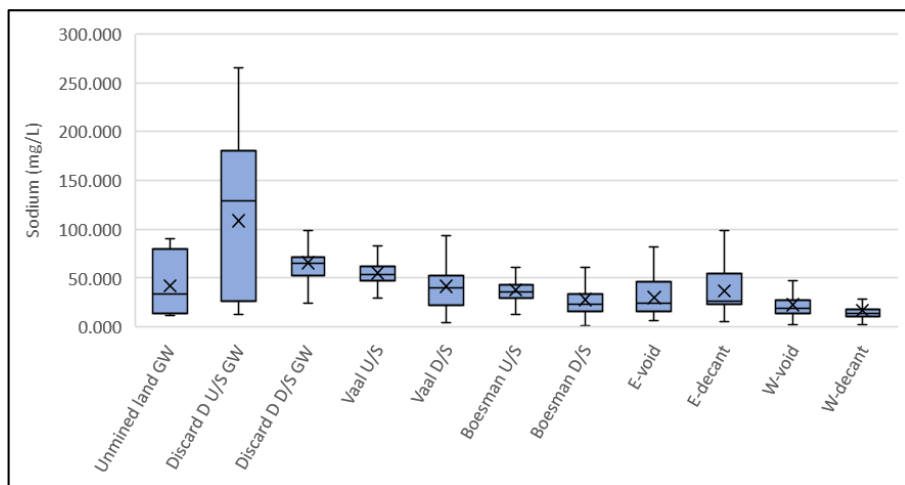
Figure 5-24: Sodium distribution within the hydrogeochemical areas.
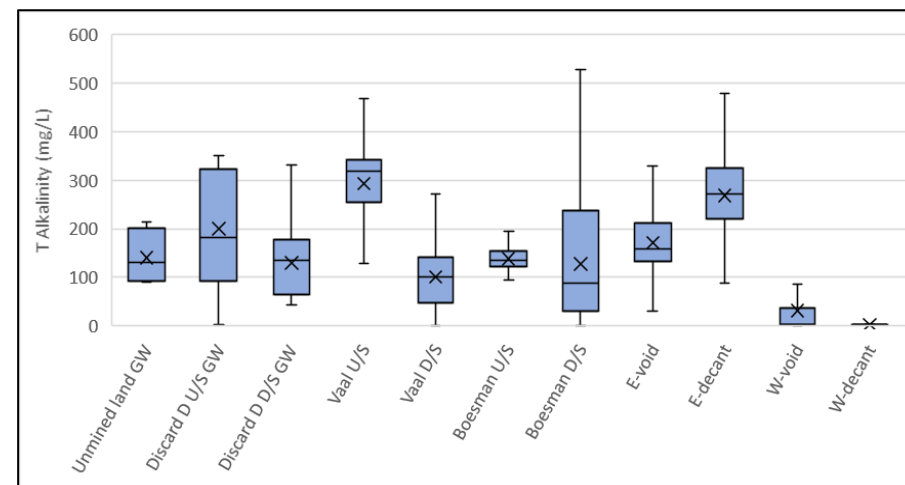
Figure 5-25: Alkalinity distribution within the hydrogeochemical areas.
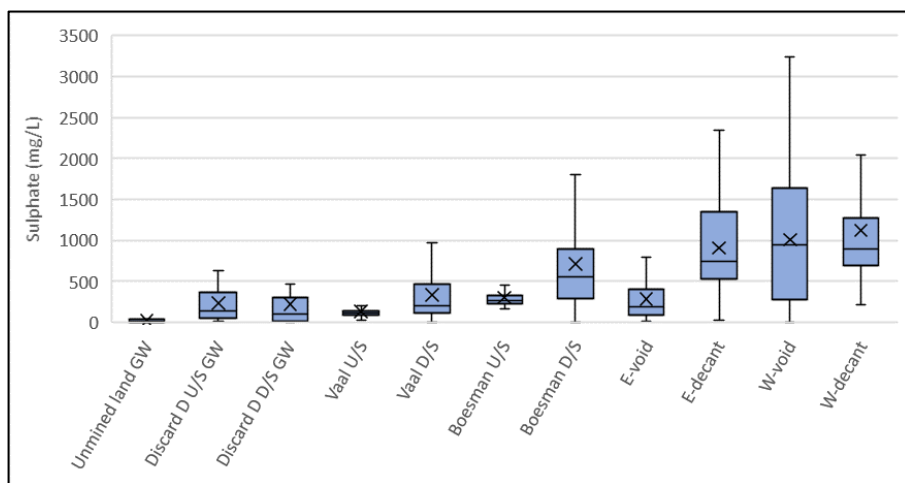
Figure 5-26: Sulphate distribution within the hydrogeochemical areas.
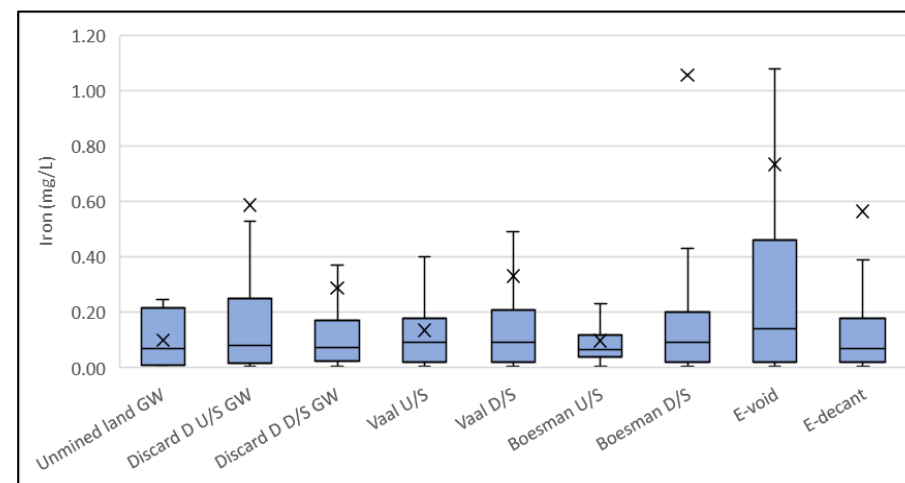
Figure 5-27: Iron distribution within the hydrogeochemical areas (excluding the western operations).
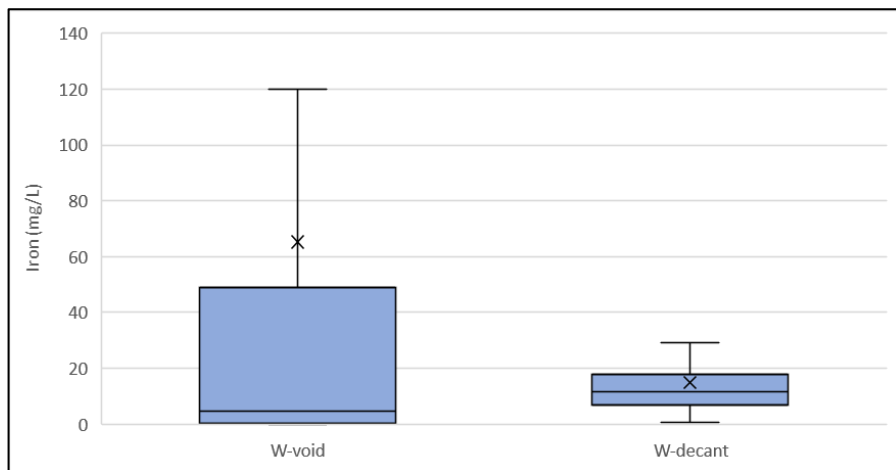
Figure 5-28: Iron distribution within the western operations.
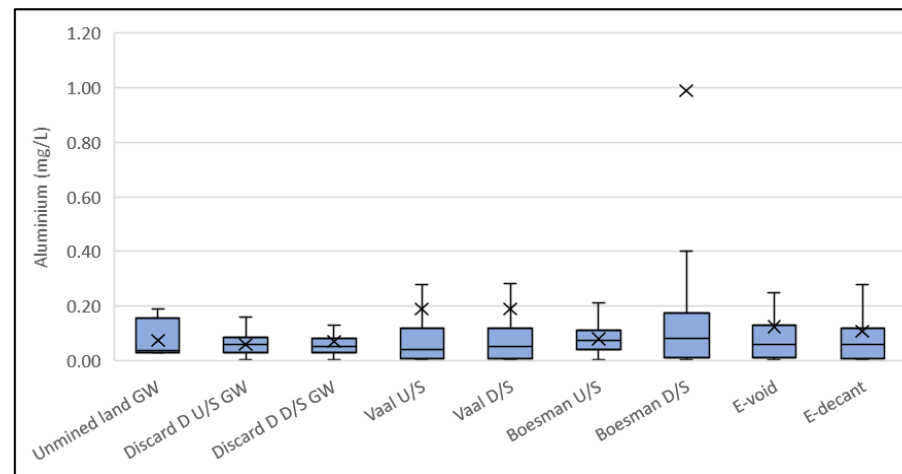
Figure 5-29: Aluminium distribution within the hydrogeochemical areas (excluding the western operations).
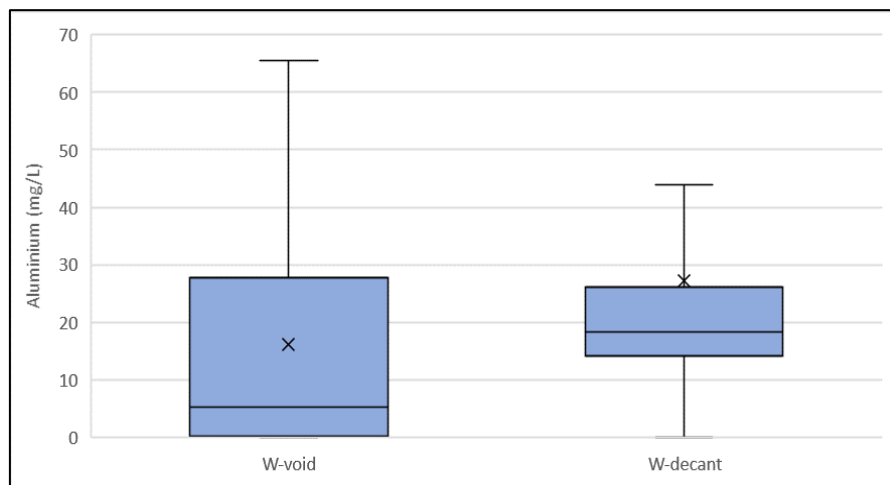
Figure 5-30: Aluminium distribution within the western operations.
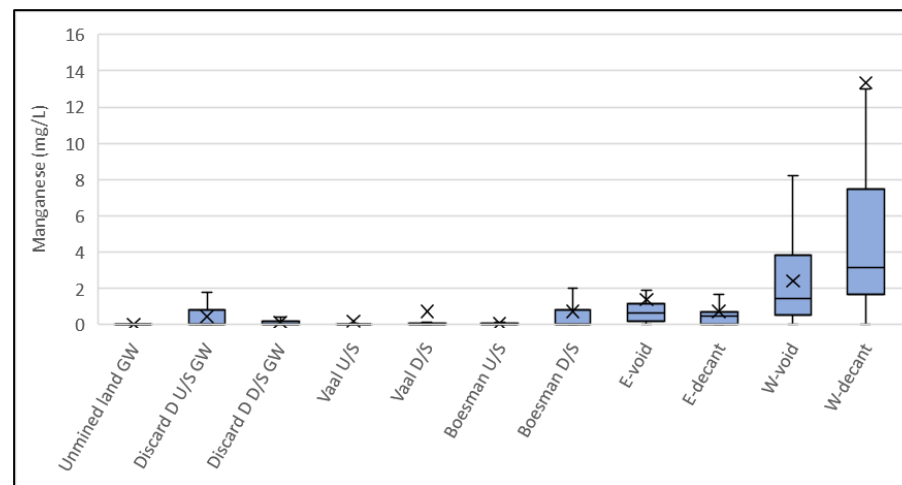
Figure 5-31: Manganese distribution within the hydrogeochemical areas.

5.5   CONCLUDING SUMMARY

The determination of baseline hydrogeochemical conditions is vital to determine the current situation and provides understanding of the dominant controls on the chemistry within the area. Moreover, the evaluation of the water quality data provides identification of representative samples which are vital inputs for geochemical models. The processes that produce changes in the chemical quality of mine waters need to be understood to inform the remedial actions necessary to alleviate any environmental impact. The following main comments can be made from the preceding discussions.

- Baseline conditions for the respective hydrogeochemical areas are reflected by the 5th and 95th percentile range. This range reflects typical concentrations for each hydrogeochemical area as it is resilient to outlier values.

- A comparison between observations and hydrogeochemical areas indicate that there is no dominant cation type in most areas. Exceptions include the groundwater regime which is dominated by sodium, and the mining-influenced waters (MIW) of both the eastern and western operations, which is dominated by calcium. In terms of the major anions, bicarbonate is a significant anion along with sulphate in the groundwater, surface water and eastern operations. Sulphate is the dominant anion in the western operations. There is a distinct trend in all areas, except for groundwater in the unmined land, to be or to become sulphate dominated.

- The pH reflects a bimodal distribution. The western operations decant water are characterised by acidic pH, whereas the other hydrogeochemical areas indicate circum-neutral to alkaline conditions. Relatively few samples display pH values between 4.0 and 6.0 since the pH will be driven towards one mode or the other depending on the relative abundance and extent of pyrite weathering and carbonate mineral neutralisation.

- The groundwater hydrogeochemical areas display elevated concentration fluxes in the dry as well as in the wetter months. Acidity, as well as sulphate and metal concentrations tend to increase in the dry season with lower values and concentrations observed in the wetter months from October to March. The latter may be ascribed to increased percolation of infiltrated water to the groundwater table during prolonged precipitation events and therefore increased mixing and dilution may occur along the flow paths. The higher concentrations observed in the wetter months may be indicative of the flushing out of built up oxidation products within the coal discard dumps after the first rain. Hereafter concentrations decrease due to mixing and dilution processes driven by further precipitation events and the circulation of shallow groundwater.

- The underground operations display increased concentration fluxes of especially sulphate, iron and manganese predominantly in the wetter months. This may indicate the flushing out of accumulated oxidation products within the mine voids due to increased infiltrated rainwater as well as shallow groundwater. When dry conditions are re-established, contaminant loads are generally lower in

comparison to the wetter seasons due to reduced flow within the mine voids. This trend is mimicked in the downstream sampling stations within the Vaalwaterspruit and Boesmanspruit tributaries.

CHAPTER 6:

GEOCHEMICAL ASSESSMENT RESULTS AND DISCUSSION

6.1   INTRODUCTION

One of the main objectives of this study was to characterise the mine wastes as the chemistry of the mining-influenced waters (MIW) will commonly reflect the composition of the mine waste. Furthermore, the author aimed to ascertain the mineralogical and chemical composition of the mine waste in order to support certain assumptions regarding the underlying geochemical processes. The mineralogical and chemical composition of the mine waste further serves as very important inputs to the geochemical models. Considering this, coal discard -and coal roof material were sampled at the Union Colliery (refer to section 4.2.2.1)

This chapter presents an overview of the mineralogy and geochemistry of the mine wastes, so that the interaction between water and mine wastes can be used to better understand the geochemical nature and origin of the waters. The results were discussed on the basis for better understanding of the mineralogical and geochemical properties of the individual components. The information presented in this chapter were used to develop representative conceptual models which serve as the basis for the development of kinetic geochemical models.

6.2   MINERALOGICAL ANALYSES OF SAMPLES

As mentioned before, the most important requirement for quantitative geochemical modelling of mine wastes is accurate and complete sets of data. According to Perkins *et al*. (1997) the mineralogy of the waste material is crucial input parameters to the geochemical models as it is associated with thermodynamic and kinetic reaction rates.

The terminology (after Usher, 2003) used to describe the semi-quantitative composition of the samples in the text is as follows:

- Dominant: >40 wt%

- Major: 10 to 40 wt%

- Minor: 2 to 10 wt%

- Accessory: 1 to 2 wt%

- Rare: <1 wt%

Table 6-1 summarises the weight percentages (wt%) of individual minerals in the coal discard -and coal samples based on XRD assessment, as reported by the Department of Geology, UFS. Only the calculated

median values for the coal discard dump samples will be discussed as these values were used as representative mineralogy of the coal discard material at the Union Colliery in the forward reaction path models.

Concerning the coal discard dump samples, the XRD revealed quartz to be the dominant phase with major quantities of mica (muscovite), gypsum, kaolinite and smectite-type clays, and minor quantities of microcline (K-feldspar), plagioclase (albite), calcite, pyroxene (enstatite), pyrite, amphibole (pargasite), ankerite (siderite), hematite, and goethite.

Furthermore, the XRD revealed quartz, mica, kaolinite and smectite-type clays as the major phases in the coal sample with minor quantities of microcline, plagioclase, calcite, pyrite, and ankerite.

The XRD results show that the minerals which are the major sources of acidity and alkalinity, namely sulphides and carbonates, are present in significant amounts. This agrees with results following the acid-base accounting (ABA) assessment (discussed under section 6.4) that show relatively high acid (AP) -and neutralisation potentials (NP) for these samples.

Based on the results, pyrite is the major sulphide mineral in the Union Colliery mining wastes. According to Zhao *et al.* (2010) the mining type employed is quite significant as normal bord-and-pillar mining results in a relatively unobstructed flow path with minimum source term of pyrite available for reaction. However, high extraction (stooping) found along the perimeter of many of the Union Colliery compartments results in a tortuous flow paths with numerous small ponds and a larger source term of pyrite due to the longer flow path. Collapsed sulphide-bearing hanging walls in the flow path may further increase the source term due to exposed pyrite mineral surfaces. Coupled to this is the process that effectively neutralises acidity and removes the bulk of mobilised metal(loid)s through precipitation as secondary minerals. The major carbonate mineral in the waste material is calcite and secondary minerals include hematite, goethite, siderite, gypsum, and the clay minerals, kaolinite and smectite.

The XRD analyses demonstrated that the principal clay mineral present was kaolinite. Weathering of all feldspars, which include muscovite, K-feldspar and albite will produce kaolinite as secondary mineral (Zhao *et al.,* 2010). The non-clay fraction of the waste material comprises abundant quartz and feldspars (K-feldspar and plagioclase). Carbonates comprise calcite [$CaCO_3$] and siderite [$FeCO_3$] in order of decreasing abundance within the coal discard material. The coal sample however indicate a higher fraction of siderite than calcite.

As explained by Sherlock *et al*. (1995), it is important to recognise that if calcite coexist with silicate minerals, calcite will pre-empt the role of acid neutralisation via dissolution. Silicate minerals may potentially have a greater neutralisation capacity through alteration processes, however, this is very dependent on the pH of the system. The rate of alteration processes is also inherently much slower than calcite dissolution rates. This ultimately suggests that in the short term, carbonates are the dominant minerals facilitating neutralisation reactions and thus influence the drainage water quality, and once depleted and under specific pH conditions, silicate alteration may become more important in the long-term. A more detailed discussion will follow in Chapter 7 of this dissertation.

Differences exist in relative proportions of the clay and non-clay minerals between the coal discard samples and the coal sample:

- The quartz content is very similar in all coal discard material analysed, however lower proportion is observed in the coal sample which can be correlated with high proportions of clay minerals (kaolinite and smectite-type clays).

- Feldspar contents are highest in the coal discard material, both in terms of prevalence as well as abundance.

- Calcite is the dominant carbonate mineral in the coal discard material, whereas siderite is the dominant carbonate mineral in the coal material. Calcite and siderite are therefore the dominant carbonate phases within the mine waste.

- Pyrite play a significant role in the composition of the coal discard material as well as in the coal sample.

- The coal discard material comprises minor quantities of pyroxene and amphibole, whereas these minerals were below detection in the coal sample.

- Secondary minerals namely, gypsum, hematite and goethite were observed as major and minor quantities within the coal discard material, whereas it is rare in the coal material.

Table 6-1: Quantitative mineral composition data (wt%) for the Union Colliery samples based on XRD.

Sample Name	Quartz	Microcline	Plagioclase	Mica	Calcite	Pyroxene	Pyrite	Amphibole	Ankerite	Gypsum	Kaolinite	Smectite	Hematite	Goethite
						Coal discard dumps								
BDD1	51	9	-	-	-	-	-	-	4	14	13	-	8	-
BDD2	38	14	-	22	6	-	-	-	-	-	20	-	-	-
BDD3	49	10	-	10	-	7	-	-	-	11	10	-	3	-
BDD4	30	27	-	12	-	-	-	-	-	15	16	-	-	-
BDD5	37	18	-	13	-	-	-	-	-	15	17	-	-	-
UD1-01	44	9	-	15	-	-	2	-	-	14	17	-	-	-
UD1-02	40	7	-	14	-	-	3	-	-	15	22	-	-	-
UD1-03	57	6	-	10	-	-	3	-	-	12	13	-	-	-
UD1-04	55	6	-	12	-	-	3	-	-	11	13	-	-	-
UD1-05	44	6	-	14	-	-	3	-	-	14	19	-	-	-
UD2-01	40	12	-	14	-	-	-	-	-	14	19	-	-	-
UD2-02	47	6	-	16	-	-	4	-	-	13	15	-	-	-
UD2-03	38	6	-	11	4	-	-	-	-	14	11	12	-	3
UD2-04	45	22	7	10	-	-	2	-	-	-	13	-	-	-
UD2-05	43	6	-	-	-	-	-	-	-	30	14	-	8	-
UD3-01	50	5	-	9	-	-	-	8	-	10	11	-	7	-
UD3-02	48	13	-	9	-	-	2	-	-	12	15	-	-	-
UD3-01N	33	-	7	10	-	-	-	10	-	16	16	-	7	-
UD3-03	39	8	5	-	-	-	-	-	-	15	25	-	7	-
UD3-04	36	12	10	-	-	-	-	-	-	23	20	-	-	-
UD3-05	37	15	9	-	-	-	-	-	-	16	16	-	7	-
Median	43	9	7	12	5	7	3	9	4	14	16	12	7	3
						Compartment coal								
Sus Coal	28	5	5	15	3	-	3	-	5	-	23	17	-	-

6.3 CHEMICAL ANALYSES OF SAMPLES

According to Zhao *et al.* (2010) the main aim when chemically evaluating solid samples during static geochemical evaluation are to yield information of the solid phase concentrations of numerous metals that may be of environmental concern given under suitable physico-chemical environment. Solid phase levels, whether high or low, are nor on their own measures of the potential aqueous concentrations in drainage or of the threat to the environment (Price, 2009). However, these measures can be used as screening tools to identify constituents with anomalous concentrations when compared to normal ranges in rocks and soils as well as in the water chemistry of the area. Furthermore, it can be used to detect when one mineral is the only source of a particular element; the concentration of the trace element can also be used to estimate the mineral concentration. Lastly, XRF data can be used to estimate trace mineral proportions to be used as input data for geochemical modelling. Overall this method is used to refine the results obtained from other static geochemical tests. In this section a brief overview of the XRF analyses of the solid samples are given.

The results of the major element analysis in wt% as determined from the XRF investigation (reported by the Department of Geology, UFS) are listed in Table 6-2, with trace elements given in Table 6-3 The XRF techniques used were regarded as only semi-quantitative of sulphur, hence the sulphur contents are not reported. Only the calculated median values for the coal discard dump samples will be discussed as these values were used as the representative geochemistry of the coal discard dump material at the Union Colliery during the development of site conceptual models and subsequent geochemical models. The XRF analyses were normalised and excludes carbon and volatiles.

The XRF analyses of the feed coal discard samples to gasification indicated that the coal discard material contains median values of 44.80% SiO_2, 10.00% Al_2O_3, 3.00% Fe_2O_2, 1.70% CaO, 1.10% K_2O, 0.60% TiO_2, 0.40% MgO, 0.10% MnO, 0.10% P_2O_5, and 0.10% Na_2O.

Bulk chemical composition as determined by XRF analysis of the coal sample material indicated that this sample contains 12.60% SiO_2, 5.10% Al_2O_3, 1.50% CaO, 0.70% Fe_2O_3, 0.50% MgO, 0.30% TiO_2, and 0.30% K_2O.

It is apparent that the waste material predominantly consists of the two oxides, SiO_2 and Al_2O_3. The coal discard material is enriched in SiO_2, Al_2O_3, Fe_2O_3, CaO, K_2O, TiO_2, MnO, P_2O_5, and Na_2O when compared to the hanging wall coal sample material. Overall, the coal discard material has slightly higher concentrations of SiO_2 (44.80 wt%), Al_2O_3, (10.00 wt%), Fe_2O_3 (3.00 wt%), CaO (1.7%), K_2O (1.10 wt%), TiO_2 (0.60 wt%), MnO (0.10 wt%) P_2O_5 (0.10 wt%) and Na_2O (0.10 wt%) than the coal material, whilst the coal discard material appears to have lower concentration of MgO.

The CaO is relatively high in all samples and is mainly accommodated in the calcite and plagioclase minerals. It thus suggests that carbonates may be significant in the sampled waste material. Calcite is the most probable mineral responsible for the NP values generated by the ABA tests. Previous investigations by Azzie (2002) indicated that the major carbonate species in the South African Coalfields are calcite and dolomite. In Figure

6-1 the correlation between reported CaO, MgO and NP is given. It was pointed out by Usher (2003) that a very good correlation exists between CaO and NP. Based on the mineralogical and chemical results during this study, it can be inferred that the NP shown in the ABA test derived mainly from the carbonate mineral, calcite.

(Usher, 2003)
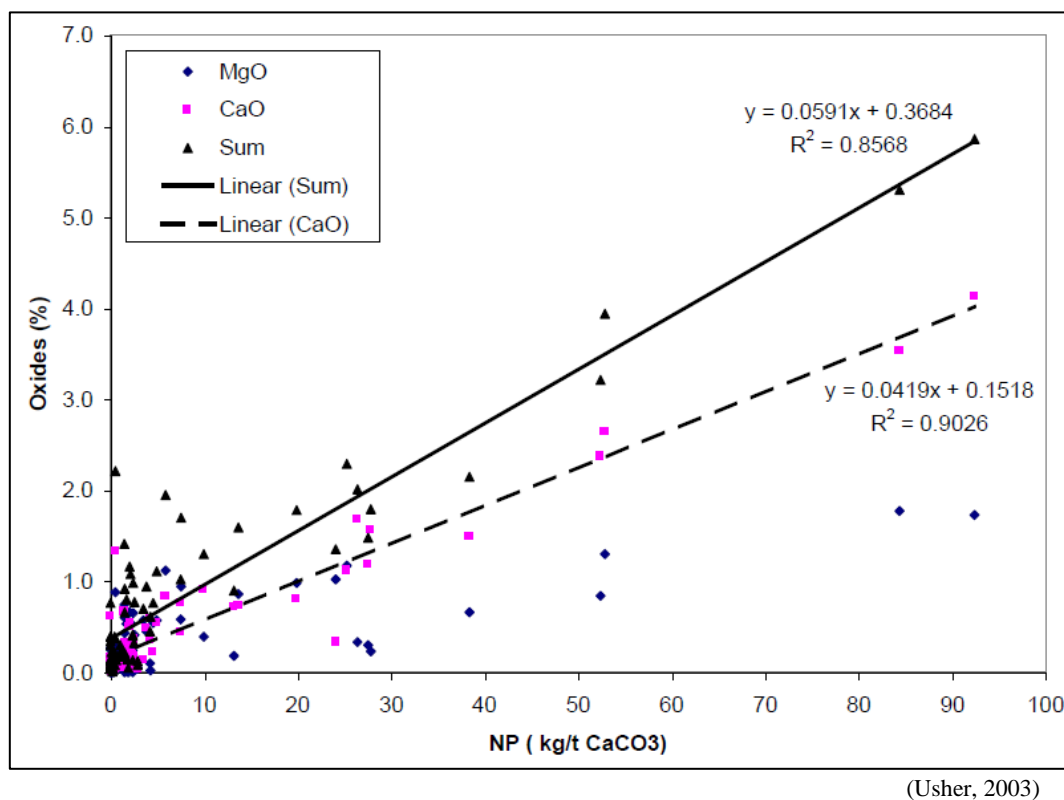
Figure 6-1: Comparison between XRF and NP results.

Fe_2O_3 (total) in the coal discard material is relatively high and exceeds the CaO, which indirectly suggests that sulphides may be present at reasonable amounts. The XRD results indicate that a high percentage of pyrite occur in the sampled material and it is further reflected by the higher AP values of these samples (ABA results presented under section 6.4). Furthermore, the sulphur speciation data indicates that sulphide-sulphur are present at percentages greater than 0.3% within the samples (presented and discussed under section 6.4). The Fe_2O_3 content is however lower than the CaO in the coal sample material and is also mirrored in the ABA results where this sample indicated a higher NP. Pyrite is nonetheless the most dominant sulphide mineral in the sampled waste material where other sulphides may only occur at trace amounts.

The trace metal analyses show that among the base metals, the median chromium [Cr] and nickel [Ni] are relatively high compared to lead [Pb] and cobalt [Co] in the coal discard -and coal sample material. Overall, the coal discard material displays higher metal concentration, except for barium [Ba], when compared to the coal sample material. According to Zhao *et al.* (2010) the XRF data can be used to identify the metals' potential to likely occur as contaminants within the area. The water quality monitoring data can further be used to confirm if these metals occur at high concentrations within the study area. Chromium and vanadium [V] may be potential contaminants that may impact on the quality of the water, provided that the physico-chemical conditions prevailing in the coal discard dumps, aquifer systems, underground compartments and adits allow

mobilisation and leaching of these metals in significant amounts. Nickel, lead and cobalt are intermediate in concentration. It is crucial that the interpretation of these results be verified by the water quality assessment, which was dealt with in Chapter 5 of this dissertation. The occurrence of nickel, lead and cobalt at worrying concentrations, in especially the underground operation hydrogeochemical areas, can be confirmed by the water monitoring data since these constituents occur at concentrations exceeding quality guidelines as well as groundwater baselines. Chromium and vanadium as potential pollutants can however not be confirmed by the water quality data. Chromium concentrations are below the standards and vanadium was mainly analysed as below the detection limit.

Table 6-2: Major elements in oxide wt% in the Union Colliery samples.

Sample name	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	K_2O	P_2O_5	Na_2O	LOI	Total
Coal discard dumps												
UD1-01	41.00	0.60	8.10	2.00	0.30	-	1.30	1.00	-	-	46.50	100.80
UD1-02	44.80	0.70	10.80	3.00	0.30	-	2.20	1.20	-	-	38.20	101.20
UD1-03	50.40	0.80	13.10	3.90	1.10	-	2.60	1.30	0.10	-	28.80	102.10
UD1-04	61.20	0.50	8.40	4.70	0.40	-	0.90	1.10	0.10	-	20.50	97.80
UD1-05	45.30	0.70	10.40	2.40	0.50	-	1.40	1.00	-	-	40.60	102.30
UD2-01	29.00	0.40	6.50	2.10	0.20	-	1.10	0.50	0.10	-	62.00	101.90
UD2-02	41.90	0.80	12.20	3.70	0.80	0.10	1.80	1.00	0.10	-	39.00	101.40
UD2-03	49.10	0.60	10.00	7.70	0.90	0.10	3.30	1.20	0.10	-	27.90	100.90
UD2-04	56.30	0.50	9.60	1.90	0.40	-	1.70	1.90	-	-	29.10	101.40
UD2-05	41.70	0.50	12.20	3.80	1.20	-	4.00	1.00	-	-	37.70	102.10
UD3-01	65.50	0.80	13.70	3.10	0.50	-	2.30	1.10	0.10	-	14.70	101.80
UD3-02	56.60	0.50	10.60	2.50	0.30	-	1.60	1.80	0.10	-	27.00	101.00
UD3-01N	47.00	0.70	12.30	3.10	0.80	-	2.40	1.10	0.10	0.10	32.00	99.60
UD3-03	28.70	4.00	7.60	2.60	0.30	-	0.90	0.60	0.10	-	58.80	103.60
UD3-04	28.50	0.30	6.20	2.70	0.10	0.10	1.50	0.70	-	-	58.50	98.60
UD3-05	40.80	0.60	9.50	3.40	0.40	-	2.50	1.10	0.10	0.10	39.50	98.00
BDD-01	47.60	0.70	13.50	2.70	0.50	-	1.70	1.60	-	-	32.80	101.10
BDD-02	23.40	0.40	7.80	4.50	0.30	-	1.20	0.70	0.10	-	62.80	101.20
BDD-03	64.30	0.70	13.90	3.40	0.90	-	1.60	2.20	0.10	-	15.60	102.70
BDD-04	39.90	0.50	9.50	3.00	0.40	-	1.30	1.40	-	-	45.30	101.30
BDD-05	32.60	0.40	8.90	2.50	0.40	-	1.80	1.20	-	-	52.50	100.30
Median	44.80	0.60	10.00	3.00	0.40	0.10	1.70	1.10	0.10	0.10	38.20	101.20
Compartment coal												
Sus Coal	12.60	0.30	5.10	0.70	0.50	-	1.50	0.30	-	-	76.10	97.10

Table 6-3: Concentration of trace elements (mg/kg) in the Union Colliery samples.

Sample name	Sc	V	Cr	Co	Ni	Br	Sr	Y	Nb	Ba	Pb
					Coal discard dumps						
UD1-01	10	57	123	19	31	3	263	12	6	310	15
UD1-02	10	50	319	16	35	2	383	13	7	384	20
UD1-03	9	55	314	22	40	3	335	15	7	357	21
UD1-04	7	85	194	31	32	4	159	9	6	360	24
UD1-05	9	58	261	19	34	3	241	16	10	317	23
UD2-01	6	60	200	18	36	3	263	19	4	289	14
UD2-02	12	93	198	27	48	5	299	14	8	367	16
UD2-03	14	127	195	35	35	1	376	12	7	516	-
UD2-04	6	63	112	14	26	2	311	9	6	599	-
UD2-05	15	64	91	24	63	3	666	26	4	515	-
UD3-01	9	54	296	17	50	3	368	19	11	421	-
UD3-02	8	37	283	11	28	2	320	13	5	523	-
UD3.01N	12	50	311	12	42	1	460	23	7	433	-
UD3-03	8	40	546	11	29	1	201	15	4	319	-
UD3-04	5	28	226	9	19	1	243	8	2	355	-
UD3-05	11	49	575	14	47	<1	442	15	7	500	-
BDD-01	12	69	73	17	43	2	356	22	9	519	-
BDD-02	9	72	62	22	45	2	231	19	5	401	-
BDD-03	11	80	71	18	36	5	388	21	9	657	-
BDD-04	10	67	60	15	32	5	250	17	5	404	-
BDD-05	9	69	148	18	39	3	244	18	5	391	-
Median	9	60	198	18	36	3	331	15	6	401	20
					Compartment coal						
Sus Coal	6	35	31	10	19	2	333	19	2	185	-

6.4 ACID-BASE ACCOUNTING AND NET ACID-GENERATION TESTS

In this study, ABA tests were performed on 22 samples (five from Union Dump 1, Union Dump 2 and Black Diamond Dump, respectively, six from Union Dump 3, and one from the Susanna compartment hanging wall). As mentioned in previous sections, the coal discard dumps were considered as homogeneous entities, therefore mean values for each of the coal discard dumps were calculated based on the different method results and will hereafter be presented and discussed. Complete results of the ABA and NAG tests for each individual sample are presented in Appendix C: ABA and NAG Results (provided on request).

Table 6-4 summarises the results obtained from the static geochemical evaluation including ABA and NAG methods for the Union Colliery samples.

The pH-levels before (paste pH) and after oxidation (NAG pH) is presented in Table 6-4. In instances where the neutralisation potential (NP) exceeds the calculated acid potential (AP), little or no drop in pH is expected (Usher, 2003). All samples have initial pH values at or above 6.43. This implies that the coal discard -and Susanna coal material have excess base material available which prevents immediate acidification under natural field conditions. In the coal discard dumps, weathering may have advanced to the stage where most of the acid producing species have been leached from the material, and thus indicate near neutral pH values. However, the coal discard material acidified under oxidising conditions, which suggests excess acid potential in comparison to base potential. Samples from Union Dump 1 and Union Dump 3 acidified to pH levels below 3.0. Many other reactions, such as the mobilisation of metal(loid)s, become significant at these low pH levels.

Usher (2003) conjectured that carbonate minerals are in nature more reactive than sulphide minerals, resulting in base potential leaching much quicker by circulating groundwater or infiltrating rainwater. This however invariably results in a long-term acid problem, despite an initial excess of neutralisation potential.

The coal discard material generally has significantly higher acid than base potentials as illustrated in Table 6-4. The higher AP of the coal discard material is also reflected by the high percentage of sulphide-sulphur analysed within the materal (Table 6-5). Higher base potential is associated with the Susanna roof coal sample. It was ascertained by IGS (2017) that the groundwater level within the Susanna compartment has not yet reached the coal roof elevations (refer to Chapter 3), and it can therefore be assumed that due to a lack of natural groundwater circulation, relatively little carbonate leaching from this horizon has occurred.

During the calculation of the AP, and consequently the net neutralisation potential (NNP), a distinction is made between open and closed conditions as mentioned in Chapter 4 under section 4.2.3.2.3. Under closed conditions, the AP is doubled due to the production of carbon dioxide [CO_2]. Carbon dioxide produces carbonic acid [H_2CO_3] upon dissolution in water. The acid reacts with the carbonate species in the rock, thus increasing the overall acid potential. Under field conditions, it can be assumed that most of the carbon dioxide end up in the water, however, instances would certainly occur where some of the carbon dioxide is released into the air. A continuum between closed and open systems, which tend towards a closed system, is therefore very likely (Usher, 2003; Hodgson & Krantz, 1998). However, it should be borne in mind for all interpretations that the assumption was made that there is free flow of oxygen and carbon dioxide to and from reactive surfaces within the coal discard dump -and underground operation systems. Open system conditions were therefore assumed.

As an initial step in the interpretation of the data, some interpretative diagrams were used (details of the screening criteria for each type of method are given in Chapter 4 under section 4.2.3.3). The first of these is shown in Figure 6-2 showing the different categories of acid-generation potential based on the neutralisation potential ratio (NPR). Figure 6-3 differentiates the samples based on their %S and NPR values.

As discussed in section 4.2.3, the interpretation of ABA test data is based on simple equations either by calculating the arithmetic difference between the NP and AP values which yields NNP values or by calculating the ratio between the NP and AP, which is termed the NPR. According to Sherlock *et al.* (1995) the latter method is preferred and is becoming more widely applied, since the derivation of NNP values can often fail to reflect the relative proportions of acid-generating and acid-consuming constituents. These proportions are more apparent in the calculation of the NPR. The NPR can provide an indication of the acid-generating potential, but since synchronism is not considered the test is not discriminatory and it merely provides an estimate of the ratio of acid-generation and acid-consumption averaged over a geologic period (Sherlock *et al.*, 1995).

Based on the mean NNP results, the coal discard material collected from all dumps can be classified as potentially acid-generating, whereas the coal sample might not generate acid. The NAG pH results reflect that coal discard material from Union Dump 1 and Union Dump 3 are high risk acid-generating, where coal discard material from Union Dump 2 and Black Diamond Dump have low risk acid-generating potentials. The roof

coal sample can be classified as non-acid-generating. The NPR ratios further indicate that the coal discard material collected from all discard dumps may be potentially acid-generating, whereas the coal sample has a low likelihood of generating acid.

Table 6-4: Summary of ABA and NAG results.

Site	Paste pH	NAG pH	AP (kg CaCO3/t)	NP (kg CaCO3/t)	NNP	NPR ratio	Assessment	Metal(loid)s of potential concern
Coal discard dumps								
Union Dump 1	6.87	2.79	17.44	8.57	-8.87	0.49	Potential acid-generating	Al, As, Se, Co, Cr, Fe, Mn, Ni, Pb
Union Dump 2	7.15	3.70	20.88	18.36	-2.51	0.88	Potential acid-generating	Al, As, Se, Co, Cr, Fe, Mn, Ni, Pb
Union Dump 3	6.43	2.32	29.03	2.29	-26.74	0.08	Potential acid-generating	Al, As, Se, Co, Cr, Fe, Mn, Ni, Pb
Black Diamond Dump	6.88	3.55	20.09	8.87	-11.22	0.44	Potential acid-generating	Al, As, Se, Co, Cr, Fe, Mn, Ni, Pb
Compartment coal								
Sus Coal	7.71	5.68	16.03	42.44	26.40	2.65	Non-acid-generating	Al, As, Se, Fe, Mn, Ni, Pb

Total sulphur content of 0.25% is regarded as a criterion to distinguish between acid -and non-acid generating materials (Brady & Hornberger, 1990). However, it was noted by Usher (2003) that a sulphide-sulphur content of 0.3% is a more accurate indication of long-term acid-generation potential. Sulphur speciation data (Table 6-5) indicate that the coal materials contain high proportions of carbon (ranging from 33-90.90%), as well as relatively high concentration of sulphur (0.55-1.07%) with high sulphide-sulphur proportions (0.51-0.93%). This suggests that the coal discard and coal sample material have sufficient sulphide to yield long-term acidity. However, the coal sample, which has a sulphide-sulphur content greater than 0.3 wt%, have an NPR value above 1.0, which recognise the importance that samples cannot unequivocally be regarded as acid-producers or non-acid producers. The minimum AP and sulphide-sulphur capable of causing acidic drainage is however not a generic number but depends on the magnitude of the effective NP. Therefore, ABA results should be interpreted in conjunction with the on-site conditions and long-term conceptual models (Zhao *et al.,* 2010).

Table 6-5: Sulphur speciation laboratory results.

Sample ID	Union Dump 1	Union Dump 2	Union Dump 3	Black Diamond Dump	Sus Coal
Total Sulphur (%)	0.64	0.76	1.07	0.77	0.55
Sulphate-sulphur (%)	0.08	0.10	0.14	0.13	0.03
Sulphide-sulphur (%)	0.56	0.67	0.93	0.64	0.51
Total Carbon (%)	33.00	33.60	40.90	41.20	90.90

Figure 6-3 demonstrates the likelihood of long-term acidification. The graph is divided into different fields, where the red field represents low NPR values with 0.3-1.0% sulphide-sulphur which indicates a high probability of long-term acidification. The green field represents an area where sufficient neutralisation potential and limited sulphide-sulphur is present that prevents acidification. The grey field represents samples with low sulphide-sulphur content but with low neutralisation potential. These samples should not in theory

have enough sulphide-sulphur to produce acidity in the long-term but can yield acidity in the short term until the sulphides are depleted. Overall, according to Figure 6-2 and Figure 6-3, acidification of the coal discard dump material is very likely, whereas uncertainty exist regarding the acidification of the roof coal sample material.

Although the ABA results suggest that the coal discard systems will become acidic, this could not be confirmed with field seepage measurements. However, as mentioned in Chapter 5 of this dissertation, groundwater downstream of the coal discard dumps are predominantly characterised by circum-neutral to alkaline pH ranges. This suggests that potential acidity produced by the coal discard material is either limited to the unsaturated zone or upper weathered zone where active groundwater flow is limited, or the acidity is neutralised by near neutral to alkaline groundwater and by carbonate minerals within the aquifer material.
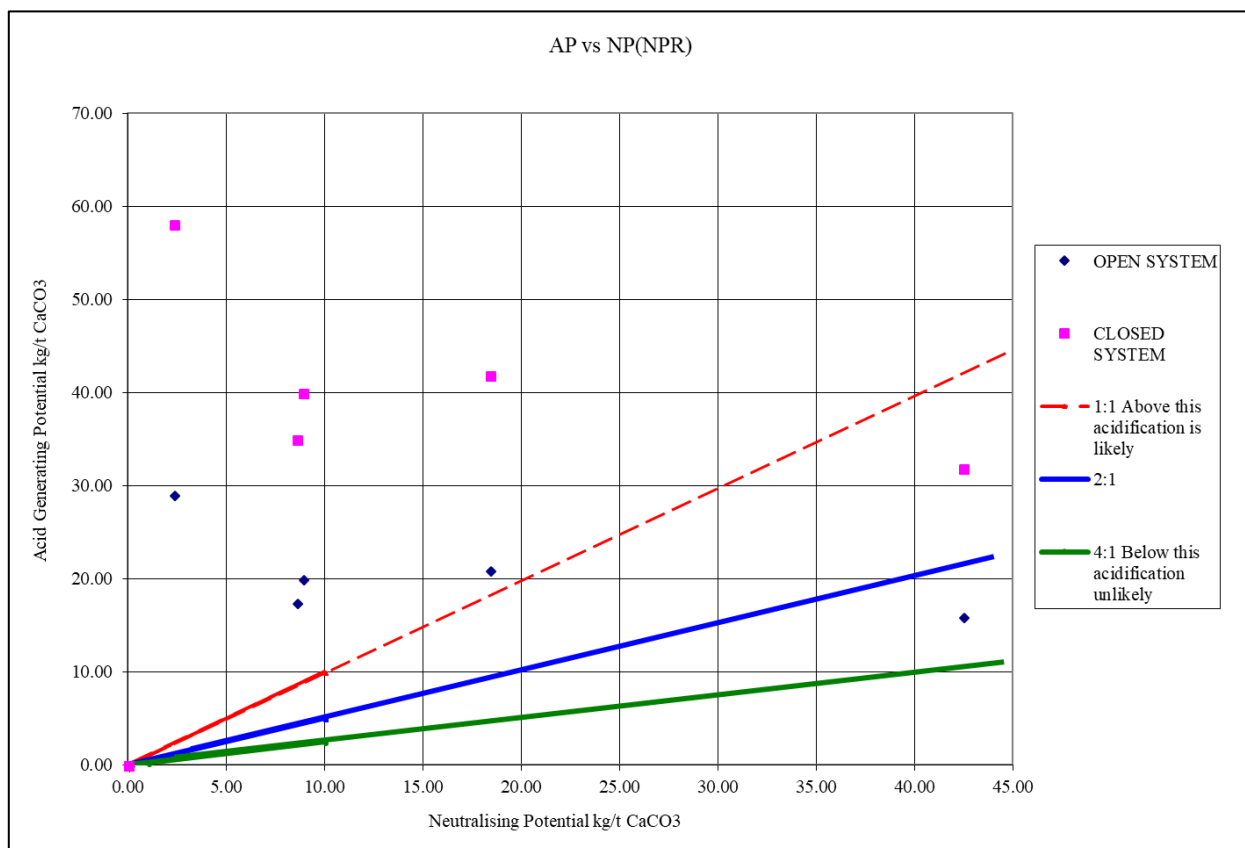
Figure 6-2: Graph showing different categories of acid-generation potentials based on NPR.
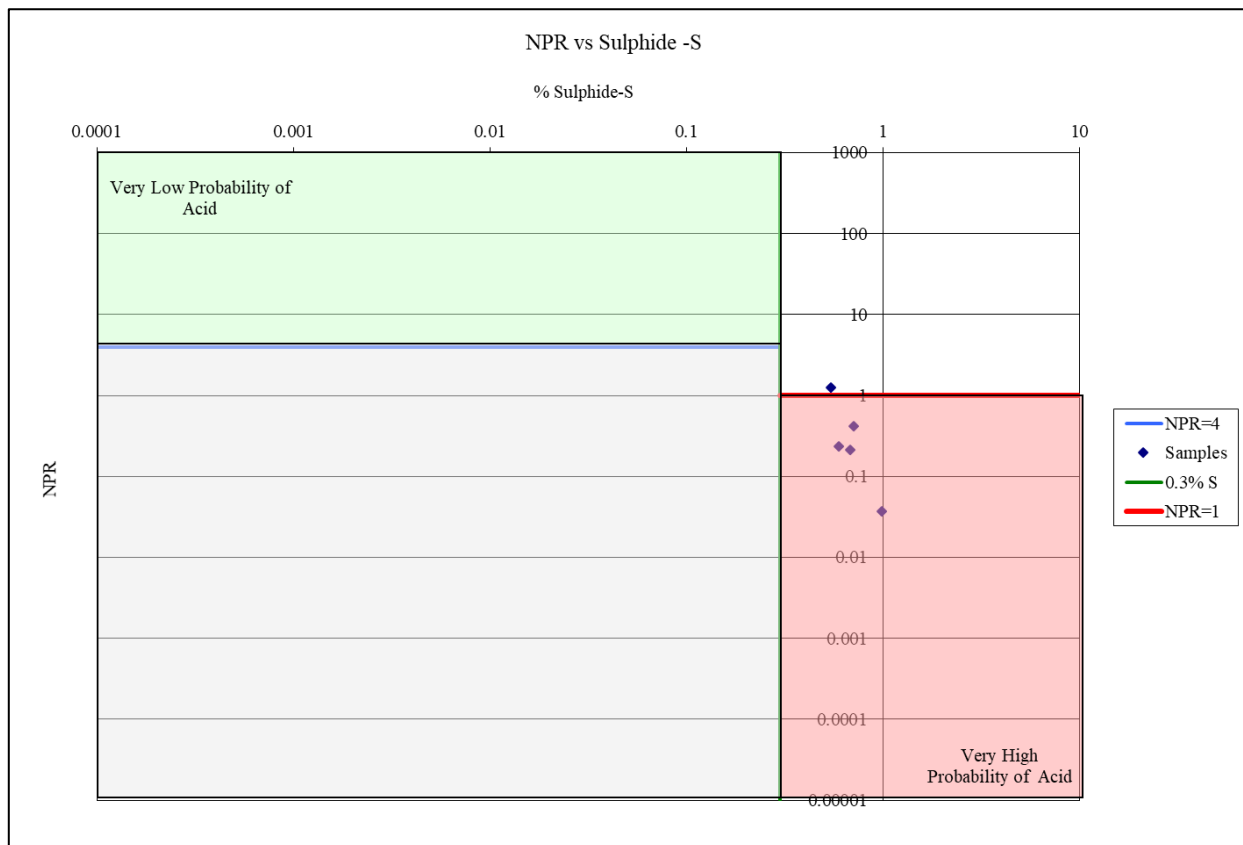
Figure 6-3: Evaluation graph using %S and NPR to differentiate samples.

6.5   CONCLUDING SUMMARY

Although it is not recommended to make conclusions based solely on static test data without cognisance of the hydrogeochemical conceptual model and encountered environmental conditions, conclusions presented in this section are based on the results presented and discussed in this chapter. Conclusions based on static tests data include the following:

- The mine waste comprises varying proportions of primary minerals, quartz, K-feldspar, albite, muscovite, enstatite, pargasite/tremolite, pyrite and calcite, and secondary minerals including, gypsum, hematite and goethite. The main clay minerals include kaolinite and smectite-type clays.

- The mine waste consists of varying proportions of two major oxides, SiO_2 and Al_2O_3. In addition, Fe_2O_3, TiO_2, MgO, CaO, MnO, K_2O, P_2O_5, and Na_2O are present in minor concentrations. MnO, P_2O_5 and Na_2O were barely present in the Susanna coal sample material. Numerous trace elements were also detected in the waste material and when compared to the water quality data, nickel, cobalt, and lead are potential contaminants.

- According to the ABA results, all samples have initial pH levels at or above 6.43. This suggests that the material does not contain readily available acidity, but alkalinity that may be readily released over time.

- Material from the coal discard dumps acidified under oxidising conditions. The Susanna coal sample is an exception. This implies that the coal discard material has excess AP over NP. However, in a laboratory scenario the milling and crushing of rock samples to a fine powder increases surface area and thus increases reaction tempos.

- The NNP values together with the NPR values, suggest that the coal discard material have a high likelihood to produce acid. This is supported by the relatively high sulphide-sulphur concentrations in this samples which implies long-term acid generation.

- The Susanna coal sample material can, according to the NNP and NPR ratios, be regarded as highly likely to maintain neutral conditions, however the sulphide-sulphur concentration of this sample suggests potential long-term acidification. The minimum sulphide-sulphur capable of causing acidic drainage is not a generic number but depends on the magnitude of the effective NP.

CHAPTER 7:
CONCEPTUAL MODEL

The prediction of mine waste behaviour, which is a necessity to design and develop management strategies to mitigate and prevent environmental impacts, largely depends on a conceptual understanding of the dynamic interaction of processes and the reactions that take place within the mine waste systems. This chapter presents the conceptual models developed for the coal discard dump -and underground operation systems at the Union Colliery as well as discussions of the different geochemical zones identified influencing the mine wastes. A conceptual model with different conceptual subjects, which is focused on the geochemical processes influencing the mine waste drainage quality over the medium to long-term, has been developed to model a written and illustrated concept of the expected conditions and processes at the Union Colliery. The basis for the geochemical conceptual model were field investigations and sampling to provide hydro-chemical and geochemical characterisation of the mine water and waste material as discussed in Chapters 4 to 6. This chapter is intended to provide an understanding of the fundamental processes and reactions involved along the evolution of the mine affected water. A review of the general concepts and definitions of sulphide mineral oxidation, acid neutralisation and alkalinity generation, silicate mineral dissolution, secondary mineral precipitation, and adsorption is thus provided. All information and literature presented in this chapter is directed towards a conceptual understanding of the waste geochemical systems at the Union Colliery.

7.1 INTRODUCTION

The modelling of geochemical processes is used as a tool to quantify the medium to long-term geochemical risks associated with the waste materials. This quantification is based on a conceptual understanding, built on the foundations of the data collected and on sound scientific principles, which is used to build numeric geochemical models that consider the geochemical processes over time.

According to several authors (Sherlock *et al*., 1995; Mayer *et al*., 2003; Maest *et al*., 2005) creation of a site-specific conceptual model is a step vital in the process of successfully predicting water quality at a mine site. Oreskes and Belitz (2001), and Bredehoeft (2005) highlighted the importance of accurate conceptualisation as errors in conceptualisation often leads to erroneous modelling and unreliable long-term predictions of mine water quality.

Usher (2003) stated that where static test data (acid-base accounting (ABA), mineralogy and geochemistry) and long-term water quality monitoring data are available, a well-defined conceptual model can be developed, which allows the prediction of expected water quality evolution. Sherlock *et al*. (1995) mentioned that historical monitoring data can successfully facilitate the prediction of future reactions. In most cases, however, sufficient data on reactive surface areas and gas fluxes cannot be obtained to accurately quantify temporal

changes in observed water quality. The overall success of a model therefore greatly depends on the measure to which the conceptual understanding reflects the site-specific processes.

Usher (2003) summarised the key factors that will influence the observed water quality in the short and long-term at any coalmine as 1) the specific mining methods employed, 2) the mineralogy of the coal, 3) the oxidation of sulphide minerals to yield acidity and sulphate [SO_4^{2-}], and 4) neutralisation of the acidity by carbonate, hydroxide, and silicate minerals with associated secondary mineral formation. Azzie (2002) further conjectured that the chemistry of the rock sequence in which the coal is found, and the quality and quantity of the natural groundwater also play a role. Sherlock *et al.* (1995), and Newbrough and Gammons (2002) emphasise the importance of understanding the relationship between mine drainage chemistry and the mineralogy of the surrounding rocks, and how these relationships can vary on a district scale.

In many coal mines, such as those studied by Bell and Bullock (1996), Bullock and Bell (1997), Bullock *et al.* (1997), Geldenhuys and Bell (1998), Hobbs (1998), and Bell *et al.* (2001), acid mine drainage (AMD) arises when sulphide minerals contained in the coal and associated rocks are oxidised due to the diffusion of oxygen and where the products are flushed and transported with water. Factors that facilitate the rate at which sulphide oxidation takes place include the temperature, pH, oxygen saturation, chemical composition of the pore water and microbial population (Ritchie, 1994; Azzie, 2002). The process of sulphide oxidation followed by transport by water, generally creates saline drainage water, which is characterised by highly acidic (<3.0) pH values unless it has been neutralised through contact with alkaline or calcareous rocks (Skousen, 1996; Gray, 1997; Azzie, 2002). Processes associated with that of sulphide oxidation thus includes the dissolution of neutralising minerals that is built in the coal seams and host rocks which provides acid buffering and subsequent precipitation of secondary minerals along the flow paths (Zhao *et al.*, 2010). The mine affected water often resides in the underground workings until water levels rise to decant elevations. The pH of the mining-influenced waters (MIW) is a crucial consideration as under extreme pH conditions, adverse effects result from the dissolution of toxic metal(loid)s and the protonation and deprotonation of other ions.

The conceptual models are graphically illustrated in Figure 7-1 to Figure 7-3 and will be used as a constant guide to the modelling of the geochemical interactions as well as the development of conceptual scenarios. The next sections will focus on the most important factors, geochemical zones and processes influencing the mine waste to provide fundamental understanding of the dominant processes and reactions influencing the mine waste drainage at the Union Colliery.
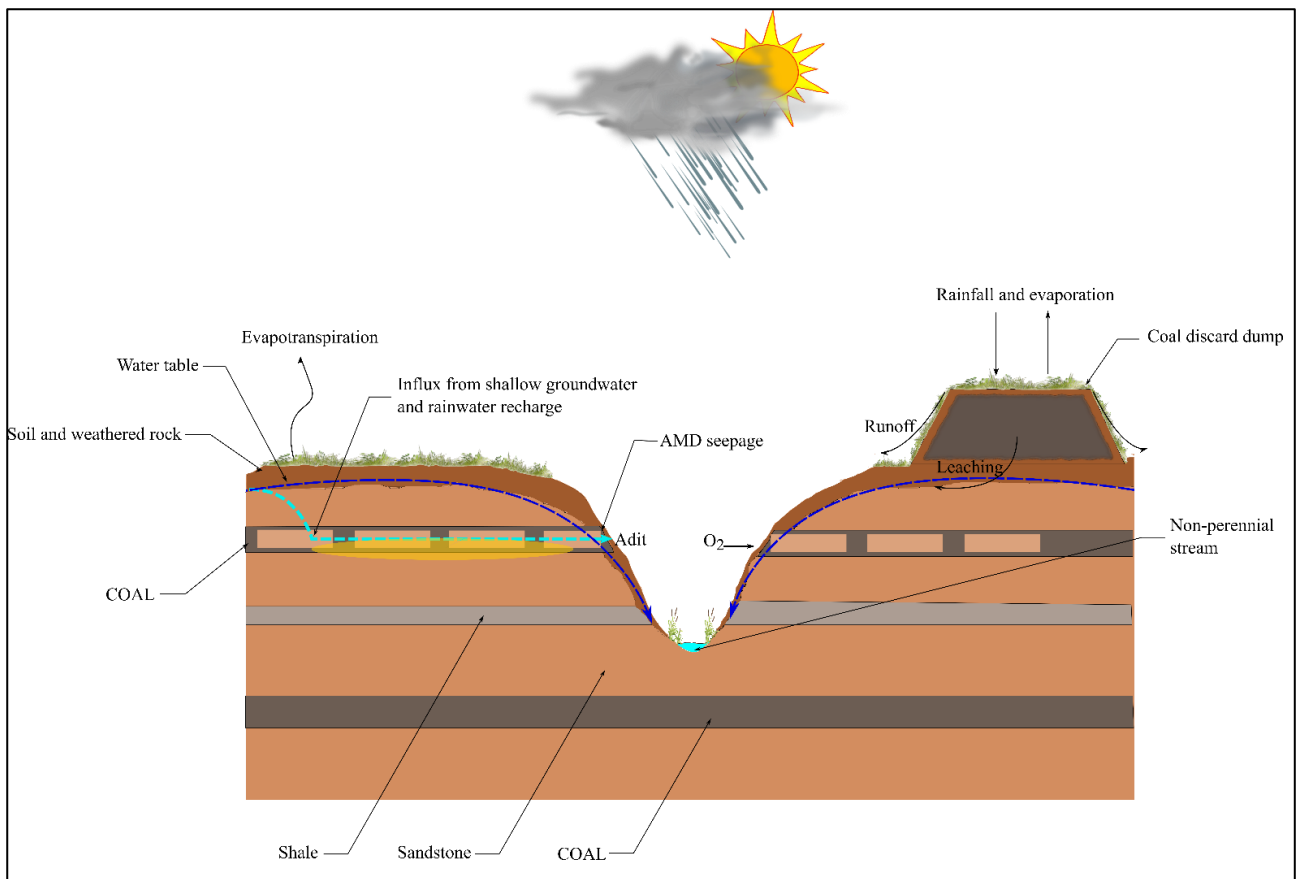
Figure 7-1: Schematic diagram of the dominant geochemical processes and flow paths influencing the mine waste.
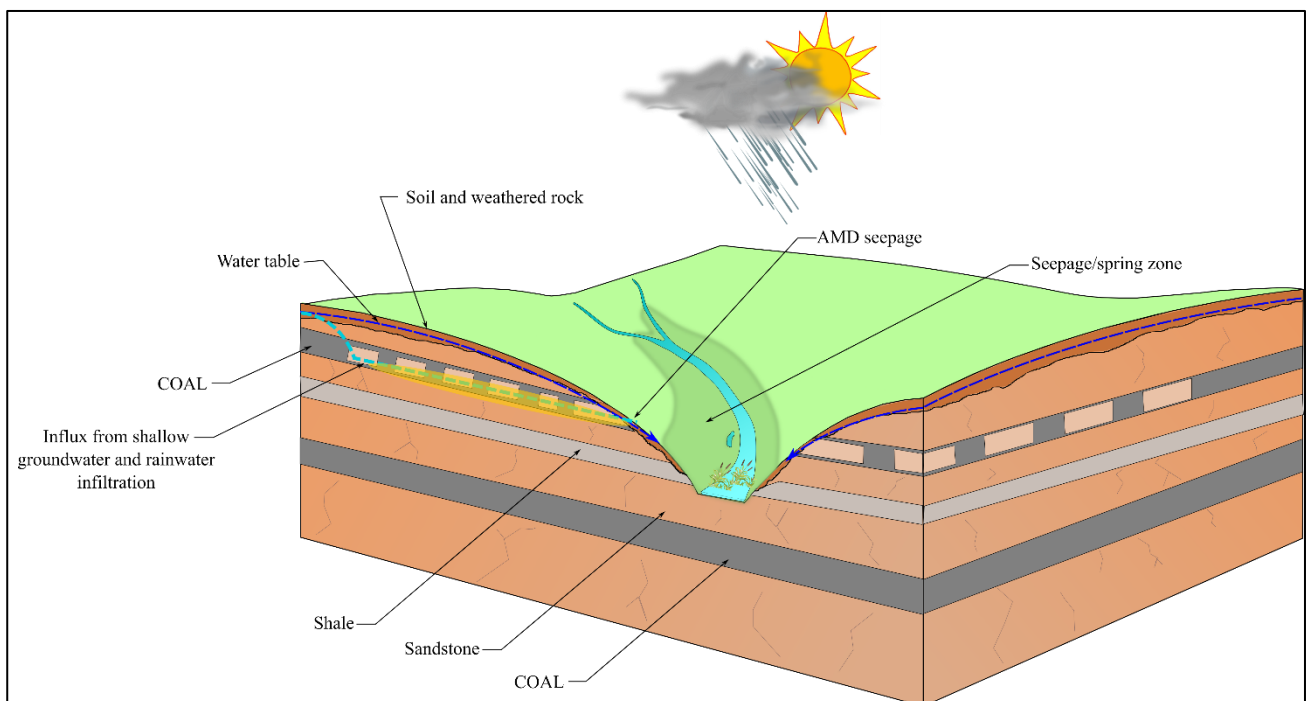
Figure 7-2: Schematic diagram of the post-mining underground operations at the Union Colliery.

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┌─────────────────────────────────────────────────────────┐
│                        Reactants                         │
│  ┌───────────────────────────────────────────────────┐  │
│  │  Recharge water (rain and shallow groundwater      │  │
│  │                  infiltration)                     │  │
│  │                       +                            │  │
│  │                       O₂                           │  │
│  │                       +                            │  │
│  │  Pyrite, carbonates (calcite), silicates and       │  │
│  │              exchangeable bases                    │  │
│  └───────────────────────────────────────────────────┘  │
│                            │                             │
│                            │         Oxidation           │
│                            │         Hydrolysis          │
│                            │         Hydration           │
│                            │         Acidification       │
│       Dominant Processes   │         Neutralisation      │
│                            │         Adsorption          │
│                            │         Dissolution         │
│                            │         Precipitation       │
│                            ▼         Complexation        │
│                        Products                          │
│  ┌───────────────────────────────────────────────────┐  │
│  │  Mine water (saline and either acidic or alkaline) │  │
│  │                       +                            │  │
│  │  Secondary minerals (silicates, hydroxides,        │  │
│  │                 sulphates)                         │  │
│  │                       +                            │  │
│  │                 Gases (CO₂)                        │  │
│  └───────────────────────────────────────────────────┘  │
└─────────────────────────────────────────────────────────┘
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After Azzie (2002)

Figure 7-3: Conceptual model for the geochemical evolution of mine water.

7.2 IMPACT OF MINING TYPE ON HYDROGEOCHEMISTRY

Numerous authors including Hodgson and Krantz (1998), Hodgson (2001), Grobbelaar (2001), and Grobbelaar *et al.* (2004) have reported on the impacts of different mining types employed in South African collieries on the hydrogeological regime and especially on the water quality. The mining method employed has a significant impact on the generation of acidity (McCarthy & Pretorius, 2009). This section therefore aims to highlight important observations made by aforementioned authors, especially in terms of recharge and subsidence, and associated impacts on water quality. These observations are viewed from a perspective of the conditions prevailing at the Union Colliery. As mentioned in Chapter 3 of this dissertation, bord-and-pillar mining was the main mining method employed at the Union Colliery with stooping, which is considered as high extraction mining, in some areas.

Sulphide oxidation and associated neutralisation processes require exposed mineral reactive surface areas. The reactive surface does not differ between the different mining methods, however flow rates and, consequently, contact periods may differ (Hattingh *et al*., 2002). During a study at Hlobane Colliery in South Africa, Hattingh *et al*. (2002) found that water-rock interaction during the vertical migration of infiltrating rainwater is small because of generally high flow rates. Horizontal flow within the mine voids, however, is controlled by the floor contours and the specific mining method which can prolong contact periods between water and exposed mineral surfaces. In bord-and-pillar mined areas, flow paths essentially consist of open channels, whereas in total extraction areas (stooping), the floor paths are more tortuous and may be braided due to collapsed roof material (Hattingh *et al.,* 2002).

Recharge into areas where bord-and-pillar mining predominates are lower than for high extraction areas due to the structural support provided by the coal pillars. The latter implies that collapse of roof material, and hence subsidence areas, in bord-and-pillar mined areas is less pronounced when compared to high extraction methods (Hodgson, 2001). This results in decreased infiltration and subsequent flooding rates in bord-and-pillar mined areas which allows the build-up of oxidation products (Grobbelaar *et al*., 2004). Moreover, the decreased infiltration rates are accompanied by slower rates of alkalinity addition to the underground workings from recharge water.

Exposed mineralised wall rock in underground adits, drifts, levels and shafts are often characterised by a multitude of sulphide bearing and secondary minerals (Majzlan *et al*., 2015). The exposed reactive surface area of bord-and-pillar areas is the lowest of all mining types even though entire walls are exposed in each pillar. Acid generation is therefore typically limited (McCarthy & Pretorius, 2009). Over time, however, scaling of the coal pillars, fracturing, and partial collapse of roof material within the coal bords result in increased reactive surface area, thus increasing acid generation (Usher, 2003; McCarthy & Pretorius, 2009). A sharp geochemical boundary between the mine atmosphere and the adit walls enables massive oxidation of the sulphide minerals and precipitation of minerals from aqueous solution. This is assumed to be the case in the Union Colliery compartments.

Grobbelaar (2001) explained that stooping is a stage during the bord-and-pillar mining method with increased pillar extraction. The degree of extraction generally varies as it depends on the geology, coal quality and common safety factors. Goafing or collapse of the roof materials can occur as a result of extensive stooping but ultimately depends on the competence of the lithology of the roof and host lithology. Various subsidence areas, of which most have been rehabilitated, have been identified at the Union Colliery especially in areas where mining depths are shallow and in areas where extensive stooping were performed. The sinkholes generally occurred along the perimeter of the mine compartments. As a result of this collapsed material, increased influx rates of water are expected. Collapse of roof materials may further create fractures that extend outwards from these areas to the surface. The rate of water infiltrations thus depends on the degree of interconnectedness and extension of the fracture zones but is nonetheless higher due to the collapsed roof material. Goafing material further results in far higher reactive surface areas, therefore reactions may proceed far quicker in these areas (Usher, 2003).

7.3 CONCEPTUAL UNDERSTANDING OF GEOCHEMICAL ZONES

7.3.1 Rainfall and evaporation

Although the processes of rainfall and evaporation are not important from a geochemical point of view, it serves as the driver of water availability within the coal discard dumps. As the dumps have been fully rehabilitated (covered with a soil layer and revegetated) this will limit the water ingress to the dumps. Rainwater infiltration and percolation to the underground voids may further influence the water levels within the underground voids. Subsidence areas, however, also rehabilitated, may be associated with higher infiltration rates to the underground voids as mentioned previously. Water is important for geochemical reactions to take place and it serves as a transport mechanism of dissolved components. Water availability within the coal discard dumps and underground voids are expected to fluctuate with the wet and dry seasons that undoubtedly influences the quality of the MIW as explained in Chapter 5 of this dissertation.

7.3.2 Runoff from the coal discard dumps' side walls

This process is not important from a geochemical perspective as much as from a suspended load perspective. However, as the coal discard dumps have been fully rehabilitated which limits erosion, the suspended load will not be significant in terms of geochemical impacts.

7.3.3 Geochemical reactions within the coal discard dump material and coal bearing lithologies

It has already been established that mining activities are important accelerators of sulphide mineral oxidation as it exposes large volumes of reactive material to atmospheric oxygen and moisture. Furthermore, blasting and crushing as well as goafing of waste material leads to considerable increase in the available surface area of reactive minerals. Hydrologic changes caused by dewatering of the underground voids and the recovery of water levels may expose large volumes of waste rock to the atmosphere where after oxidative products are transported by the water.

The coal discard dumps as a geochemical system can be visualised using Figure 7-1. As water is the transport medium of potential dissolved contaminants in the coal discard dumps, the most important water flow paths are shown in Figure 7-1, which corresponds to the contaminant flow paths.

Water quality data from monitoring boreholes located upstream and downstream of the coal discard dumps (refer to Chapter 5) as well as the mineralogical composition of the coal discard material (refer to Chapter 6), were used to determine the most important processes and reactions dominant within the waste material. The mineralogical data indicated that the most important primary mineral phases are quartz, K-feldspar, plagioclase (albite), mica (muscovite), calcite, pyroxene (enstatite), pyrite, and amphibole (pargasite/tremolite), and the

most important secondary phases include hematite, goethite, ankerite (siderite), gypsum, kaolinite, and smectite-type clays.

The coal-bearing lithologies can be visualised as two systems in one including the underground mine voids themselves from which coal has been extracted, and those areas that are coal-bearing, but have not been extracted and includes the coal pillars left behind to prevent collapse of the subsurface. The mineralogical data from the sample collected from the Susanna compartment roof indicated that the most important primary mineral phases are quartz, K-feldspar, plagioclase (albite), mica (muscovite), calcite, and pyrite, and the most important secondary phases are ankerite (siderite), kaolinite, and smectite-type clays. Mine water quality is strongly related to oxidation of sulphide minerals in the coal seams and roof materials in terms of acidity, sulphate$^-$, and metal(loid)s. This process includes the dissolution of neutralising minerals within the mine workings resulting in the removal of acidity and precipitation of secondary minerals along the flow paths. Mine void water and decant monitoring data indicate distinct differences in the water quality of the eastern and western underground operations (refer to section 5.4). Monitoring data of the eastern operations decant water indicates that the mine voids, although not acidic, contain elevated concentrations of sulphate as well as sufficient alkalinity. Monitoring data of the western underground operations decant water, however, indicates prevailing acidic conditions which is further associated with elevated concentrations of sulphate and a depletion of alkalinity. Therefore, as the mineralogical data of the underground operations are sparse, certain assumptions are made regarding processes dominant in the eastern and western underground operations based on the water chemical analyses monitoring data.

The mineralogical data indicated that some mineral phases, namely pyrite, are redox sensitive, implying that exposure to oxygen is expected to be a driving force in the oxidation of the mineral phase. Mining has created a new water table within the voids with new flow vectors, allowing oxygen and water to come in contact with sulphide minerals, resulting in contaminated water which then seeps to the surface (Figure 7-2). The oxygen content in the mine voids are elevated above the unmined baseline due to mining processes and oxygen ingress through adits, and monitoring boreholes intersecting the mine voids. It is however assumed that the oxygen content is multiple orders lower than that of the atmospheric fugacity. As mentioned before, an "open system" assumption is made for both the coal discard dumps and the underground compartments as the discard pore water and the underground waste material are in contact with a gas phase (Sherlock *et al*., 1995). The increased oxygen causes sulphide minerals to oxidise, thereby generally decreasing pH values and increasing, amongst other things, dissolved iron and sulphate. However, if sufficient buffer capacity is available in the form of carbonate minerals, then the system may have the capacity to neutralise the acid formed. This seems to be the case in the eastern underground operations, hence leading to increased bicarbonate concentrations in the mine void -and decant water concomitant with elevated sulphate concentrations. It is therefore assumed that the main difference between the eastern and western underground operations is the availability of neutralisation capacity. It is supposed that carbonate minerals were present in the western operations that depleted over time or alkalinity generated by the dissolution of calcite slowly depletes along the flow paths to final discharge.

It is clear that the water quality emerging from the mine waste materials mainly depends on the balance between the acid-generating oxidation reactions and the neutralising reactions taking place within the waste materials as a function of time (Sherlock *et al*., 1995).

Dissolution and secondary mineral precipitation due to contact with water are expected to be the dominant geochemical processes. In addition, adsorption to secondary and primary mineral phases is also expected to be important. These processes are thought to be contributory in the evolution of the MIW in the study area and will be discussed in more detail in the following sections and sub-sections.

7.3.4   Geochemical evolution of mine waste drainage water quality

In mine waste material containing pyrite, AMD may be produced due to natural oxidation reactions involving exposed reactive surfaces of pyrite, air, water, and soil micro-organisms. Of primary concern is the low-quality drainage from mine wastes that leads to adverse effects on the surrounding environments and ecosystems. Mine drainage quality is collectively affected by different physical, geochemical, microbiological and electrochemical processes (Nordstrom *et al*., 2015). The quality of drainage emerging from the wastes as surface runoff or subsurface seepage, largely depends on the reactions with minerals capable of neutralising the acidic water as it migrates through the waste along flow paths. The complex chemical and biochemical reactions and interactions responsible for mine water quality have been interpreted by many authors (Nordstrom, 1982; Sherlock *et al*., 1995; Nordstrom & Alpers, 1999; Azzie, 2002; Usher, 2003; Nordstrom, 2011; Brough *et al*., 2013). Several of these processes and accompanying reactions are discussed in the following sub-sections. It should be noted that the following sections only include highly simplified descriptions of the basic chemistry of AMD and neutralisation reactions, as well as secondary mineral precipitation and adsorption processes.

7.3.4.1   Sulphide oxidation

According to Nordstrom (1982) the oxidation of pyrite plays a significant role in the formation of acid mine waters, the source and distribution of sulphate in natural waters, and the source and distribution of metal(loid)s in the aquatic environment. The processes leading to pyrite oxidation is very complicated involving several oxidation-reduction reactions, hydrolysis and complex ion formation, solubility controls, and kinetic effects (Nordstrom, 1982; Nordstrom & Alpers, 1999; Azzie, 2002; Nordstrom, 2011). To accurately interpret these reactions in natural field systems, a fundamental understanding of microbial ecology, hydrology, and geology is required. However, it is not the purpose of this sections to review all these processes and additional role-players in detail, but to rather paint a picture of the reactions thought to be dominant within the Union Colliery mine wastes.

The overall equation which contemplates the formation of acid mine waters is often written in the form of the incongruent reaction given in Equation 7-1 (Nordstrom, 1982):

$$FeS_2(s) + \frac{15}{4}O_2(aq) + \frac{7}{2}H_2O(l) \rightarrow Fe(OH)_3(s) + 2H_2SO_4(aq) \qquad \text{Equation 7-1}$$
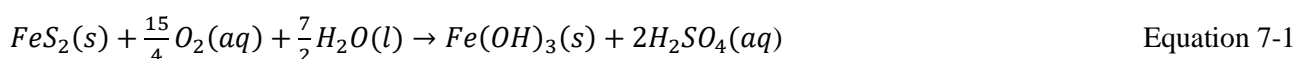
The generation of acid mine waters is best illustrated as a result of the oxidation of reactive sulphide minerals when they are exposed to an oxidant (O_2 or Fe^{3+}) and water under oxic or anoxic conditions, depending on the oxidant (Muniruzzaman et $al.$, 2018). The oxidation of pyrite, which is the most abundant sulphide mineral in the Earth's crust, is considered to be the most common mechanism responsible for acid generation in mining wastes (Blowes et $al.$, 2014; Muniruzzaman et $al.$, 2018). According to Nordstrom & Alpers (1999), although Equation 7-1 suggests that oxygen [O_2] is the ultimate driving force for the oxidation of pyrite and the final products are an insoluble form of oxidised iron [$Fe(OH)_3$] and an aqueous sulphuric acid [H_2SO_4] solution, it is an oversimplification of the process which takes place in true field conditions. Amongst other shortcomings, Equation 7-1 fails to explain geochemical mechanisms or the rates at which the reactions take place. It further does not reflect the slow oxidation of aqueous ferrous iron [Fe^{2+}] in acid solutions that often results in high ferrous iron concentrations in acid mine waters. Furthermore, it was mentioned by Nordstrom and Alpers (1999) that factors such as microbial catalysis, neutralisation reactions, sorption reaction, and climatic effects have an unavoidable effect on the weathering processes of pyrite but are not considered explicitly in the above equation. Moreover, many other minerals may form in addition to or instead of ferric hydroxide [$Fe(OH)_3$] (Nordstrom, 1982).

It was noted by Younger (2001) that chemical reactions during the processes and stages of AMD generation may seem simple and straightforward, however the chemistry of these processes may become very complicated as the geochemistry and physical characteristics of mine wastes are very site specific (Sherlock et $al.$, 1995). The acid-generation processes and stages as a consequence of sulphide oxidation have been the primary focus of many studies (Kleinmann et $al.$, 1981; Nordstrom, 1982; Morin et $al.$, 1991). The different stages in the development of acidic drainage from mine wastes as well as some of the factors mentioned above will be discussed in the following sub-sections with reference to the conditions at the Union Colliery.

7.3.4.1.1 *Basic chemistry and reactions during AMD generation*

The oxidation of pyrite by atmospheric oxygen in the presence of water that ultimately results in the generation of AMD can be described by the following oxidation and reduction reactions (Stumm & Morgan, 1970; Evangelou, 1995):

$$FeS_2(s) + \frac{7}{2}O_2(aq) + H_2O(l) \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$ Equation 7-2

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O \ (rate\ limiting\ step)$$ Equation 7-3

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$ Equation 7-4

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$ Equation 7-5
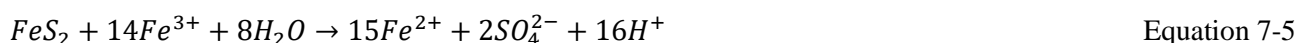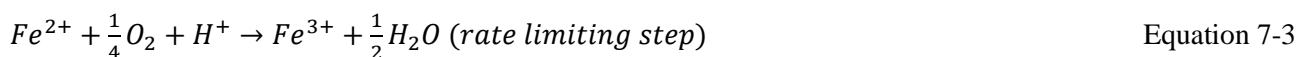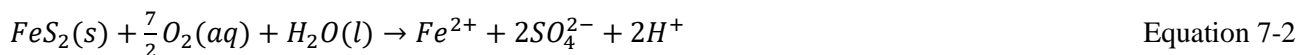
The mineralogical data indicated that the coal discard and roof coal material contain ~3 wt% pyrite which is unstable in the presence of oxygen and react according to the reaction depicted by Equation 7-2. Upon exposure of pyrite-bearing mine waste to oxygen, pyrite is oxidised leading to the release of dissolved ferrous iron [Fe^{2+}], sulphate [SO_4^{2-}] and protons [H^+] (Nordstrom, 1982) to the discard pore water and underground mine void water. This reaction is shown as irreversible, due to the presence of dissolved oxygen in the major part of the

coal discard dump facility as well as in the underground compartments. Pyrite is thus expected to be unstable. If the oxidising conditions persist, dissolved ferrous iron is oxidised to ferric iron [Fe^{3+}] according to Equation 7-3 (Nordstrom, 1982). The iron oxidation mechanism is usually sustained by microbial activity (Muniruzzaman *et al.*, 2018). The oxidation of Fe^{2+} to Fe^{3+} (Equation 7-3) is considered the rate limiting step in the pyrite oxidation process. This was explained by Singer and Stumm (1970) that since oxidation of Fe^{2+} to Fe^{3+} in the pH range of 3.0 is extremely slow, the oxidation of pyrite in this pH range will also be very slow, unless oxidation of Fe^{2+} is catalysed by micro-organisms. According to Jaynes *et al.* (1984) *Thiobacillus ferrooxidans,* which is an acidophilic chemolithotrophic organism that is ubiquitous in geologic environments containing pyrite (Nordstrom, 1982), can rapidly oxidise Fe^{2+} to Fe^{3+} in the pH range of 2.5 to 3.5. Singer and Stumm (1970) explained that iron-oxidising bacteria can accelerate the rate of Fe^{2+} oxidation by a factor of 106 (Usher, 2003). The microbial oxidation rate is thus clearly greater than the abiotic oxidation rate. Therefore, where *T. ferrooxidans* exist and acidic pH conditions persist, pyrite oxidation can be described by Equation 7-3 and Equation 7-5. The detailed role of microorganisms in sulphide mineral oxidation, as well as in the overall geochemistry of mining environments, has been widely described and reviewed by Singer and Stumm (1970), Evangelou and Zhang (1995), Nordstrom and Southam (1997), Nordstrom (2000), Baker and Banfield (2003), Johnson and Hallberg (2003), Dold (2010), and Blowes *et al.* (2014), among others.

Ferric iron is not soluble above pH values of ~3.0. Therefore, Fe^{3+} will precipitate as ferrihydrite, of which ferric hydroxide [$Fe(OH_3)$] is a proxy, according to Equation 7-4. Evangelou (1995) stated that the reaction described by Equation 7-4 is a readily reversible reaction of dissolution and precipitation that serves a source/sink term for Fe^{3+} when taking place at pH values below 3.0. This reaction further describes a major step in acid generation in the environment. Equation 7-4 is however shown as irreversible as the buffering capacity of the carbonate minerals within the coal discard dumps and eastern compartments prevent pH values to drop below 3.0. Iron oxides and hydroxides were identified in the mineralogical analyses, which indicate that this process is already taking place. This assumption is however not valid when considering the western underground operations as pH values below 3.0 has been observed at Butter Adit Decant (refer to section 5.4).

It is therefore clear that for every mole pyrite, four H^+ are released, when considering that one H^+ is consumed for the oxidation of Fe^{2+} to Fe^{3+}. The Fe^{3+} can be reduced by pyrite upon the initiation of pyrite oxidation as displayed in Equation 7-5. Pyrite can thus also be oxidised by the dissolved ferric iron species, especially under low pH conditions (Muniruzzaman *et al.*, 2018). Pyrite therefore continues to be oxidised as long as Fe^{3+} is generated. Appelo and Postma (1993) explained that at a pH value below 4.5, pyrite is oxidised by Fe^{3+} much more rapidly than by O_2, and faster than dissolved Fe^{2+} is oxidised by O_2 to Fe^{3+}. Nordstrom and Alpers (1999) compared the oxidation rate of pyrite by O_2, Fe^{3+}, and by hydrogen peroxide [H_2O_2] and found that the rate of pyrite oxidation by Fe^{3+} as oxidant can be two to three orders of magnitude faster than by O_2 as oxidant. In the process all Fe^{3+} is rapidly consumed and pyrite oxidation would eventually cease unless Fe^{3+} is replenished by the oxidation of Fe^{2+} by O_2 as described by Equation 7-3. The faster rate of pyrite oxidation by Fe^{3+} when compared to oxidation by O_2 have been shown in many studies (Garrels & Thompson, 1960; McKibben & Barnes, 1986; Williamson & Rimstidt, 1994; Mylona *et al.*, 2000; Muniruzzaman *et al.*, 2018).

Therefore, it is thought that pyrite oxidation is initiated by O_2 as oxidant at near-neutral pH values (Equation 7-2), however as the pH values reduce to ~4.0, the rate of oxidation becomes governed by Equation 7-5 (Nordstrom, 1982). According to Stumm and Morgan (1981) dissolved oxygen does not have to diffuse all the way to the pyrite surface, and that it is possible for pyrite to oxidise in the absence of O_2. Nevertheless, the rate at which pyrite is oxidised within mine wastes will largely be determined by the rate of oxygen transport. It has also been established that pyrite oxidation is mediated by the Fe^{2+}/Fe^{3+} system.

It is clear from the reactions presented above that in addition to pyrite, the presence of both O_2 and H_2O is critical for process progression (Nordstrom, 1982; Evangelou, 1995; Mills, 1998a). Mills (1998a, 1998b) explained that this has important consequences as this suggests that removal of the oxygen source, or the water source, will cause a cessation of AMD generation. Moreover, the termination of the activity of *T. ferrooxidans* may halt the pyrite oxidation process, and hence AMD generation, even more. Azzie (2002) had the impression that although no definite statement can be made regarding the inhibition of pyrite oxidation in South African coal mines, it is presumed that pyrite oxidation is limited in older workings, which have been fully flooded due to the cessation of pumping and ventilation. However, as mentioned before, it is unlikely that the Union Colliery underground compartments will ever become fully flooded due to decant elevations below that of the compartment roof elevations (refer to Chapter 3). Oxygen diffusion and transport within the mine compartments can therefore not be avoided.

The complexity of the processes arises from the dynamics between chemical, biological and electrochemical reactions which varies from site to site according to the environmental conditions. It is prevalent from the above discussion that factors that have an impact on the rate of oxidation include pH, the partial pressure of oxygen [PO_2], specific surface and morphology of pyrite, the presence or absence of bacteria and/or clay minerals, as well as hydrological factors. Therefore, there is no single rate law available to describe the overall kinetics of pyrite oxidation for all studies. Although Nordstrom and Alpers (1999) found that oxidation rates can range over three orders of magnitude, they are demonstrably faster than the dissolution rates for aluminosilicate minerals by one to several orders of magnitude (White & Brantley, 1995).

In summary, from the initiation of pyrite oxidation, the pH drops quickly and typically stabilises at values in the range of 2.5 to 3.0. Mills (1998b) explained that the pH of stabilisation is generally determined by the optimal habitat requirement of the site-specific strain of bacteria. Many metal(loid)s are often present at trace levels within pyrite source minerals. Oxidation of this mineral therefore lead to the release and mobilisation of these trace elements. The acidic environment associated with AMD further creates an environment for metal(loid) solubilisation as discussed in Chapter 2 of this dissertation. The simultaneous reactions of the dissolution of pyrite by Fe^{3+} and the oxidation of Fe^{2+}, constitute a cycle of continuous pyrite oxidation (Singer & Stumm, 1970). The net consequence is an increase in the total dissolved solutes, including Fe^{2+} and SO_4^{2-}, and the release of acidity in the drainage water emanating from the mining wastes.

7.3.4.2 Acid neutralisation, alkalinity generation and pH buffering

Sherlock *et al*. (1995) explained that the development and the geochemical evolution of acid mine waters is a complex combination of inorganic and organic processes and reactions and is generally the net difference between acid-generating and acid-neutralising reactions. Numerous minerals can neutralise acidic mine waters, but their reactions are less well understood and, in general, simple assumptions are made regarding their role. Neutralising minerals generally include, 1) calcium and magnesium bearing carbonates, 2) oxides and hydroxides of calcium, magnesium, aluminium and iron, 3) soluble, non-resistant silicate minerals, and 4) phosphates, primarily apatite. Sherlock *et al*. (1995) and Azzie (2002) highlight that the rate and extent to which minerals react when subjected to acid mine waters in the environment has enormous practical significance both for the overall weathering behaviour of mining and processing wastes and the steps required to develop and maintain waste management plans.

For severe acidic drainage (pH <3.0) to occur, the sulphide minerals present in the waste material must create such an environment where rapid oxidation is favoured. Furthermore, for waters to remain acidic, oxidation processes should continue for a sufficient time to exhaust all the neutralisation capacity provided by the coal and host rocks (Usher, 2003). This is evident in the western underground operations where all neutralisation capacity is exhausted along the flow path to the specific decant points (refer to Chapter 5). The potential of sulphide rock to generate acid is therefore strongly related to the neutralisation capacity yielded by often calcareous material in the host rock (Sherlock *et al*., 1995).

Broughton *et al*. (1992) explained that in the event of initial exposure of sulphide bearing rocks to flowing water and oxygen, the process of sulphide oxidation and consequently acid generation begins. Ochieng *et al*. (2010) ascertained that pyrite is responsible for the initiation of acid generation and metal(loid) mobilisation. The increased acidity in the aqueous phase promotes the dissolution of acid-neutralising minerals along flow paths of water containing acidic solutions (Muniruzzaman *et al*., 2018). Such acid-neutralising reactions generally result in the progressive buffering of pH, often which is accompanied by the precipitation of metal-bearing oxyhydroxides and oxyhydroxide sulphates. The most common pH buffering minerals in mining environments include carbonates, aluminium and ferric hydroxides, and aluminosilicates (Muniruzzaman *et al*., 2018).

According to Sherlock *et al*. (1995) the resultant acidic plume migrating through and away from the mine waste is neutralised along the flow path in regions based on various mineral equilibrium pH, which describes the pH above which the mineral precipitates and below which it dissolves. Any calcium-based carbonate minerals in the host rock will immediately neutralise the small amount of acidity produced and will maintain neutral to alkaline conditions in the water passing over the rock. Among these carbonate minerals, calcite is found to be not only the most common, but also the fastest reacting carbonate mineral in mining environments (Muniruzzaman *et al*., 2018). Calcite dissolution raises the pH of the water to between 5.5 and 6.9 (Sherlock *et al*., 1995). Iron -and aluminium hydroxides and siderite will precipitate since the pH is above the individual equilibrium pH values. As acid generation continues and the buffering agent is consumed or rendered ineffective in further neutralisation, the pH of the water will decrease, which will in turn enhance the conditions

for further acid generation. Thus, over time with continued influx of acidic water and upon calcite mineral depletion, the pH would then be buffered by siderite [$FeCO_3$] dissolution to a pH between 5.1 to 6.0 (Sherlock *et al*., 1995). However, siderite may act as both an acid neutraliser and acid producer, depending on the prevailing chemical conditions (Dold, 2010). After all carbonates are depleted, the pH decreases until equilibrium is reached with most soluble secondary hydroxides formed. Aluminium hydroxides will buffer first, where after iron hydroxides will become dominant. The dissolution of aluminium hydroxides, such as amorphous $Al(OH)_3$ (Equation 7-6) or crystalline form gibbsite, maintain the pH in the region of 4.0-4.5. The following soluble iron hydroxide phases (Equation 7-7 and Equation 7-8), including ferrihydrite or goethite, buffer the pH values in the range of 2.5-3.5 (Blowes *et al.,* 2014).

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O \hspace{3cm} \text{Equation 7-6}$$

$$Fe(OH)_3 + 3H^+ \rightarrow Fe^{3+}3H_2O \hspace{3cm} \text{Equation 7-7}$$

$$FeO(OH) + 3H^+ \rightarrow Fe^{3+} + 3H_2O \hspace{3cm} \text{Equation 7-8}$$

These mineral dissolution processes complement a buffering sequence and as the rate of acid generation accelerates due to the exhaustion of neutralisation capacity, the pH will start to decrease in a progressive step-like manner as explained by Durkin and Herrmann (1996) and Usher (2003). Each stage of relatively steady pH represents the dissolution of a neutralising mineral that becomes soluble at the specific pH range (Figure 7-4). In the event that the system maintains a rate of sulphide oxidation, and hence acid generation, the pH-value will decrease to below 3.0 and AMD conditions will become dominant. The stages of relatively steady pH as described by Durkin and Hermann (1996), Morin (1983) and Usher (2003), may last for weeks, months and centuries, until the sulphide mineral is completely oxidised or until specific management strategies are introduced to counteract the effects of AMD. The pH stages are highly mineralogically dependent and according to Usher (2003) the observed water quality in South African mines is often associated with neutral pH's with high salt content due to carbonate neutralisation. Once the initial alkalinity has been depleted, the pH values tend to fall relatively rapidly which leads to a relatively bimodal distribution of pH in coal mine waters (refer to section 5.4).

Aluminosilicates (muscovite, plagioclase and amphibole) provide the last leg of buffering capacity in the pH buffering sequence (Figure 7-5), however reaction rates ae not rapid enough to neutralise acid and buffers pH values to ≥1.3. The rate of aluminosilicate mineral dissolution is kinetically controlled, except at very low pH values and is generally much slower than that of carbonates. Nonetheless aluminosilicate dissolution has the potential to mobilise a range of elements in pore water, including aluminium, potassium, sodium, calcium, magnesium and manganese (Muniruzzaman *et al*., 2018).
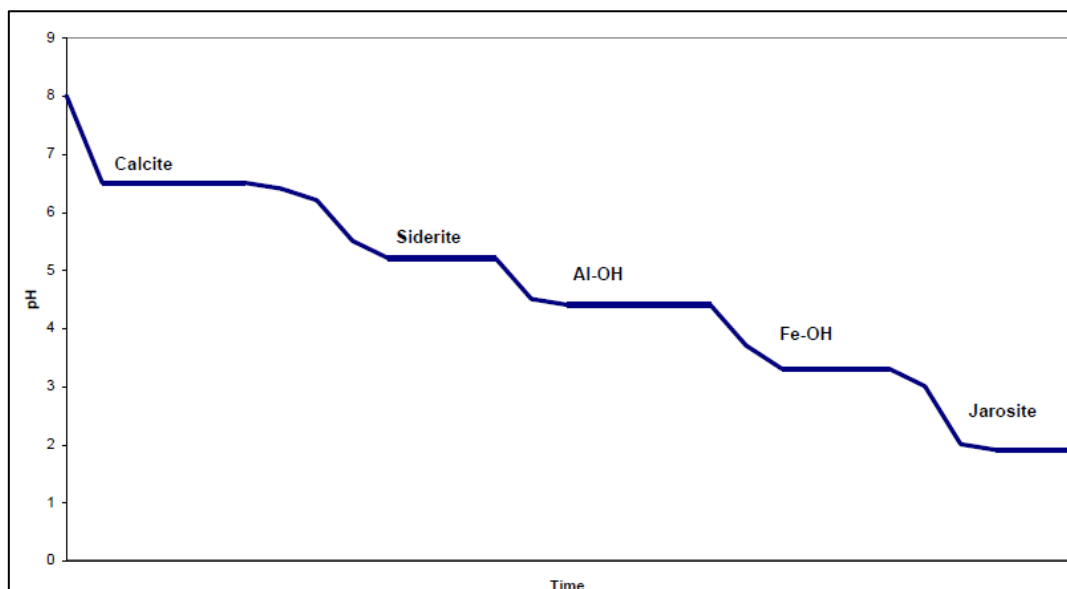
(Usher, 2003)

Figure 7-4: Stages in pH-evolution because of different neutralising minerals.
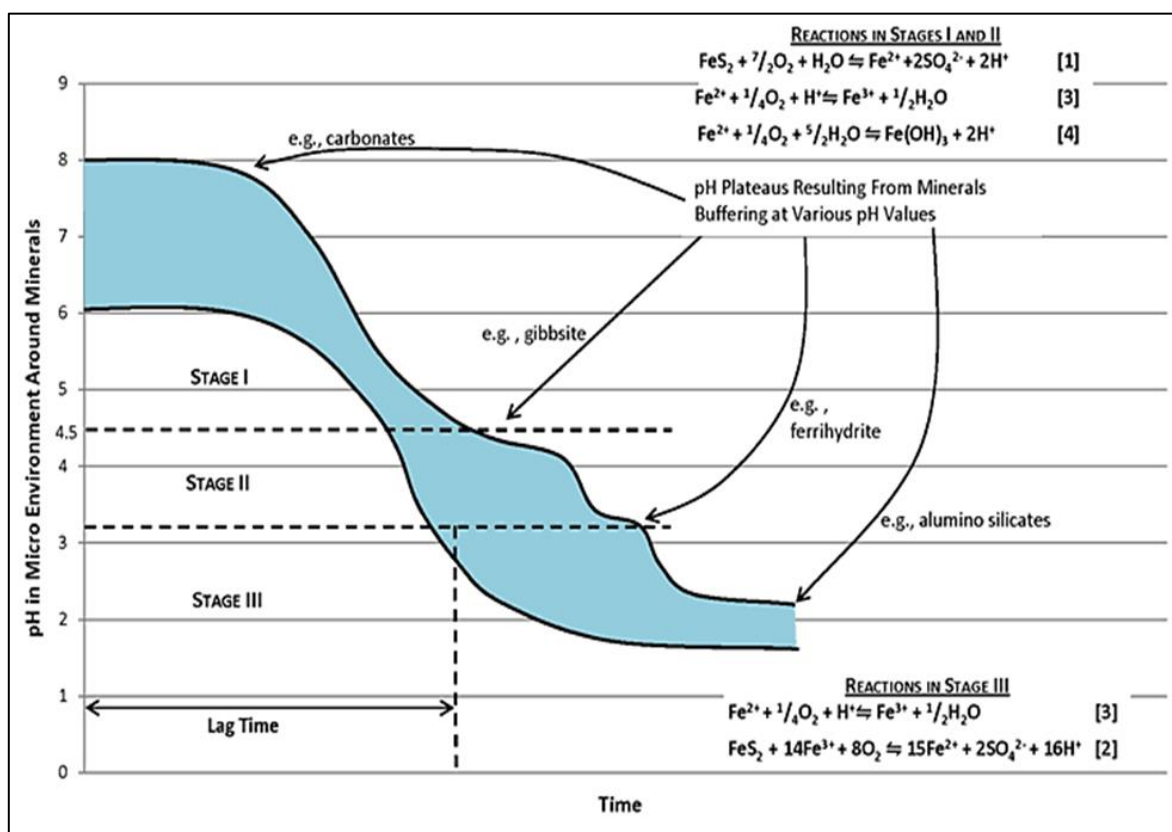
(Broughton & Robertson, 1992)

Figure 7-5: Acid neutralisation sequence of buffering minerals.

7.3.4.2.1   *Carbonate dissolution*

In nature pyrite often occur in close association with acid-neutralising minerals such as calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$], and siderite and acid produced as a result of pyrite oxidation is neutralised in situ by these minerals. Carbonates within mine wastes may either occur as an accessory gangue mineral that accompanies the mineral deposit and mine waste, or as a secondary product from weathering of wastes.

Carbonate minerals may therefore occur as either primary or secondary minerals in mine wastes and generally include calcite, dolomite magnesite, siderite, rhodocrosite and strontianite (Azzie, 2002). The importance of carbonate minerals in terms of their neutralisation capacity of acid mine waters have been reported by Blowes and Ptacek (1994), Sherlock *et al.* (1995), Nordstrom and Alpers (1999), Azzie (2002), and Usher (2003). Blowes and Ptacek (1994) ascertained that siderite forms as a secondary phase in mine wastes where calcite reacts with solutions containing elevated concentrations of iron.

Acid-neutralising capacity provided by fractured carbonate-containing waste rock and continuous infiltration of recharge water and shallow groundwater may exceed the overall acid-generating capacity of the acid forming rock which remains in contact with the water. Given sufficient recharge and reaction time, the acidity present will be neutralised, and the system would be expected to turn alkaline eventually. However, it has been explained by Azzie (2002) that in many South African mines there is insufficient acid-neutralisation capacity to maintain the alkaline system, and so the waters eventually turn acidic.

The mineralogical analyses of the Union Colliery mine waste indicated that the carbonate minerals, calcite and ankerite (siderite), occur in the coal discard -and roof coal material. Calcite is the most abundant primary carbonate phase whereas it is assumed that siderite occur as a secondary mineral within the mine wastes. According to Sherlock *et al.* (1995) the dissolution of calcite can be of the same order of rate as the redox reactions responsible for acid generation in the mine wastes. These minerals have the capacity to neutralise acid formed from the dissolution of the sulphide minerals according to the following reactions:

$$CaCO_3(s) + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$$
<div align="right">Equation 7-9</div>

$$FeCO_3(s) + H^+ \leftrightarrow HCO_3^- + Fe^{2+}$$
<div align="right">Equation 7-10</div>

Carbonate minerals are expected to dissolve at first (Equation 7-9), then neutralise the acidity and consequently generate alkalinity in the mine waters and may finally precipitate at the end of the flow path. Siderite is considered as an exception as it has the potential to oxidise and hydrolyse the iron. According to Lottermoser (2007) the capacity of siderite to neutralise acidic drainage depends on the redox conditions of the weathering environment. Under reducing conditions, siderite dissolves to form bicarbonate [HCO_3^-] and Fe^{2+} ions (Equation 7-10). However, in an open system under oxidising conditions, the dissolution of siderite has no neutralising effect as the generation of HCO_3^- consumes H^+, and any Fe^{2+} generated will undergo hydrolysis and precipitation as explained in Equation 7-4 (Ptacek & Blowes, 1994).

Equations 7-9 and 7-10 are shown above as reversible due to the overabundance of carbonate minerals relative to the sulphides indicating that the buffer capacity of the waste material far outstrips the acidity produced by the oxidation of sulphides. Note that this assumption is only applicable in the coal discard dump systems and in the eastern underground operations where the alkaline pH suggests the presence of sufficient alkalinity and thus reversible reactions. Therefore, the amount of calcium [Ca^{2+}] and HCO_3^- ions added to the discard pore water and underground void water will depend on the solubility of these minerals in the specific systems. The western compartments predominantly indicate prevailing acidic conditions with almost no alkalinity present in the drainage water at the specific decant points. This suggests that all neutralisation capacity is depleted

along the flow path. This assumption is made based solely on the water quality monitoring data discussed in Chapter 5 of this dissertation and cannot be confirmed with mineralogical data of the floor and roof materials of the western underground compartments (refer to section 4.6). It is therefore assumed that carbonate minerals were present within the western operation system and depleted over time. It is also possible that carbonate minerals provide neutralisation in isolated areas within the mine workings which is consumed along the different flow pathways to the discharge points.

According to Drever (1997) the depletion of neutralisation capacity often displayed by acidic mine waters occurs as a result of neutralising carbonate [CO_3^{2-}] and HCO_3^- ions producing carbonic acid [H_2CO_3] according to the following reactions:

$$H^+ + CO_3^{2-} \rightarrow HCO_3^-$$
<div align="right">Equation 7-11</div>

$$H^+ + HCO_3^- \rightarrow H_2CO_3$$
<div align="right">Equation 7-12</div>

As explained by Drever (1997) once the system reflects AMD conditions, the neutralisation capacity yielded by the system is not as efficient in controlling changes in the pH value. When the system reaches a pH below ~4.2, all CO_3^{2-} and HCO_3^- ions have been converted to H_2CO_3 (Equation 7-11 and 7-12). Therefore, no additional buffering can be achieved by CO_3^{2-} and HCO_3^- ions. The generated H_2CO_3 subsequently dissociates into water and carbon dioxide [CO_2] according to the reaction displayed in Equation 7-13:

$$H_2CO_3 \rightarrow H_2O + CO_2$$
<div align="right">Equation 7-13</div>

In the event the water comes in contact with basic minerals such as calcite or infiltrating groundwater of higher alkalinity along the flow path, carbonates and sulphates and their hydrated and/or hydroxy-complexes will generally precipitate. Neutralisation may further cause metallic ions such as Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and As^{3+} to react to eventually precipitate as hydroxides and is reflected by the general reaction:

$$Mn^+ + nOH^- \rightarrow M(OH)n$$
<div align="right">Equation 7-14</div>

In Equation 7-14 the OH^- represents a hydroxyl ion, and $M(OH)n$ the metal hydroxide that precipitates.

7.3.4.2.2 *Silicate mineral dissolution*

Aluminosilicate minerals are common components in mine wastes and reactions of aluminosilicates when in contact with acidic waters are a well-known part of rock weathering processes (Stumm & Morgan, 1981). These reactions are typically acid-consuming and result in the release of some constituents into solution and the transformation of other constituents into more acid stable and commonly less reactive minerals. Silicate dissolution can therefore be described as either congruent or incongruent (Sherlock *et al*., 1995). The mineral structure and composition as well as environmental factors embody some of the controls that determine whether silicate dissolution is congruent or incongruent.

Variable silicate resistance to weathering is well documented in literature (Goldich, 1938; Sverdrup, 1990; Kwong, 1993). Azzie (2002) explained that minerals that crystallise from magmas at high temperature, such as anorthite, tend to be more reactive (reaction rates are faster) than minerals that crystallise at lower

temperatures, such as albite, muscovite, and quartz. Moreover, clay minerals such as kaolinite have relatively low reactivity.

Table 7-1 displays the relative reactivities of carbonate and rock-forming minerals commonly encountered in coal mining environments. Note that dissolving minerals refer to those whose components are taken completely into solution, whereas weathering minerals indicate that components are only partially subjected into solution and partially converted into secondary minerals (Azzie, 2002). According to Sherlock *et al.* (1995) the common end products of chemical weathering and alteration processes of many silicates are clay minerals (kaolinite or smectite-type clays) which represents incongruent dissolution.

Table 7-1: Relative reactivities of common rock-forming minerals in coal environments, listed in order of decreasing reactivity. Carbonate minerals are included for comparison.

Mineral group	Typical minerals encountered in coal environments
Readily dissolving	Calcite, aragonite
Less readily dissolving	Siderite, dolomite, magnesite
Fast weathering	Anorthite
Intermediate weathering	Chlorite, biotite
Slow weathering	Albite, montmorillonite (smectite), kaolinite
Very slow weathering	K-feldspar, muscovite
Inert	Quartz, zircon

(Azzie, 2002)

According to Sherlock *et al.* (1995) the evidence of silicate weathering is thus demonstrated in the presence of secondary alteration minerals such as kaolinite. The dissolution and reaction of aluminosilicates with acidic drainage as a result of sulphide oxidation at mine sites is also reflected by the high aluminium concentrations found in AMD waters. Aluminium concentrations exceeding 10 000 mg/L is not uncommon in acid mine waters according to Nordstrom and Alpers (1999) and Plumlee *et al.* (1999). It would however suggest that although aluminosilicate minerals are usually found in abundance in mine wastes, the aluminium observed in the waters was brought through relatively limited acid consumption by very slow aluminosilicate weathering reactions (Azzie, 2002).

Albite (plagioclase) is a slow weathering silicate mineral (Table 7-1) commonly found in coalfields. Albite generally weathers to yield sodium, aluminium and silica species. Under favourable conditions kaolinite will form. The weathering of all feldspars, including K-feldspar, muscovite, and albite, will form kaolinite which has been reported by Azzie (2002) as the principal clay mineral in local coalfields. Kaolinite is also the principal clay mineral found in the Union Colliery mine wastes (refer to section 6.2).

According to Sherlock *et al.* (1995) silicate weathering serves a primary sink for acidity and therefore chemical weathering results in the dissolution of species that contributes to the alkalinity of the water under certain pH conditions. The rate at which naturalisation takes place considering non-carbonates can however be orders of magnitude slower than pyrite oxidation rates, therefore, Shaw and Mills (1998) stated that the oxidation reactions will dominate. Cravotta *et al.* (1999) noted that bimodal pH frequency distributions often observed in coal mine waters (also refer to section 2.1.2.1.2), which are either in the circum-neutral or acidic range with

minimal values in between, reflect the slow reaction rates of non-carbonate minerals which fails to prevent acidification.

Ritchie (1994) described some of the reactions of silicate minerals that may contribute to the neutralisation capacity of the system, which becomes dominant at specific pH conditions (Equation 7-15 to Equation 7-17). Note that Equation 7-18 describes the dissolution of iron oxy-hydroxide minerals that may also buffer the system under given pH conditions. Only the reactions of the minerals identified in the Union Colliery mine waste will be referred to and include:

Muscovite dissolution:

$$KAl_2(AlSi_3O_{10})(OH)_2\ (s) + H^+ + \frac{3}{2}H_2O \rightarrow K^+ + \frac{3}{2}Al_2Si_2O_5(OH)_4\ (s) \qquad \text{Equation 7-15}$$

Albite dissolution:

$$NaAlSi_3O_8\ (s) + H^+ + \frac{9}{2}H_2O \rightarrow Na^+ + 2H_4SiO_4 + \frac{1}{2}Al_2Si_2O_5(OH)_4\ (s) \qquad \text{Equation 7-16}$$

K-feldspar dissolution:

$$KAlSi_3O_8\ (s) + H^+ + \frac{9}{2}H_2O \rightarrow K^+ + 2H_4SiO_4 + \frac{1}{2}Al_2Si_2O_5(OH)_4\ (s) \qquad \text{Equation 7-17}$$
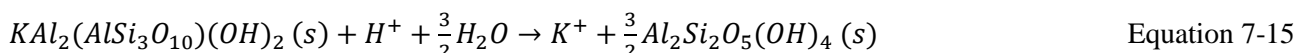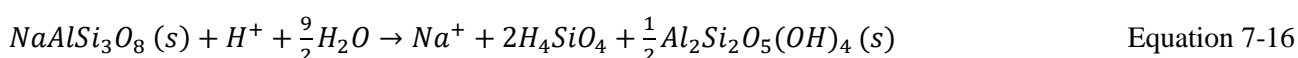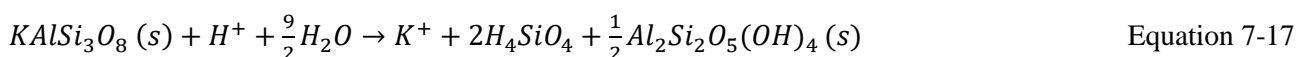
Iron oxy-hydroxide dissolution:

$$Fe(OH)_3\ (s) + 3H^+ \rightarrow Fe^{3+} \qquad \text{Equation 7-18}$$

Lappakko (1994) clarified that the dissolution rates of the minerals described above are comparatively slower in the neutral pH-range than in waters with lower pH values. Therefore, these minerals will provide more neutralisation capacity under extremely acidic conditions. The dissolution rate of silicate minerals is too slow to maintain the pH of MIW above 6.0. These minerals therefore usually serve to contribute to more neutral pH values in water if pyrite oxidation is terminated. In general, the role of carbonates is very important because of the reactivity of these minerals and the resultant neutralisation capacity. Some silicate weathering reactions are identified based on elevated concentrations of silica and aluminium in acid mine waters specifically observed in the western underground operations (refer to section 5.3.3.2).

The inference can be made that important factors that mainly determine the rate at which neutralisation takes place by carbonate, hydroxide, and silicate minerals include pH, the partial pressure of carbon dioxide [PCO₂], equilibrium conditions, temperature, and the presence of foreign ligands (Usher, 2003). Smith (2007) defines a ligand as an anion or neutral molecule that can combine with a cation to form a complex. Sherlock *et al.* (1995) concluded that when comparing reaction rates, sulphide minerals react fastest, followed by carbonates and then silicates.

It is thus well established that silicate minerals, including plagioclase feldspars, may also yield neutralisation capacity however limited in a certain pH range. As mentioned in section 7.3.4.2, the water quality observed at the decant points is controlled by depletion of sequential buffering phases which generally occurs in the order, carbonates, hydroxides, followed by aluminosilicates (Jurjovec *et al.*, 2000). It is assumed that the eastern

operations are effectively buffered by carbonate minerals, whereas within the western operations, dynamic equilibrium between dissolution and precipitation of aluminium -and iron hydroxide minerals control the pH range of the system. Thus, within the AMD conditions observed in the western operations where the carbonate neutralising capacity is depleted, aluminium -and iron hydroxide dissolution play a role in long-term acid neutralisation. In the event that the pH further drops, buffering by silicate minerals may become more dominant as explained in section 7.3.4.2.

7.3.4.3 Secondary mineral precipitation

Due to the highly reactive nature of acid mine waters, most primary minerals will dissolve when in contact which indices the formation of a variety of secondary minerals. Secondary minerals are those that predominantly forms during weathering of the primary minerals. Four important processes that lead to the formation of secondary minerals from acid mine waters have been identified by Nordstrom and Alpers (1999) and include, 1) iron oxidation and hydrolysis, 2) reaction of acid solutions with sulphides, gangue minerals and host rock, 3) mixing of acid mine waters with more dilute waters, and 4) evaporation of acid mine waters.

As mentioned earlier, the reaction of acid mine waters with country rock and gangue minerals such as carbonates, hydroxides and silicates will lead to buffering reactions as well as precipitation of metals. Evaporation may further concentrate the acid, sulphate and metal(loid)s generally associated with acid mine waters. Metals and sulphate may reach mineral saturation at a point forming sulphate salts, a common feature associated with oxidising sulphide-bearing mine wastes (Nordstrom & Alpers, 1999). It is well known that metal oxides such as iron, aluminium, copper, nickel and manganese are closely associated with acid mine drainage. Various authors, including Nordstrom and Alpers (1999), Bigham and Nordstrom (2000) and Jambor *et al*. (2000b) give an in-detail overview of amongst others, iron and aluminium oxides.

Iron occurs in two oxidation states in mine waters, namely Fe^{2+} and Fe^{3+}. It further occurs as solid phases in several oxide, hydroxides and hydroxy sulphates. According to Nordstrom (1982) many iron minerals may be associated with mine wastes and have a wide range of properties, from being very insoluble iron hydroxides to very soluble iron sulphate hydrates. The formation of iron sulphates is an important intermediate step preceding the precipitation of the more common insoluble iron minerals including hematite [Fe_2O_3], magnetite, goethite [$FeO(OH)$], lepidocrocite, ferrihydrite [$Fe(OH)_3$], schwertmannite and jarosite [$KFe_3(SO_4)_2(OH)_6$]. Acid mine waters, where iron becomes fully oxidised, will eventually reach saturation with respect to either ferrihydrite or jarosite. Ferrous hydroxide is according to Nordstrom and Alpers (1999) more soluble than its ferric iron equivalent in a given pH range. Ferrihydrite can be described as a poorly crystalline form of hydrous ferric oxide hydroxide that generally forms first upon neutralisation of ferric iron-bearing solutions where low temperatures and surficial conditions prevail. According to Bigham (1994), ferrihydrite in the mining environment is commonly associated with waters in the pH range of 5.0 to 8.0. Mine waste in equilibrium with ferrihydrite may provide a buffer system at a pH of approximately 3.19 (Miller, 1979). Hematite and goethite are probably the most common and most stable forms of ferric oxide and oxyhydroxide. Ferrihydrite is therefore known to weather to hematite if pH conditions are maintained in the range of 5.0 to 9.0. According to Schwertmann and Murad (1983), ferrihydrite will dissolve and precipitate as goethite in conditions outside

of this pH range. Goethite forms at pH values generally less than 6.0 from the dissolution of previously mentioned minerals, including early-formed goethite, and generally accumulates farther from sources of acidity (Montero *et al.*, 2005). Hematite forms in a pH dependent process that may involve the dehydration and transformation of earlier precipitates, such as those of goethite and ferrihydrite (Nordstrom, 1982; Montero *et al*, 2005).

The Log O_2-pH diagram as depicted by Figure 7-6 shows the stability of iron phases and dissolved species in sulphate-rich waters. The diagram shows that Fe^{3+} is soluble only at pH values less than ~3.0 and under oxidising conditions. At higher pH, it precipitates as some form of ferric hydroxide or ferric oxyhydroxide. Goethite is the most stable phase according to Figure 7-6. Similar observations were made by Monterroso *et al.* (1999). It is clear that Fe^{2+} is more soluble under reducing conditions.
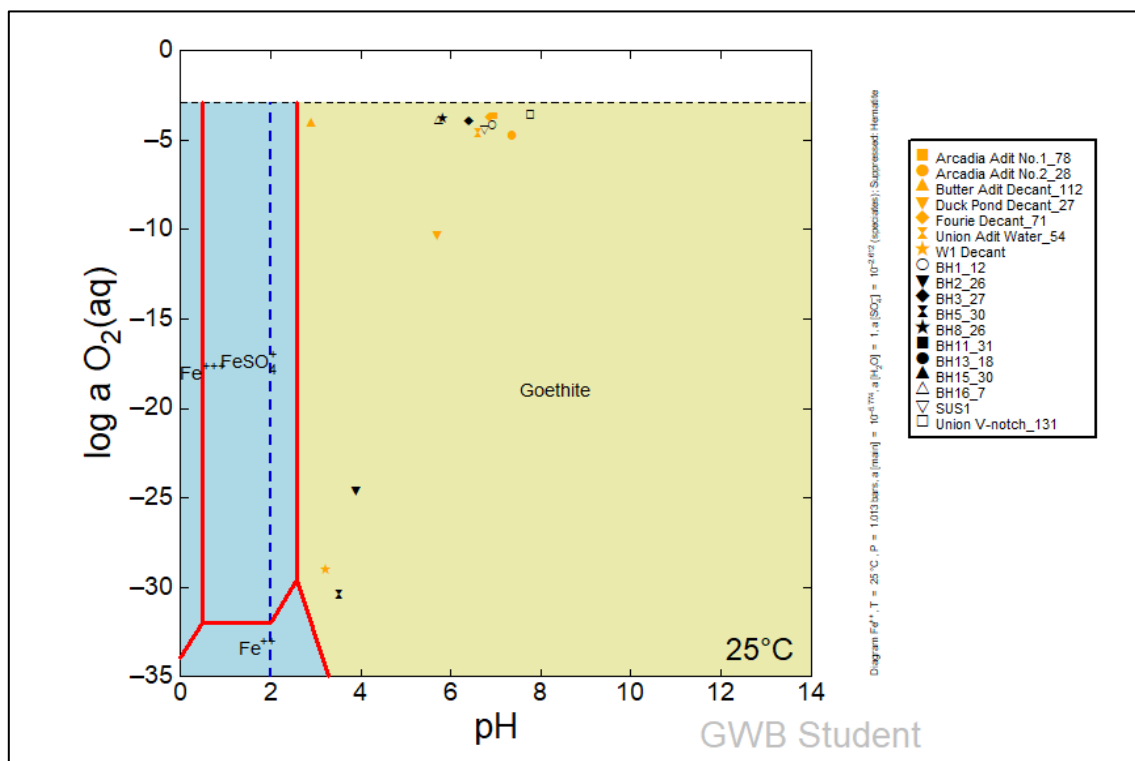
Figure 7-6: Log O_2-pH diagram for iron, showing fields of solubility of dissolved species (blue) and solid species (tan).

Common aluminium oxide, hydroxide, and hydroxysulphate minerals include boehmite, gibbsite, alunite, jurbanite, and basaluminite. Nordstrom (1982) specified that aluminium-sulphate and hydroxy sulphate minerals become more stable in acid mine waters than common soil minerals that includes gibbsite and kaolinite. Nordstrom and Ball (1986) extensively described the behaviour of aluminium in acid mine waters and some of their findings are presented in section 2.1.2.3.1.

As a result of elevated sulphate concentrations due to pyrite oxidation, as well as calcium introduced to the system through carbonate mineral dissolution, it is likely that the mineral gypsum [$CaSO_4.2H_2O$] will form in the coal discard dump facilities according to:
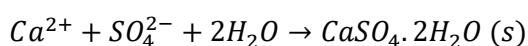
$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4.2H_2O \ (s)$$
<div align="right">Equation 7-19</div>

The formation of gypsum in the coal discard facilities (Equation 7-19) are confirmed by the mineralogical data (refer to section 6.2). The formation of gypsum will depend on the solubility product of the mineral under the specific conditions within the coal discard dumps and it is unlikely that enough will precipitate to completely buffer the discard pore water sulphate concentrations.

7.3.4.4   Adsorption

According to Smith (1999), sorption reactions which generally involves both inorganic and organic particulates, are a significant control on the transport and fate of many trace elements in natural systems. These processes generally limit metal(loid) mobility in most aqueous natural systems (Hem, 1985; Smith, 1999).

Smith (1999) noted that secondary minerals that form due to primary mineral weathering, as discussed in the previous section, often serve the most effective sorbent material. Nordstrom and Alpers (1999) stated that insoluble secondary minerals with large surface areas can effectively immobilise many contaminants associated with acid mine waters which provides an important attenuation and detoxifying mechanism. The phenomenon described above is known as adsorption and refers to two-dimensional accumulation of an adsorbate at a surface (adsorbent). Adsorption is therefore known as a surface-phenomenon.

Various iron-minerals can form as a result of iron oxidation and hydrolysis, which have low solubility and can adsorb or co-precipitate significant quantities of trace elements. Smith (1999) noted that metal-oxide minerals comprise some of the most important sorbent minerals in natural systems.

The main factors influencing adsorption include the pH of the system, the sorbate identity and concentration, formation of solution complexes, sorbent composition, and the concentration of sorbent surface binding sites (Smith, 1999; Azzie, 2002). Smith (1999) explained that when a metal-oxide mineral comes in contact with water, hydroxyl functional groups (OH^-) form on the surface. Neutral or alkaline pH conditions will generally result in a net negatively charged surface (attract cations); whereas under acidic conditions, excess protons are generally retained at the surface yielding a net positively charged surface (attract anions). Hem (1985) and Sherlock *et al.* (1995) defines the pH at zero-point charge (pH_{zpc}) as the pH at which the mineral surface is electrically neutral (the number of positively charged sites are equal to the number of negatively charged sites). Above the pH_{zpc}, the surface will be negatively charged and attract cations and below the pH_{zpc}, the surface will be positively charged and attract anions. Some representative values of pH_{zpc} are displayed in Table 7-2.

Table 7-2: The pH of zero-point charge for certain minerals.

Mineral	pH$_{zpc}$
Amorphous HFO [Fe$_2$O$_3$.H$_2$O]	8.1
Goethite [α-FeOOH]	6.0-7.0
Hematite [α-Fe$_2$O$_3$]	4.2-6.9
Gibbsite [α-Al(OH)$_3$]	10
Birnessite [α-MnO$_2$]	1.5-2.8
Amorphous [SiO$_2$]	3.5
Kaolinite [Al$_2$Si$_2$O$_5$(OH)$_4$]	4.6
Montmorrillonite (smectite)	2.5

(Smith, 1999)

Factors that affect the pH$_{zpc}$ include the concentration and type of ions in solution and the impurities of the solid. In general, the pH$_{zpc}$ usually corresponds to the pH of minimum solubility (Sherlock *et al.*, 1995).

It has been established that iron hydroxides have the capacity to adsorb potential contaminants from solution. This is generically shown by the following equation for cations and anions.

$$> OH + Me^{2+} \leftrightarrow Me + H^+ \qquad\qquad \text{Equation 7-20}$$

$$> OH + L^{2+} + H^+ \leftrightarrow > L^- + H_2O \qquad\qquad \text{Equation 7-21}$$

In Equations 7-20 and 7-21 above, >OH represents the mineral surface with associated hydroxyl group, Me is the metal(loid) and L is the anionic ligand, of which sulphate would be an example. The equations are also written as reversible, as adsorption is a completely reversible process, depending on the local physicochemical conditions as mentioned earlier.

Figure 7-7 presents sorption capacity provided by different abundances of sorbent material, namely hydrous ferric oxide (HFO), after a study done by Smith *et al.* (1992). Field data were compared with computer model predictions for metal(loid) sorption at ten diverse mine drainage sites. The consequences of limited amount of sorbent material was clear. Where abundant sorbent material was present the result was well-defined adsorption edges. However, where the sorbent material was sparse, competition for binding sites with major cations became dominant. The latter is commonly the case in mine drainage systems where less-defined adsorption edges are observed and zinc [Zn], cadmium [Cd] and nickel [Ni] tend not to sorb at all. According to Plumlee *et al.* (1999) zinc, cadmium, and nickel are expected to remain mobile in many mining environments and is supported by the observations made by Smith *et al.* (1992).
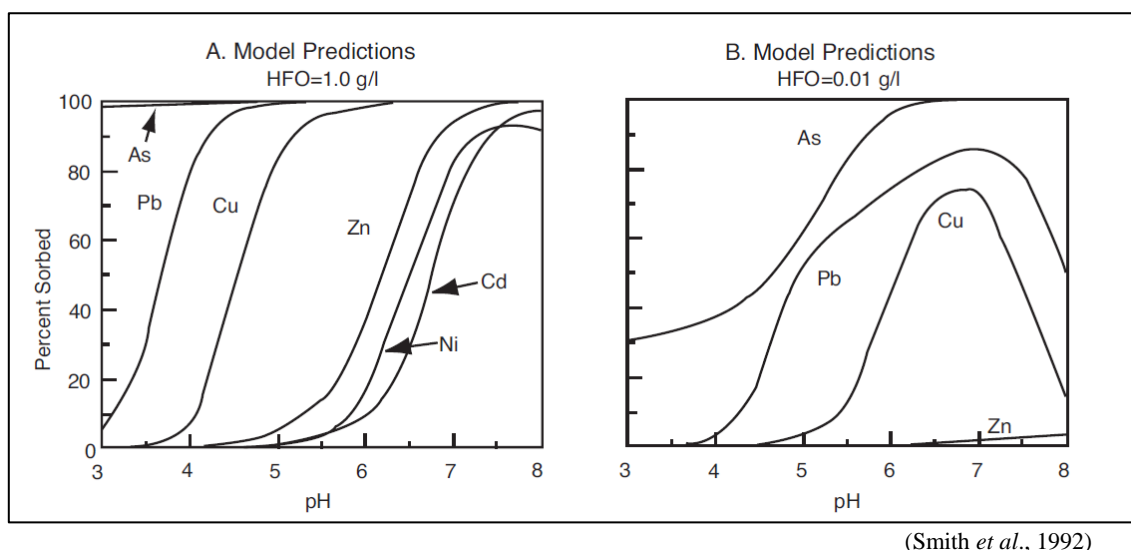
Figure 7-7: Model predictions of metal sorption on hydrous ferric oxide (HFO) as a function of pH for two different sorbent concentrations (A and B).

7.3.5   Leaching and direct flow to sensitive receptors

The shallow weathered and deeper fractured Ecca aquifer are for the purposes of this study considered from a hydrogeochemical perspective to aid in the quantification of geochemical risks to the environment. From this perspective the aquifer systems should be considered sensitive receptors as well as an important transport pathway for potential contaminants.

From a hydrogeochemical perspective, the most important processes in the aquifers are expected to be mixing, dilution, ion exchange and precipitation. The geology of the site consists of sandstone, siltstone, shale, coal and dolerites. Adsorption is deemed to be likely, as the iron content in the sandstone aquifer water is expected to be high and thus also the amount of iron oxides and hydroxides, which could act as mineral substrates for dissolved constituents (refer to previous section).

The most important fluid fluxes influencing the underground mine waste is indicated in blue in Figure 7-1 and Figure 7-2 and suggest that rainfall infiltration and groundwater ingress to the underground voids will be accompanied by water level rise within the compartments leading to eventual mine discharge at adits (some of which were sealed and fitted with drainage pipes), sinkholes and weaker geological structures. Subsidence, together with sinkholes also play an important role in surface infiltration.

The mine discharges contaminated water into two important river catchments and is expected to continue discharging water into these rivers in perpetuity. Apart from seeps, seven significant discharge points in well-defined flow channels affects two primary river systems, namely the Vaalwaterspruit and the Boesmanspruit. In these seven major discharges, seepages drain towards three tributaries of the Vaalwaterspruit and a single tributary of the Boesmanspruit. As described by various authors (Stumm & Morgan, 1996; Mosley *et al*., 2014; Mosley *et al*., 2015) there is a general tendency for metals to oxidise (Fe^{2+} and Mn^{2+}), hydrolyse and precipitate as pH and redox potential increases when acidic mine drainage enters receiving water bodies. The protons produced from these reactions can result in acidification of the water courses should the neutralising capacity

of the system be insufficient. As well as pH, the dissolved metal(loid) speciation following mixing will determine bioavailability and risks to aquatic organisms (Mosley *et al*., 2015).

7.4 GROUNDWATER AND MINE WATER HYDRO-CHEMICAL DESCRIPTION

Both groundwater and mine water chemistry in terms of baseline ranges, water quality types, and seasonal variability were discussed in detail in Chapter 5 of this dissertation. The groundwater and mine water discussion in this section only includes general descriptions of the water compositions that will be used as inputs in the geochemical models. The specific assumptions and input data will further be discussed in Chapter 8.

Distilled water was used as the initial water flux to the coal discard dump system, whereas recent (2017) monitoring data of the underground mine void water was used as the initial water quality in the underground workings. This was done to evaluate the incremental change of the mine water chemistry as a result of geochemical processes along the flow paths up until it discharges at the surface. Hence, only the input data used for the eastern and western geochemical models will briefly be discussed in the following sub-sections.

7.4.1 Mine water characterisation

During the selection of input parameters and concentrations for the geochemical models, only the most recent water quality data for the year 2017 were considered as this data is most representative of the system at that moment. Future change can be simulated accordingly by means of forward reaction path models. As mentioned earlier, the mine void water for the respective eastern and western underground operations served as input to the geochemical models and were calibrated against the respective operations' decant water chemistry.

7.4.1.1 Eastern operations

The mine void water observations considered to be used as input parameters for the eastern operation forward reaction path models included the sampling stations, BH11 (February, March, June), BH16 (June), BH9 (March, June). The months indicated in brackets after each monitoring station reflect the months for which water quality data was available. These monitoring boreholes intersect the eastern underground operations. The Susanna compartment was excluded from this assessment as this compartment is currently not decanting. The six mine water observations therefore represent a variable distribution of the water quality within the mine voids.

BH11 (February and March), BH16 (June) and BH9 (March and June) have ion distributions that dictate Ca-SO_4 water types, whereas BH11(June) reflects a Ca-HCO_3 facie. This is evident in the Durov diagram (Figure 7-8) that shows that the dominant ions in the mine water are principally SO_4^{2-} and Ca^{2+}. The difference in ion distributions are also shown by the Stiff diagrams in Figure 7-9.
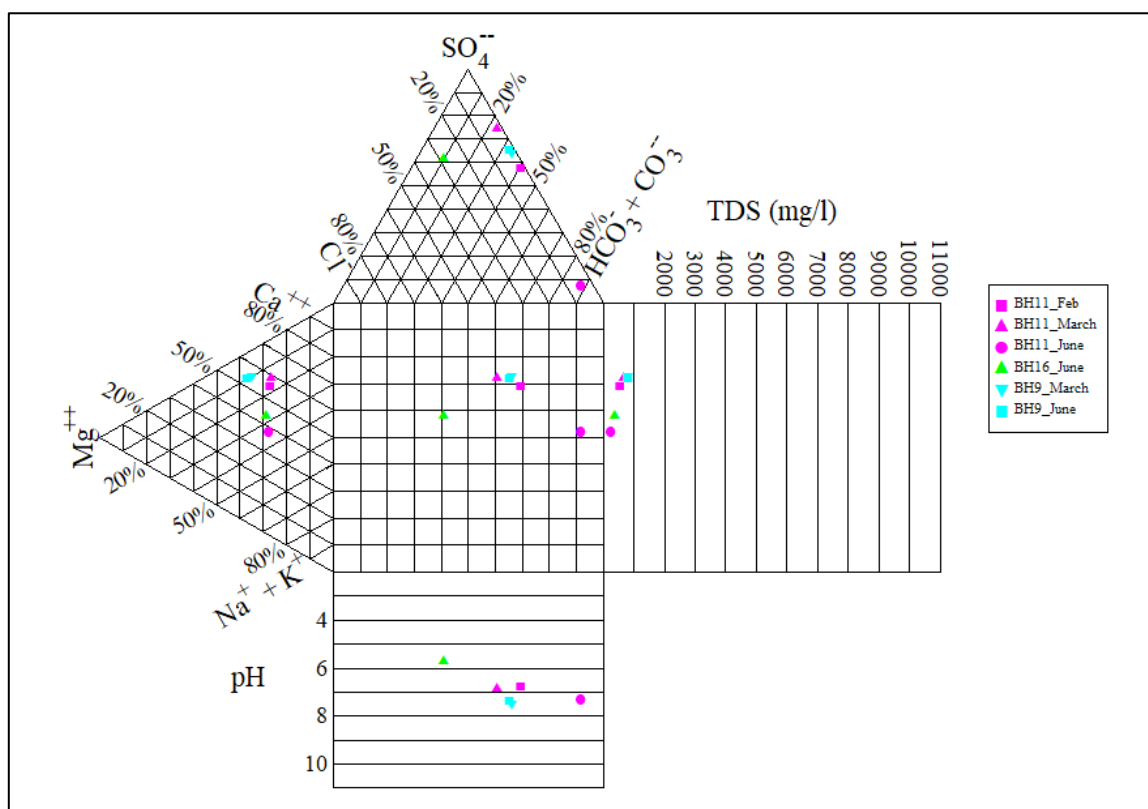
Figure 7-8: Durov diagram of eastern operation mine void water samples.

The pH of the mine void waters is in the circum-neutral range, except for BH16 which displays a pH <6.0. The TDS values average at 572 mg/L (Figure 7-8). The processes yielding the high sulphate and calcium concentrations have been discussed in Chapter 5 of this dissertation and in preceding sections.
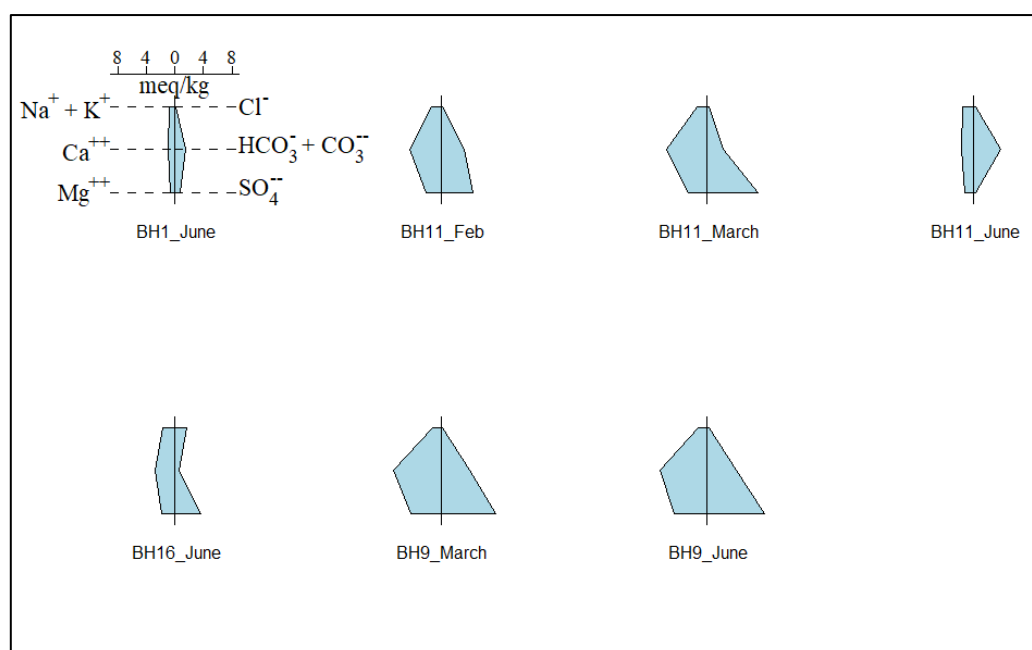
Figure 7-9: Stiff diagrams of the eastern operation mine void water.

During the geochemical model setup, mine void water chemistry representative of the eastern operations had to be selected to serve as input to the geochemical models. The median values for all constituents were

calculated and the observation that displayed concentrations closest to the median values were selected as input water quality for the eastern operation geochemical models. A detailed chemical analysis of the input mine water chemistry is given in Chapter 8 of this dissertation. Specific metal(loid)s of concern (excluding iron and aluminium) as observed in the eastern operations' decant water chemistry that displayed concentrations above the unmined groundwater baseline as well as given guideline standards included manganese, nickel and selenium (refer to Appendix B: Water Quality Data).

7.4.1.2   Western operations

The mine void water observations considered to be used as input parameters for the western operation forward reaction path models included the sampling stations, BH1 (June), BH2 (February, March, June), BH3 (February, March, June), BH5 (February, March, June), BH7 (March, June), BH8 (February, March, June) and BH15 (February, March, June). These monitoring boreholes intersect the western underground operations and represent a variable distribution of the water quality within the mine voids.

BH2 (February, March and June), BH3 (February and March), BH5 (February, March and June), BH7 (March and June) and BH15 (March and June) have ion distributions that demonstrate Ca-SO$_4$ water types. BH8 (February and June) shows a Mg-SO$_4$ facie, BH8 (March) a Na-SO$_4$ water type, BH1 and BH3 (June) Ca-HCO$_3$ water types, and BH15 (February) a Fe-SO$_4$ water type. The dominant Ca-SO$_4$ water type is evident from the Durov diagram (Figure 7-10). The ion distributions of the different observations are also shown in the Stiff diagrams presented in Figure 7-11 to Figure 7-13.
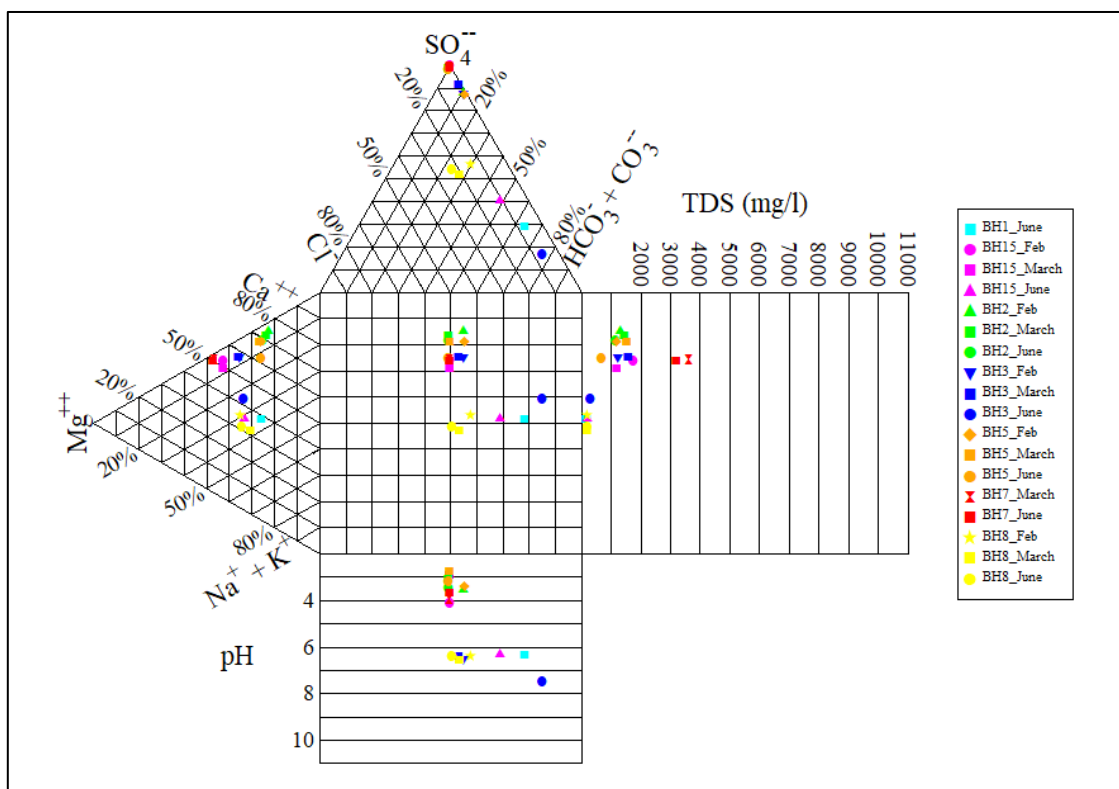
Figure 7-10: Durov diagram of western operation mine void water samples.

The pH of the mine void water displays a bimodal distribution with values predominantly between 2.0 and 4.0, and between 6.0 and 8.0. Relatively few samples have pH values between 4.0 and 6.0. This may be attributed to various factors which is mentioned in Chapter 5 of this dissertation. The samples display an average TDS value of 1 175 mg/L (Figure 7-10).
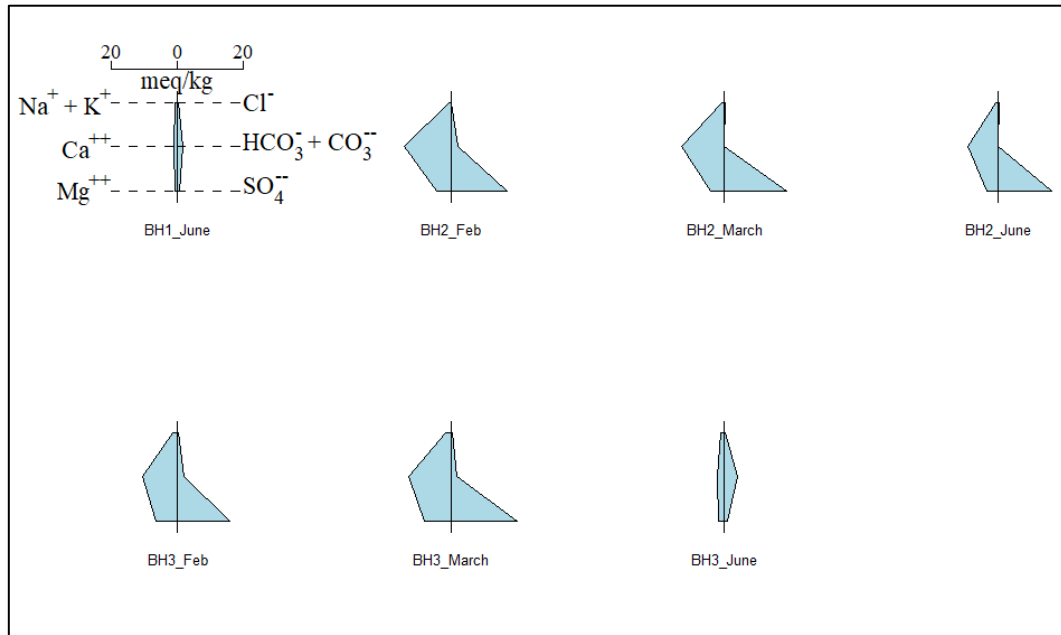
Figure 7-11: Stiff diagrams for boreholes, BH1, BH2 and BH3, within the western operations.
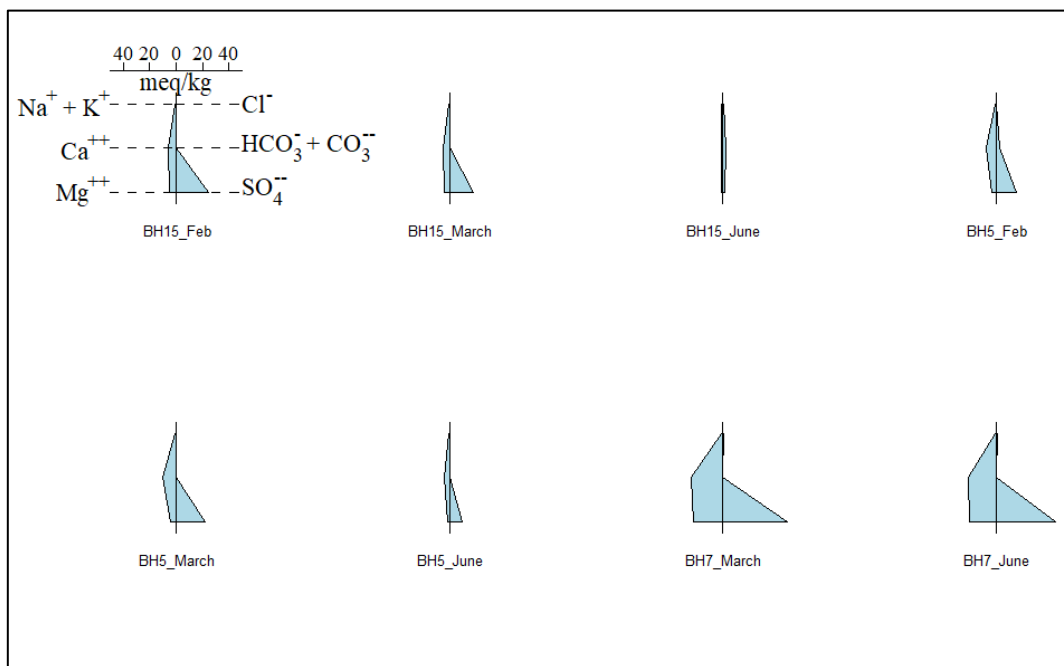
Figure 7-12: Stiff diagrams for boreholes, BH15, BH5 and BH7, within the western operations.
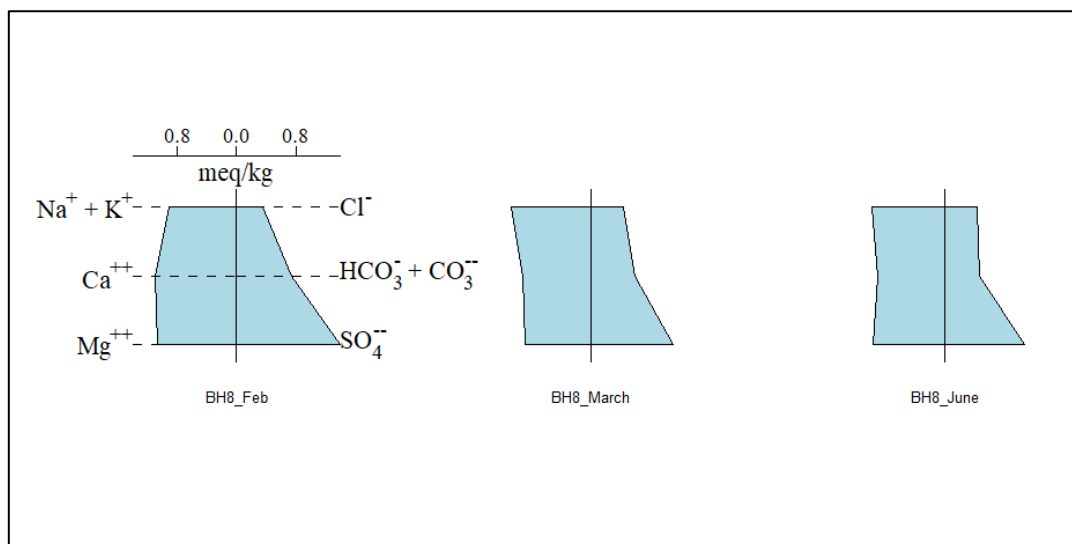
Figure 7-13: Stiff diagrams for BH8 within the western operations.

Similar to the eastern operations geochemical model setup, representative mine void water chemistry for the western operations had to be selected to serve as input to the geochemical models. A detailed chemical analysis of the input mine water chemistry is given in Chapter 8 of this dissertation. Specific metal(loid)s of concern that displayed concentrations above the unmined groundwater baseline as well as given guidelines included manganese, nickel, lead, arsenic and selenium (also refer to Appendix B: Water Quality Data).

7.5 CONCLUDING SUMMARY

The development of site conceptual models is a vital step in predicting water quality at mine sites. Most uncertainty related to the prediction of water quality at mine sites derives from inadequate or inaccurate conceptual models, hydrologic and geochemical characterisation data, and input data to hydrogeochemical models. In order to create a well-defined and representative conceptual model, the collection and interpretation of hydrogeologic and geochemical data from the mine is a necessity.

The discussions presented in this chapter are highly simplified descriptions of the basic chemistry of sulphide oxidation, AMD generation and associated neutralisation, secondary mineral formation and adsorption processes. The chemistry and reactions of processes that take place in true mine water systems are extremely complex. Nonetheless, the following conclusions can be drawn from the conceptual models:

- Rainfall and evaporation serve as the drivers of water availability within the coal discard dumps. Rainwater infiltration and percolation to the underground voids influence the water levels within the workings. Subsidence areas along the perimeter of the mined compartments may be associated with higher infiltration rates. Water serves a necessity for geochemical reactions and is a crucial transport mechanism of dissolved components.

- Shallow groundwater infiltration to the underground mine voids further influence the water levels and allow mixing of infiltrated groundwater with built up oxidation products. The increased water flux leads to mine decant at adits and sinkholes.

- Adits (most of which have been sealed and fitted with drainage pipes), subsidence areas as well as boreholes intersecting the mine voids provide pathways for oxygen diffusion. The coal discard dump systems as well as the underground voids are therefore assumed to represent open systems as the mine wastes are in contact with a gas phase.

- Mining has created a new water table within the mine voids with new flow vectors, allowing oxygen and water to mix with pyrite resulting in drainage characterised by either circum-neutral or acidic pH, and elevated sulphate and metal(loid)s which then discharge at the surface.

- Reactions assumed dominant within the coal discard dumps and along flow paths within the eastern operations include pyrite oxidation, carbonate neutralisation, secondary mineral precipitation and adsorption. The reactions assumed to be dominant along flow paths within the western underground operations include pyrite oxidation, hydroxide dissolution and neutralisation, secondary mineral precipitation and dissolution, and adsorption.

- Ultimately, the rate of oxidation and acid generation varies depending on the accessibility of air, moisture, and microbes to the pyrite surfaces and the neutralisation capacity of available buffering materials.

- The mine discharges contaminated water into two important river catchments and is expected to continue discharging water into these rivers in perpetuity. Apart from seeps, seven significant discharge points in well-defined flow channels affects two primary river systems, namely the Vaalwaterspruit and the Boesmanspruit. Apart from the aquifer systems affected through leaching from the coal discard dumps and subsurface seepage from the underground operations, three tributaries of the Vaalwaterspruit and one Boesmanspruit tributary were identified as sensitive receptors.

Conceptual models are not unique and can change over time. It is therefore necessary to revisit conceptual models and modify predictive models based on new site-specific information. However, for the purposes of this study and due to time constraints water quality monitoring data only up to June 2017 were considered in the conceptual models and subsequent selection of input water chemistries for the geochemical models.

CHAPTER 8:
NUMERIC GEOCHEMICAL MODELS

This chapter is dedicated to the predictive modelling of the quality of drainage emanating from the mine waste systems, including the coal discard dumps, eastern -and western underground operations, to quantify long-term mine waste drainage stability and analyse risk. Prediction of acid generation and metal(loid) mobility are undertaken with the aim of reducing uncertainty to a level at which potential risk and liability can be quantified. This will inform appropriate monitoring, mitigation and contingency plans. Short discussions regarding the model components, assumptions, and inputs, as well as short presentations on the model outcomes are given to numerically quantify any impacts from an environmental geochemistry point of view. With the conclusion of this chapter it will form part of a full discussion of the results in Chapter 9.

All model results are presented in Appendix D: Model Results and are available on request.

8.1   INTRODUCTION

Conceptual models, as discussed in the preceding chapter, are aimed to provide a simplified but complete representation of the observed natural conditions and processes in a way to conceptually understand all dynamic phenomena of the study area (Van Coller, 2013). Numerical geochemical modelling refers there to that most factors and processes from the conceptual models are divided into various mathematical models. All mathematical models are combined in a systematic and simplified numerical model accordingly, with certain assumptions being made to accommodate data gaps as well as uncertainties in the models. It is unavoidable that the degree to which the models accurately portray the true field processes and conditions and the decisions made based on their outcomes, is greatly dependant on the quality and quantity of the data as well as the assumptions made (Bethke, 1996; Swart *et al*., 1998; Bethke, 2008).

Kinetic geochemical modelling is a superior modelling approach since the models consider the kinetic rates of the chemical oxidation of sulphide minerals present in the mine waste. Kinetic models further account for chemical processes such as kinetic or equilibrium-controlled dissolution, complexation (from equilibrium and stoichiometry of several complexes), precipitation, and formation of complexes and secondary minerals (Swart *et al.,* 1998). Through mass balance equations and solubility constraints the model keeps track of the evolution of chemical species and provides estimates of the quality of seepage. The models also include the dissolution (thermodynamic and sorption equilibrium), adsorption and co-precipitation of several metal(loid)s (Swart *et al.,* 1998).

It should be emphasised before commencing with the model setup and results that numeric geochemical models do not simulate reality and cannot be considered and applied with the idea that the outcomes are accurate or completely true (refer to section 2.3.1). However, geochemical models should be applied as tools in establishing a working and visual understanding of the processes and variables at hand in a certain scenario,

ultimately used as a decision-making tool (Van Coller, 2013). According to Swart *et al*. (1998) geochemical modelling provides long-term estimates (+100 years) of the possible changes or trends of the quality of seepage from mine waste. The results obtained from quantitative modelling improves the understanding of interactions between geochemical processes. The models presented in this chapter should therefore not be considered as concrete evidence or predictions of what will happen to the mine waste drainage quality over time. The model outcomes are aimed to provide understanding and reduce uncertainty regarding the dominant processes influencing the mine waste drainage over time. Referring to section 2.3 of this dissertation, the modelling process and model results should thus be treated as heuristic tools rather than sources of absolute truth.

Numeric geochemical modelling was used as a tool to quantify the medium to long-term behaviour of the mine waste material to identify and quantify the risks to the local environment, including soil, groundwater and surface water. Models based on different conceptual scenarios were developed respectively for the coal discard dumps and the eastern -and western underground operation components.

The following sections and sub-sections present the methodology, assumptions, input data, and the scenario setups of the geochemical models for each waste component. Furthermore, simulated results are listed and shortly discussed with some minimal interpretations. More comprehensive discussions of the model results will follow in Chapter 9 of this dissertation to culminate in the final objectives of this study.

8.2   MODEL SETUP

The mine area was divided into different geochemical systems or components (coal discard dumps, eastern - and western operations), each with defined specific geochemical conditions as discussed in Chapter 7 of this dissertation. Drainage chemistry were predicted or simulated for each component based on its unique combination of system conditions and design. As mentioned before, the seepage emanating from the mine waste within the different systems were modelled using GWB (Bethke, 1996).

8.2.1   Model input data and assumptions

As mentioned in section 7.4 of this document, distilled water was used as input water chemistry to the coal discard dump system. Representative mine void water chemistry was selected as inputs to the respective eastern -and western operations. The specified input water chemistries were reacted with mineral phases with acquired reaction rates (forward reaction path models) to simulate the water chemistry downstream of the coal discard dumps and that of the decanting mine water at the respective eastern -and western operations. Special focus was placed on metal(loid) mobility. To remain both conservative in approach while remaining true to the system view as developed in the conceptual models and to compensate for data limitations, certain assumptions were made in reference to certain model inputs.

It should be highlighted that assumptions made during data processing, data input and model setups and simulations were made to follow a conservative approach to simulate realistic processes within the limits of the software. These assumptions are presented in Table 8-1.

Table 8-1: Compilation of main model assumptions.

Assumption	Description	Data	Source
Data processing			
Data on detection limit	All laboratory water analyses data with values below laboratory detection limits were assumed to be half of the detection limit	All laboratory results	South 32 and IGS Laboratory
Zero value data	All laboratory water analyses data with zero values were assumed to be half of the laboratory detection limit	All laboratory results	South 32 and IGS Laboratory
XRD and XRF data	All compartments will exploit the same mineral resources and coal as the Susanna compartment. Mineralogical data following the geochemical assessments of the Susanna compartment roof material were assumed to be the same for the remaining eastern and western coal mineralogy	Laboratory results	Department of Geology, UFS
Elemental compound conversion	PO_4, As, B, and Si were converted to HPO_4^{2-}, $As(OH)_4$, $B(OH)_3$ and SiO_2 respectively due to software and simulation constraints on aqueous species	All laboratory results	South 32 and IGS Laboratory
Models			
Rock mass water interaction	1 L of water will be in contact with 1 kg of mineralogy during rainwater infiltration, groundwater flow and geochemical interactions	Model input	Author assumption
Reactive surface area of mineral phases	$100 \ cm^2.g^{-1}$ of mineral surface area will be exposed for reactions to take place	Model input	Author assumption
Oxygen availability within discard dumps	The maximum oxygen fugacity within the discard dump system was assumed to be 0.18, which is lower than the atmospheric value	Model input	Author assumption
Oxygen availability in underground operation	The maximum oxygen fugacity within the underground voids was assumed to be 0.018, which is multiple orders lower than in true open systems	Model input	Author assumption
Adsorption by hydrous ferric oxide (HFO)	HFO is assumed to be the sole sorbent material in the model simulations	Model input	Smith (1999), author assumption

8.2.2   Input sampling points and water chemistry

Distilled water was used as input water quality to the coal discard dump geochemical model to simulate the natural weathering of the mineralogy of the coal discard material. The resultant chemistry of groundwater affected through leaching from the coal discard dumps were subsequently evaluated.

As mentioned before, representative mine void samples within the respective eastern and western operations were selected to serve as input water quality to the geochemical models. As will be mentioned, the nitrate concentrations of the samples will not be included in the models or used for comparison as outside sources like blasting and agricultural activity can lead to these parameters being elevated (Van Coller, 2013). Weathering models for the eastern -and western underground operation systems were simulated to compare with field decant monitoring data to evaluate the transient effect of weathering products on the water chemistry and the evolution of mine void water until final discharge. The geochemical models were focused on the geochemical processes influencing the mine waste drainage quality over the medium to long-term. Distilled water and mine void water chemistry used as input to the respective geochemical models are shown in Table 8-2. Considering the coal discard dumps model, GWB requires some type of electrolyte (basis species) to calculate reactions, therefore sodium and chloride was added as the major constituents and the rest of the parameters were included in trace amounts. GWB requires basis species and initial concentrations of all constituents to be evaluated over the long-term. The groundwater monitoring data did not reflect significant arsenic, nickel and lead concentrations; therefore these constituents were not included in the coal discard dumps models.

Table 8-2: Input sample chemistry used in geochemical models.

Geochemical system		Coal discard dump	Eastern underground operations	Western underground operations
Sample ID		Distilled water	BH11 (February 2017)	BH2 (June 2017)
Water Type		Na-Cl	Ca-SO$_4$	Ca-SO$_4$
pH	pH units	7	6.80	3.46
TDS	mg/L	-	533.67	1126.00
Ca	mg/L	1.00E-06	90.14	188.00
Mg	mg/L	1.00E-06	26.69	41.90
Na	mg/L	1	30.09	14.10
K	mg/L	1.00E-06	4.22	5.93
HCO$_3$	mg/L	1.00E-06	161.00	2.50
Cl	mg/L	1	4.96	10.10
SO$_4$	mg/L	1.00E-06	216.12	781.00
Al	mg/L	1.00E-06	0.01	6.75
Fe	mg/L	1.00E-06	0.09	17.30
Mn	mg/L	1.00E-06	0.56	1.69
As(OH)$_4$	µg/L	-	5.00	0.001
Ni	µg/L	-	15.00	0.001
Pb	µg/L	-	7.50	0.001
Se	µg/L	0.001	23.00	0.001
SiO$_2$ (aq)	mg/L	0.001	11.17	18.70

8.2.3   Mineralogical data

The laboratory XRD mineralogical analyses of the coal discard and roof coal material were used to calculate representative mineralogical composition and abundances of the waste material within the coal discard dump and underground operation systems. The calculated median weight percentage (wt%) were used to convert mineral abundances to grams which were used as representative mineralogy in the forward reaction path models. With regards to the underground operations' models, chemical analyses data of the discharging mine water for the eastern and western components were used to augment decisions made in terms of mineral abundances, especially in terms of calcite abundances.

The reaction rate constants of the various mineral phases were acquired from literature (Palandri & Kharaka, 2004). Laboratory mineral reaction rates are generally up to three orders of magnitude faster than natural reaction rates (Banwart *et al*., 2002). Therefore, the models were set up from a conservative perspective, as faster reaction rates imply more dissolved solids added to the solution per unit time.

The input water qualities for the different modelled systems, as discussed in the previous section, were allowed to react with the primary mineral phases observed within the mine waste. The mineral abundances were determined based on the XRD result weight percentages as mentioned before. Only the primary minerals were assigned kinetic rates within the models to confirm if the models precipitate the secondary minerals identified by the XRD analyses. The exception is kaolinite which was included as a kinetic mineral in the eastern and western operation models. It was assumed that kaolinite occur as a primary mineral within the host rocks and aquifer material. Kinetic rates were assigned to all primary minerals except for calcite, which was included as a simple reactant as its reaction rate was assumed to be very fast (Sherlock *et al*., 1995). All oxides were also included as simple reactants. It should therefore be noted that the buffering provided by calcite is under equilibrium control, whereas the buffering provided by aluminosilicates is under kinetic control (depends on pH conditions) (Swart *et al.,* 1998).

The systems under consideration had the following main characteristics:

- Largely inert mass;

- pyrite being oxidised to generate acidity; and

- a small quantity of carbonates to react (only applicable in the eastern -and western operation systems).

The mineral proportions and assigned kinetic rates for the different system components are presented in Table 8-3 and Table 8-4.

Table 8-3: Mineral proportions for coal discard dump forward reaction path models.

Mineral	Input (g) Discard dumps model	Surface area $(cm^2.g^{-1})$	Dissolution/weathering rate	Reference/comment
Quartz	452.61	100	5.75E-19	Palandri & Kharaka (2004)
Albite	73.68	100	9.12E-18	Palandri & Kharaka (2004)
Pyrite	31.58	100	3.00E-15	-
K-feldspar	94.73	100	3.89E-17	Palandri & Kharaka (2004)
Muscovite	126.31	100	2.82E-18	Palandri & Kharaka (2004)
Pargasite	94.73	100	2.51E-17	Palandri & Kharaka (2004)
Enstatite	73.68	100	1.91E-17	Palandri & Kharaka (2004)
Calcite	52.63	-	Simple reactant	
Total	999.95			
Metal(loid) oxides				
MnO	5.00E-05		Simple reactant	
SeO_2	3.00E-05		Simple reactant	
HFO				
$Fe(OH)_3$ ppd	0.10			

Table 8-4: Mineral proportions for respective eastern -and western operations' forward reaction path models.

Mineral	Input (g) E-operations	Input (g) W-operations	Surface area $(cm^2.g^{-1})$	Dissolution/weathering rate	Reference/comment
Quartz	345.64	345.69	100	5.75E-19	Palandri & Kharaka (2004)
Albite	86.37	86.42	100	9.12E-18	Palandri & Kharaka (2004)
Pyrite	37.01	37.04	100	5.50E-15	-
K-feldspar	61.69	61.73	100	3.89E-17	Palandri & Kharaka (2004)
Muscovite	185.07	185.19	100	2.82E-18	Palandri & Kharaka (2004)
Kaolinite	283.77	283.96	100	6.61E-18	Palandri & Kharaka (2004)
Calcite	0.25	-	-	Simple reactant	
Total	999.80	1000.03			
Metal(loid) oxides					
MnO	5.00E-09	4.00E-04		Simple reactant	
SeO_2	3.00E-05	3.00E-05		Simple reactant	
NiO	1.00E-05	0.002		Simple reactant	
PbO	-	4.00E-05		Simple reactant	
As_2O_5	-	2.00E-05		Simple reactant	
HFO					
$Fe(OH)_3$ ppd	0.10	0.10			

As mentioned in section 7.4, the most recent monitoring data were used to identify elevated concentrations of certain metal(loid)s within the different geochemical systems with reference to the unmined groundwater baseline (refer to Appendix B: Water Quality Data). Within the coal discard dumps system, metal(loid) contaminants were identified as manganese [Mn] and selenium [Se]. The tendency of these constituents to remain in solution, and hence mobile, was evaluated by adding the specified metal(loid)s as simple reacting oxides. Manganese, nickel [Ni] and selenium were identified as contaminants in the eastern operation system. The aforementioned constituents as well as lead [Pb] and arsenic [As] were identified within the western operation system. The mobility of these constituents within the discharging mine water and hence its potential to cause contamination over the long-term were thus evaluated by including the specific metal(loid)s as simple reacting oxides within the models (refer to Table 8-3 and Table 8-4).

Adsorption capacity was further added to the models. This is due to the presence of clay as well as iron oxides, both of which have the capacity to remove potential contaminants from solution through the process of

adsorption. When modelling sorption reactions in natural systems, the assumption is often made that most of the reactive metal-binding surfaces are natural organic matter and hydrous oxides of iron, manganese, aluminium and silica. Crystalline minerals and clay minerals are of lesser importance (Smith, 1999). In natural systems low in organic matter, metal sorption is commonly thought to be controlled by iron -and aluminium-oxide coatings on particle surfaces (Davis & Kent, 1990; Smith, 1999). According to Smith (1999), iron oxide minerals are generally the primary sorbent for transition metals in oxic environments and in the absence of evidence of sorptive dominance by a particular component, the bulk can be modelled. Therefore, due to the high levels of iron in these systems, they may represent a case in which metal sorption reactions are dominated by a single component, hydrous ferric oxide (HFO). Smith (1999) further explained that although the iron-rich precipitates in mine drainage systems consist of a variety of iron-oxide minerals, it is possible to consider them in bulk and combine them under the "HFO definition". HFO is therefore assumed to be the sole sorbent material in the model simulations. A total of 0.1 free grams adsorption capacity was added to the systems in the form of iron oxides $[Fe(OH)_3]$ (refer to Table 8-3 and Table 8-4). The GWB software uses the adsorption data of Dzombak and Morell (Bethke, 2008) for modelling adsorption to HFO using the double diffusion surface complexation model. Therefore, the surface complexation model of adsorption to HFO (Bethke, 2008) which has predictive capabilities beyond the measured conditions (Smith, 1999), was used to simulate sorption processes.

8.2.4   Note on continuous model calibration

Modelling of natural systems is associated with calibration of models through evaluating correlation coefficients and mean square root errors between simulated and measured data. However, with regards to geochemical modelling, the calibration approach is slightly different due to the measurement of change in parameters being controlled by a vast range of factors, which have impacts on the equilibrium of both the hydro-chemical system and the equilibrium of equations with the interaction of the various phases within the model (Van Coller, 2013).

It was therefore recommended that constant and continuous monitoring of input parameters and the simulated model results should be done with scientific and chemical knowledge being the main calibration tools. The accuracy of parameters and variables was also evaluated through sensitivity analysis, which evaluates the effect of small changes to the system. The scientific design of the system and whether the system is behaving like it should, will ultimately determine the accuracy of the model simulations and the calibration (Van Coller, 2013). Therefore, a systems-thinking approach was maintained throughout the modelling exercise.

An iterative approach was followed during the modelling of the systems with constant sensitivity analysis and changes to parameters and rates to achieve outputs that most closely match the measured parameters in the monitoring data set.

8.2.5 Modelling scenarios description

As mentioned, an iterative approach was followed during the modelling of the different systems with constant sensitivity analysis. The sensitivity analyses were focused on alterations of mineral weathering rates, increase and decrease of reactive mineral surface areas, as well as alterations of the oxygen content available to react within the system. As the oxygen availability and redox state within the different systems play an integral role in which geochemical processes are dominant, only scenarios and simulations in reference to alterations made to oxygen fugacity will be included in the main body of this document.

Nine scenarios in total were simulated which included three scenarios for the coal discard dump system and three scenarios respectively for the eastern -and western underground operations. The scenarios were developed to evaluate the sensitivities on parameter change, specifically oxygen fugacity, and the processes involved in the general weathering of the mineralogy to generate the sampled downstream groundwater and decant mine water. The scenarios follow the iterative calibration path as mentioned before to augment understanding of the geochemical processes involved and are discussed in the following sections.

8.2.5.1 Coal discard dumps system

The maximum oxygen content within the coal discard dump system was assumed at a fugacity of 0.18. Although the coal discard dumps are open to the atmosphere (maximum fugacity of 0.21) the oxygen content within the coal discard material were assumed to be lower due to rehabilitation and associated compaction processes. The soil and vegetation cover will ultimately reduce oxygen diffusion and hence availability within the coal discard material.

The following scenarios were assessed:

1. Scenario 1: Assessment of the reaction of the system and resultant fluid chemistries under fixed fugacity representing a system where oxygen continually diffuses to the coal discard material over a 100-year period.

2. Scenario 2: Assessment of the reaction of the system and resultant fluid chemistries under a sliding fugacity, from 0.18 to 1% of the atmospheric fugacity (0.0021), over a period of 100 years. This conceptually represents a system in which the oxygen content between the coal discard particles, which is a major role player in sulphide oxidation, is reduced due to the continuous compaction of overlying material, thus reducing oxygen diffusion. As the drainage emanating from the coal discard dumps leaches to the groundwater table, it creates conditions for decreased oxygen availability.

3. Scenario 3: Assessment of the processes and outcomes under a fugacity of 0.18 that is allowed to linearly decrease and eventually rapidly deplete over a period of 100 years (oxygen fugacity rapidly decrease after a period of 80 years). This conceptually represents a system where the compaction processes of the overlying material have progressed to such an extent that oxygen diffusion to the coal discard material is greatly inhibited. Oxidation of pyrite mediated by oxygen will therefore decline over the 100-year period. Scenario 3 further simulates an environment with depleting oxygen content

with almost no oxygen available except for oxygen already consumed and dissolved by the system. It therefore represents the reducing environment of the receiving groundwater systems.

From these three scenarios certain results and outcomes were obtained based on the conservative approaches and assumptions.

8.2.5.2   Underground operations

The maximum oxygen content within the underground voids was assumed at a fugacity of 0.018. A much lower oxygen content was assumed as the underground operations are not in its entirety open to the atmosphere. However, other oxygen diffusion pathways do exist which account for oxygen availability within the voids.

The following scenarios were assessed:

1. Scenario 1: Assessment of the reaction of the system and resultant fluid chemistries under fixed fugacity for 100 years. This represents a system in which water level fluctuations within the underground mine voids are not significant.

2. Scenario 2: Assessment of the reaction of the system and resultant fluid chemistry under sliding oxygen fugacity from 0.018 to 1% of atmospheric fugacity (0.0021) over a period of 100 years. This conceptually represents water level fluctuations within the underground voids over time.

3. Scenario 3: Assessment of the reaction of the system and resultant fluid chemistry under a fugacity of 0.018 that is not fixed over a period of 100 years, therefore supplementary in simulating water level rise within the underground voids to such a degree where the underground workings becomes flooded.

Similar to the coal discard dump component, certain results and outcomes were obtained from aforementioned scenarios based on the already mentioned conservative approach and assumptions.

8.3   MODEL RESULTS

The following sub-sections aim to present the main results in a logical way where after discussions will follow in Chapter 9 of this dissertation. The modelling results will be presented respectively for the different geochemical system components. Only a summary of the model and its main results are presented in the main body of the document. For more detail regarding the model setup and determination of model sensitivities, the reader is referred to Appendix E: Sensitivity Analysis (provided on request).

8.3.1   Coal discard dumps system

With an iterative approach and constant sensitivity analyses used as the main calibrators to understand the system with regards to fluid-mineral interaction, simulations with the steadiest reaction tempos and system parameters were simulated to evaluate the modelled system.

During the sensitivity analyses, the mineral surface area and mineral weathering rates were altered. Parameter values with outcomes that most closely match the monitoring data set were used. Table 8-3 shows the weathering rates and mineral surface areas for the different mineral phases which was used to model the different scenarios to simulate and evaluate processes under different oxygen fugacity conditions. The aim of the sensitivity analyses was to develop an understanding of the system dynamics to conclude with a calibrated system. The calibrated systems were then simulated to evaluate the system parameters and processes with a focus on metal(loid) mobility.

Scenarios 2 and 3 represent simulations displaying outputs that most closely match the measured parameters in the monitoring data set. These calibrated systems do not resemble the same concentrations as those observed in the monitoring data set due to time constraints as well as limits to understanding processes that cannot be seen and are therefore not accounted for which is a common modelling constraint (Van Coller, 2013). However, the processes and the proportional contents of the simulated results do fairly resemble the monitoring data set.

The results of the weathering simulations of the different scenarios are summarised in Table 8-5. Also shown in the table is the upper range concentrations (95th percentile) observed in the downstream groundwater monitoring data (refer to section 5.3.1.2). The model results were constantly calibrated against the calculated median values of the most recent (2017) downstream monitoring data which is also shown in Table 8-5. Only boreholes located directly downstream of the coal discard dumps were included in the calibration data set. These boreholes included BD02/02, UN01/02, UN02/02 and UN06/02.

From the aforementioned model setup parameters, weathering simulations for 100 years at an average temperature of 25°C were simulated to evaluate the effect of time and weathering on the fluid chemistry as it migrates through the discard dumps and eventually seep to the groundwater table. The end result, as demonstrated by Scenarios 2 and 3, is a water sample resembling a groundwater sample with a pH of 7.87 to 8.26 and a TDS between 532 and 668 mg/L. The calibrated system displays a Ca-SO$_4$ water type resembling that of the monitoring data.

Table 8-5: Summary of 2017 groundwater monitoring data together with model results following each scenario simulation for the coal discard dump component.

Parameter	Units	D/S boreholes (95th percentile)	COV (%)	Scenario 1	Scenario 2	Scenario 3	Calibration data (median)
		Value	Value	Value	Value	Value	Value
pH	pH units	8.64	8.00	7.70	7.87	8.26	7.81
TDS	mg/L	1016.22	51.32	947	668	532	537
Ca	mg/L	89.53	63.79	208	153	124	47.70
Mg	mg/L	102.66	65.03	26	11	4	43.90
Na	mg/L	79.51	33.81	23	23	23	43.10
K	mg/L	18.99	55.03	7	5	5	10.11
Cl	mg/L	37.11	65.31	2	2	2	14.05
HCO$_3$	mg/L	182.10	51.12	35	28	13	73.45
SO$_4$	mg/L	644.05	75.47	633	441	357	296
Fe	mg/L	5.72	207.88	0.97	0.44	0.22	0.12
Al	mg/L	0.28	168.63	<0.001	<0.001	<0.001	0.03
Mn	mg/L	0.49	70.76	<0.001	<0.001	0.038	0.41
Se	mg/L	0.03	19.99	0.034	0.034	0.069	0.03

Potential metal(loid) contaminants, i.e. manganese and selenium were evaluated. Model results following Scenario 1 indicate that although circum-neutral pH values and adsorption capacity were provided by the presence of iron oxides and hydroxides, selenium are mobile under oxidising conditions and become more mobile under the more reducing and alkaline conditions of the groundwater (Scenario 3). Considering Scenarios 1 and 2, the mobility of manganese is constrained by the oxygen availability within the coal discard material and will most likely precipitate as pyrolusite [MnO_2]. However, manganese become more mobile under reduced atmospheric influence, which point to more reducing conditions, and therefore pose a risk to groundwater users. The increased mobility of selenium and manganese under more reducing alkaline conditions is also reflected in Figure 8-3. The reader is referred to section 2.1.2.3 for solubility controls on selenium and manganese.
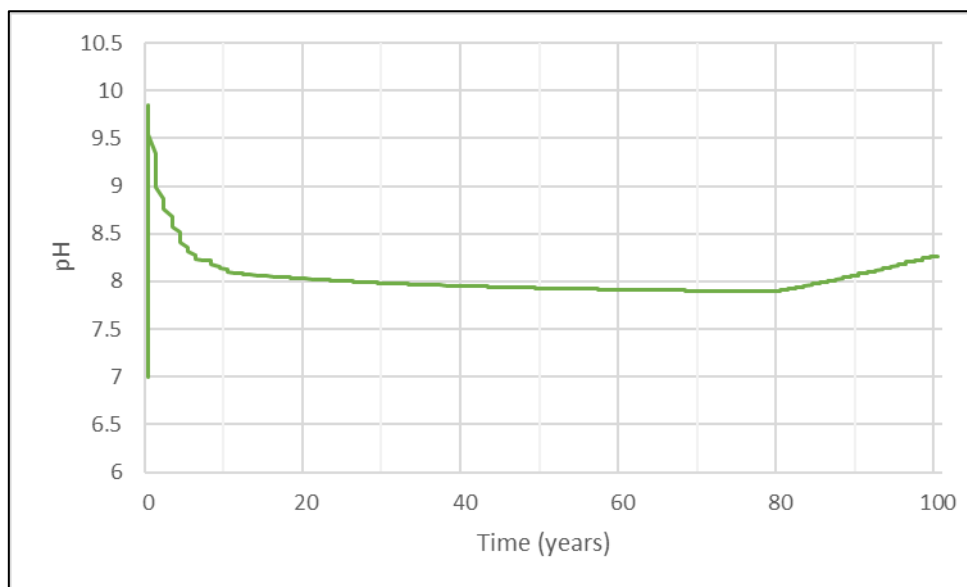
Figure 8-1: Transient evolution of pH during weathering reaction sequence over 100 years at a steadily depleting oxygen fugacity in Scenario 3 for the coal discard dump system.

Figure 8-2: Fluid composition after weathering over a period of 100 years subjected to a steadily depleting oxygen fugacity in Scenario 3 for the coal discard dump system.

Figure 8-3: Fluid metal(loid) composition after weathering over a period of 100 years subjected to a steadily depleting oxygen fugacity in Scenario 3 for the coal discard dump system.
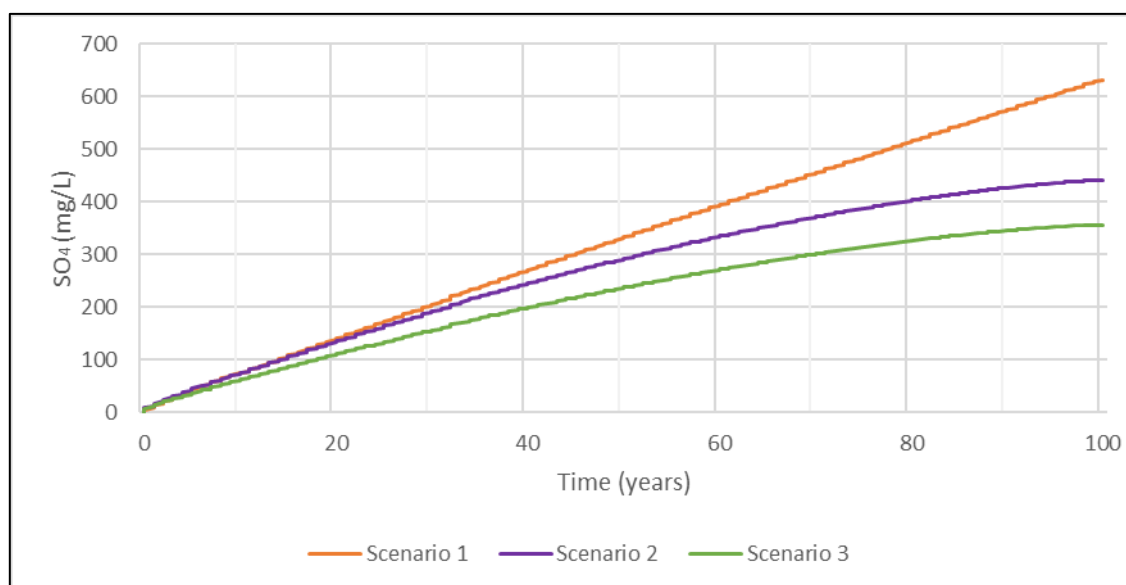
Figure 8-4: Fluid composition in terms of sulphate [SO₄] after weathering over a period of 100 years under the different fugacity scenarios for the coal discard dump system.

With an evaluation of the mineralogy at hand in the forward reaction path models, it is shown that pyrite oxidation, the dissolution and buffering effect of the carbonate mineral, calcite, and precipitation of super saturated states are the main influences on the chemical species concentrations and the system parameters. Initial dissolution of feldspar group minerals allowed for rapid increase of the pH in the 100-year transient simulation as indicated in Figure 8-1. During the simulation, the pH rises from 7.0 to a maximum of 9.85 very rapidly. The sudden rise in pH may be due to the contribution of OH^- ions by initial weathering of the silicate minerals where after the system stabilises at pH ~8.26 in Scenario 3. Neutralisation reactions due to increased activity of carbonates (calcite) in the system leads to low concentrations of bicarbonate [HCO_3^-] in the system (Figure 8-2). A decrease in bicarbonate correlates with a neutralising effect allowing for higher and more basic pH readings in solution (Van Coller, 2013; Witthueser, 2016). Along with the increase and decrease in pH,

various other chemical species also reacted and dissolved to be present in various concentrations as shown in Table 8-5 (refer to Figure 8-2 and Figure 8-3). After initial period of increased dissolution, the system reaches equilibrium with forward and backward reactions balancing with dissolution as well as precipitation. Calcite, kaolinite, pyrolusite, saponite-Ca, siderite and tridymite are present in saturated states.

The weathering/dissolution rates of especially pyrite as well as the fugacity of oxygen is most sensitive and controls the outcome of both the resultant groundwater chemistry and the pH of the system after weathering reactions has reached a state close to equilibrium. Figure 8-4 shows the sulphate concentrations as a result of different oxygen fugacities. The sensitivity of pyrite oxidation to the amount of oxygen available within the system is clear.

8.3.2   Eastern underground operations

Forward reaction path models were simulated to compare with field decant monitoring data to evaluate the transient effect of weathering products on the water chemistry as the mine void water evolves along the flow path until final decant.

As described previous sections, the main purpose of the sensitivity analyses was to facilitate understanding of the system dynamics especially in terms of the available oxygen content within the underground mine workings. Based on the conceptual model the mine voids are only partially flooded. Floor gradients and decanting elevations are such that only small portions of the coal floors will eventually be flooded. Pathways for oxygen ingress exist at adits, sinkholes, and monitoring boreholes intersecting the mine voids. Water level rise within the underground workings are expected to influence the oxygen fugacity.

Scenarios 1 and 2 conceptually account for the dynamic nature of water level fluctuation, and hence oxygen availability, within the underground mine voids. These scenarios display most resemblance with the calibration monitoring data set. Once again, these calibrated systems do not reflect the same concentrations as those observed in the monitoring data set due to time constraints as well as limits to understanding processes that cannot be seen and are therefore not accounted for. However, the processes and the proportional contents of the simulated results do reasonably resemble the monitoring data set.

The results obtained from the different scenario weathering simulations are summarised in Table 8-6. Also shown in the table is the upper range (95th percentile) concentrations observed in the mine void and decant monitoring data. The model results were constantly calibrated against the calculated median values of the 2017 decant water quality monitoring data set. The model results with the calibration data is presented in Table 8-6.

From the model setup parameters, weathering simulations for 100 years at an average temperature of 25°C were simulated to evaluate the effect of time and further chemical weathering on the fluid chemistry along flow paths to eventual decant. The end result, as demonstrated by Scenarios 1 and 2, is a concentrated mine water sample with a pH between 7.17 and 7.62 and a TDS between 1 340 and 1 493 mg/L. The calibrated systems have a Ca-SO$_4$ water type resembling that of the monitoring data set.

Table 8-6: Summary of 2017 mine void and decant monitoring data with the model results following the different scenario simulations for the eastern operation component.

Parameter	Units	Mine void (95th percentile)	COV (%)	Decant (95th percentile)	COV (%)	Scenario 1	Scenario 2	Scenario 3	Calibration data (median)
		Value	Value	Value	Value	Value	Value	Value	Value
pH	pH units	7.47	9.18	8.27	6.67	7.17	7.62	9.12	7.62
TDS	mg/L	799	39.29	2761.60	52.08	1493	1340	913	1172
Ca	mg/L	134.75	44.68	514.40	48.94	189	189	188	226
Mg	mg/L	56.15	49.56	180.20	50.30	26	26	24	84.70
Na	mg/L	35.30	14.25	63.20	49.88	69	60	40	24.80
K	mg/L	7.10	36.83	7.56	41.00	0.14	0.12	0.07	5.25
Cl	mg/L	47.86	127.77	9.92	21.31	5	5	5	7.40
HCO_3	mg/L	205	45.20	423.40	31.44	410	410	410	279
SO_4	mg/L	386	57.40	1643	64.30	574	484	217	548
Fe	mg/L	0.09	84.65	4.86	76.65	105	78	0.45	0.1
Al	mg/L	0.05	46.15	0.14	76.75	<0.001	<0.001	0.044	0.045
Mn	mg/L	3.67	117.49	2.22	190.21	0.53	0.43	0.24	0.395
Se	mg/L	0.02	-	0.04	23.37	0.057	0.057	0.033	0.022
Ni	mg/L	0.015	-	0.36	168.42	0.015	0.007	0.002	0.034

The model results of Scenario 2 show that the sulphate concentration in the mine decant water, although lower than that simulated by Scenario 1, still exceed regulatory (SANS 2015) as well as groundwater baseline values. This is due to the oxidation of sulphide minerals within the underground mine voids, which suggests that although the oxygen fugacity was allowed to linearly decrease over the simulation period, enough oxygen is still available in the system to mediate sulphide oxidation. This further suggests that the system is sensitive to changes in oxygen availability (Figure 8-8). Scenario 3 conceptually simulates conditions where the mine is flooded after active mining has ceased which, as already established, is not possible. However, it indicates that the sulphate levels are below regulatory standards which can be ascribed to reduced oxygen availability resulting in slower pyrite oxidation rates.

Potential metal(loid) contaminants, i.e. manganese, selenium and nickel were evaluated. Model results following Scenario 1 indicate that although circum-neutral pH values and adsorption capacity were provided by the presence of iron oxides and hydroxides, manganese, selenium and to a lesser extent nickel, are mobile under oxidising conditions. Upon mine flooding, as simulated in Scenario 3, the concentrations of these constituents are reduced. However, these metal(loid)s remain mobile and therefore pose risks. Manganese and selenium are mobile under oxidising and more reducing conditions and therefore pose a risk to groundwater users. Nickel pose a negligible risk to the local environment under more reducing conditions.

Figure 8-5: Transient evolution of pH during weathering reaction sequence over 100 years in Scenarios 1 and 2 for the eastern operation system.
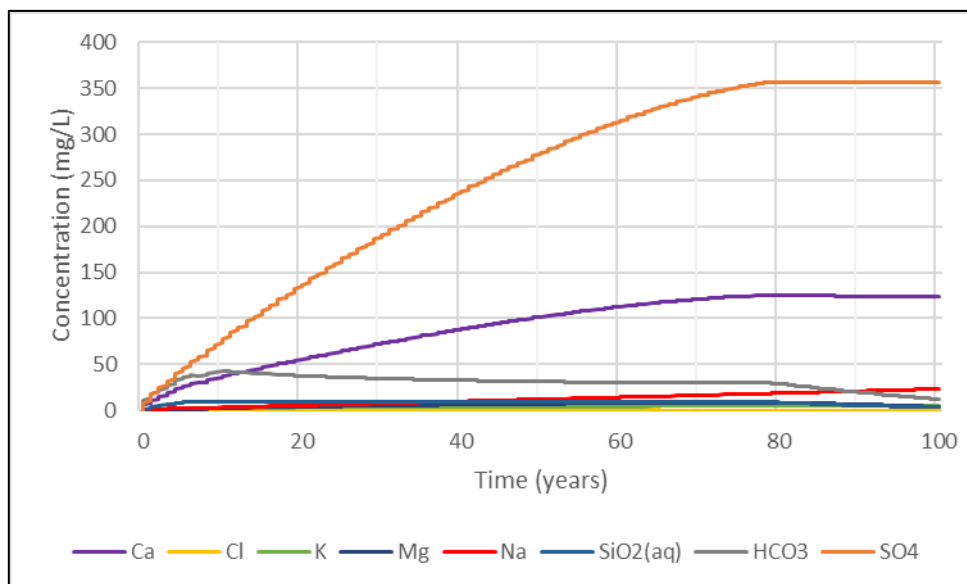

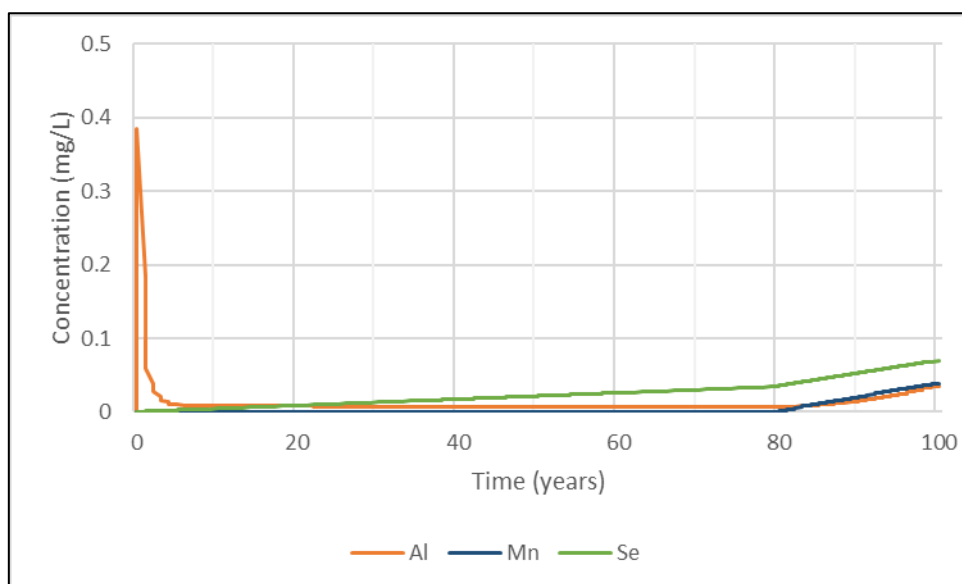**Figure 8-6: Fluid composition after weathering over a period of 100 years subjected to a steadily decreasing oxygen fugacity in Scenario 2 for the eastern operation system.**

Figure 8-7: Fluid metal(loid) composition after weathering over a period of 100 years subjected to a steadily decreasing oxygen fugacity in Scenario 2 for the eastern operation system.

Figure 8-8: Fluid composition in terms of sulphate [SO₄] after weathering over a period of 100 years under the different fugacity scenarios for the eastern operation system.

After evaluation of the system mineralogy and parameters, it can be deduced that pyrite oxidation and the buffering effect of calcite are the main influences on the chemical species concentrations and the system parameters. When considering Scenario 2, the buffering reactions of calcite allowed for steady increase of the pH in the 100-year transient simulations as indicated in Figure 8-5. During the simulations, the pH rises from 6.80 to a maximum of 7.62 very gradually. Along with the increase in pH, various other chemical species also reacted and dissolved to be present in various concentrations as shown in Table 8-6 (refer to Figure 8-6 and Figure 8-7). Ferric hydroxide minerals are present in saturated states.

The weathering rates of the minerals, especially pyrite, as well as the fugacity of oxygen (refer to Figure 8-8) is most sensitive and controls the outcome of both the resultant decant water chemistry and the pH of the system after reactions has reached a state close to equilibrium.

8.3.3   Western underground operations

Similar to the eastern operation models, forward reaction path models were simulated to compare with field decant monitoring data to evaluate the transient effect of weathering products on the water chemistry and the evolution of mine void water until final discharge.

As already described in the previous sections, sensitivity analyses were used as a constant calibrator tool and the systems' sensitivity to oxygen fugacity alterations were focused on. Like the eastern operation models, Scenarios 1 and 2 conceptually represent simulations that account for the dynamic nature of water level fluctuation, and hence oxygen availability, within the underground mine voids. These scenarios display most resemblance with the calibration monitoring data set. Once again, these calibrated systems do not resemble the same concentrations as those observed in the monitoring data set due to time constraints as well as limits to understanding true environmental processes which cannot be accounted for.

The results of the weathering simulations of the different scenarios are summarised in Table 8-7. Also shown in the table is the upper range (95th percentile) concentrations of water quality observed in the mine void and decant water monitoring data. The model results were constantly calibrated against the calculated median values of the 2017 decant water quality monitoring data. The model results together with the calibration data is presented in Table 8-7.

As described in the previous section, from the model setup parameters, weathering simulations for 100 years at an average temperature of 25°C were simulated to evaluate the effect of time and further chemical weathering on the fluid chemistry. The end result, as demonstrated by Scenarios 1 and 2, is an enriched mine water sample with a pH between 3.61 and 3.64 and a TDS between 1 361 and 1 423 mg/L. The calibrated system has a Ca-SO$_4$ water type resembling that observed in the monitoring data set.

Table 8-7: Summary of 2017 mine void and decant monitoring data with the model results following the different scenario simulations for the western operation component.

Parameter	Units	Mine Void (95th percentile)	COV (%)	Decant (95th percentile)	COV (%)	Scenario 1	Scenario 2	Scenario 3	Calibration data (median)
		Value	Value	Value	Value	Value	Value	Value	Value
pH	pH units	6.68	34.38	3.32	5.62	3.60	3.64	3.80	2.97
TDS	mg/L	3254.50	83.75	2850.60	73.59	1423	1361	1202	992.07
Ca	mg/L	441.30	87.21	393.34	58.25	185	185	185	174
Mg	mg/L	250.90	118.84	43.51	91.69	41	41	41	43.51
Na	mg/L	28.22	34.82	16.42	17.76	20	20	20	12.75
K	mg/L	10.80	28.38	8.48	19.23	41	41	41	6.90
Cl	mg/L	15.82	39.92	6.70	19.64	10	10	10	5.02
HCO_3	mg/L	124.60	119.64	2.50	0.00	2	2	2	2.50
SO_4	mg/L	2226.05	92.19	2053.97	79.11	914	874	769	680.19
Fe	mg/L	155.36	187.30	120.16	140.99	59	48	17	19.59
Al	mg/L	36.98	119.46	71.66	133.38	14	11	4	12.55
Mn	mg/L	6.34	105.84	6.88	122.80	1.98	1.98	1.98	1.34
As	mg/L	0.005	n/a	0.021	n/a	0.005	0.005	0.004	0.021
Pb	mg/L	0.027	n/a	0.035	n/a	0.033	0.033	0.028	0.035
Se	mg/L	0.02	n/a	0.01	n/a	0.034	0.034	0.020	0.01
Ni	mg/L	0.43	80.58	2.47	120.87	1.57	1.57	1.57	1.397

The model results of Scenario 2 (Table 8-7) show that the sulphate concentration in the mine decant water, although lower than that simulated by Scenario 1, exceed regulatory as well as groundwater baseline values. This is due to the oxidation of sulphide minerals within the underground mine voids, which suggests that although the oxygen fugacity was allowed to linearly reduce over time, enough oxygen is still available in the system to facilitate sulphide oxidation. This suggests that the system is sensitive to changes in oxygen availability (Figure 8-12). Scenario 3, which conceptually simulates ideal flooding conditions, suggests that even if the mine could be flooded, sulphate levels and pH values would still not comply with regulatory guidelines (SANS 2015).

Potential metal(loid) contaminants, i.e. manganese, lead, nickel, arsenic and selenium were evaluated. Model results following Scenario 1 indicate that due to the acidic nature of the mine water, manganese, lead, nickel, selenium and to a lesser extent arsenic are mobile under oxidising conditions. Upon water level rise and eventual mine flooding as simulated in Scenarios 2 and 3, respectively, the concentrations of these constituents are lowered; except for manganese and nickel. However, these constituents remain in solution, hence mobile, and therefore pose risks. Due to the adsorption capacity provided by the presence of iron oxides and hydroxides arsenic poses a negligible risk to the local environment under more reducing conditions.
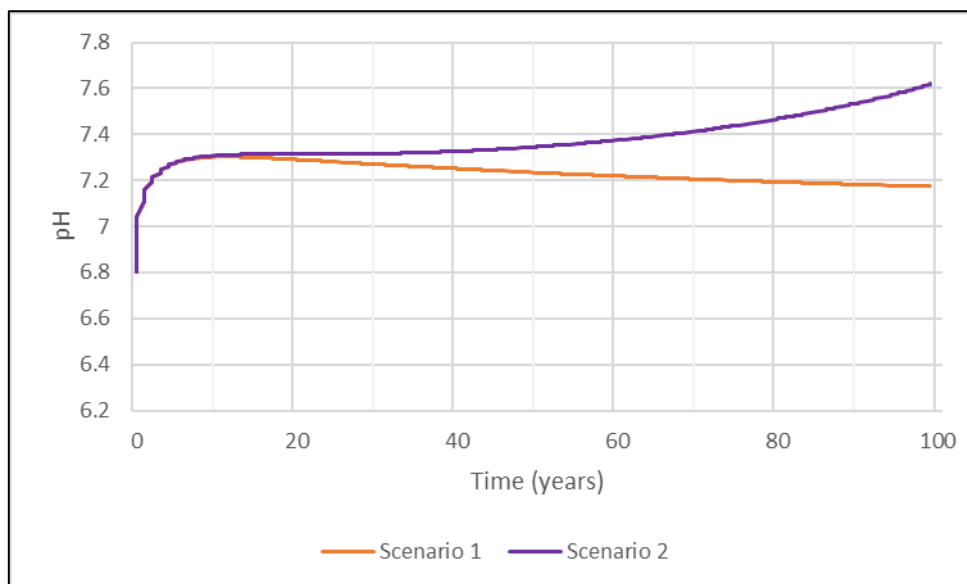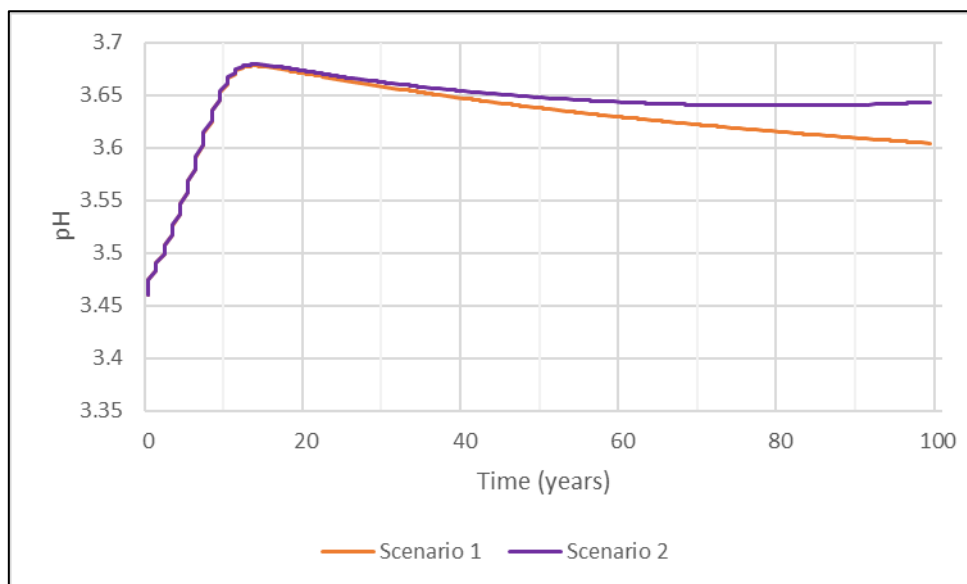
Figure 8-9: Transient evolution of pH during the weathering reaction sequence over 100 years in Scenarios 1 and 2 for the western operation system.
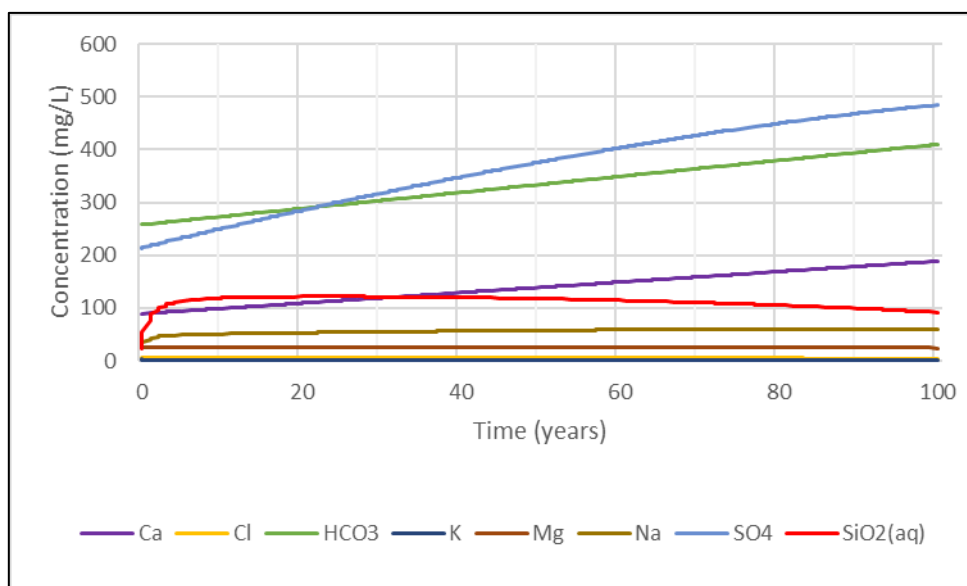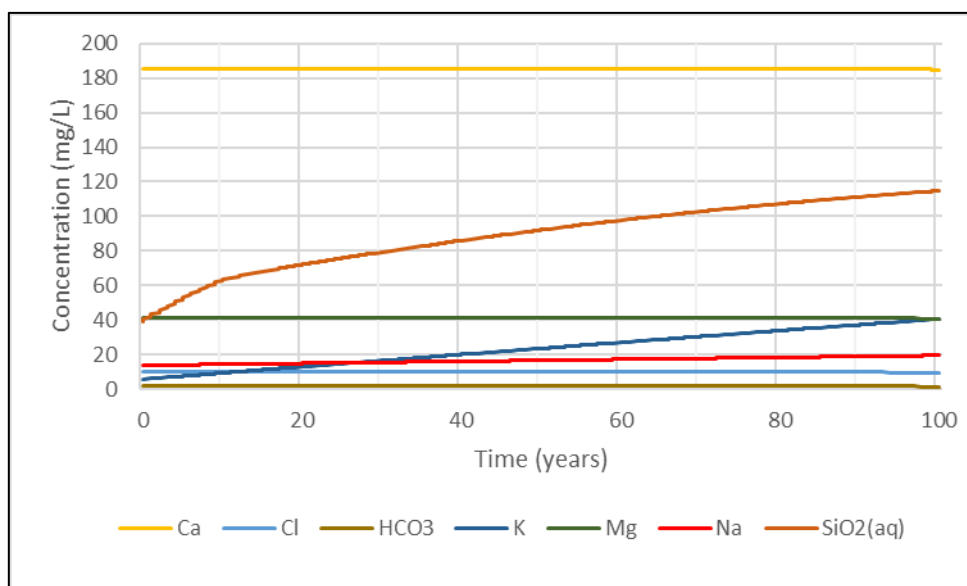

Figure 8-10: Fluid composition after weathering over a period of 100 years subjected to a steadily decreasing oxygen fugacity in Scenario 2 for the western operation system.
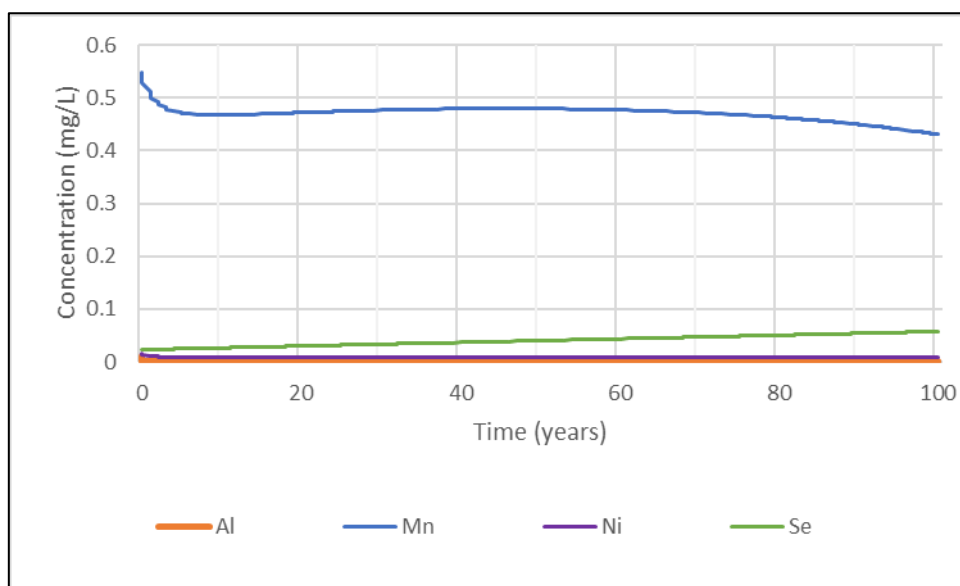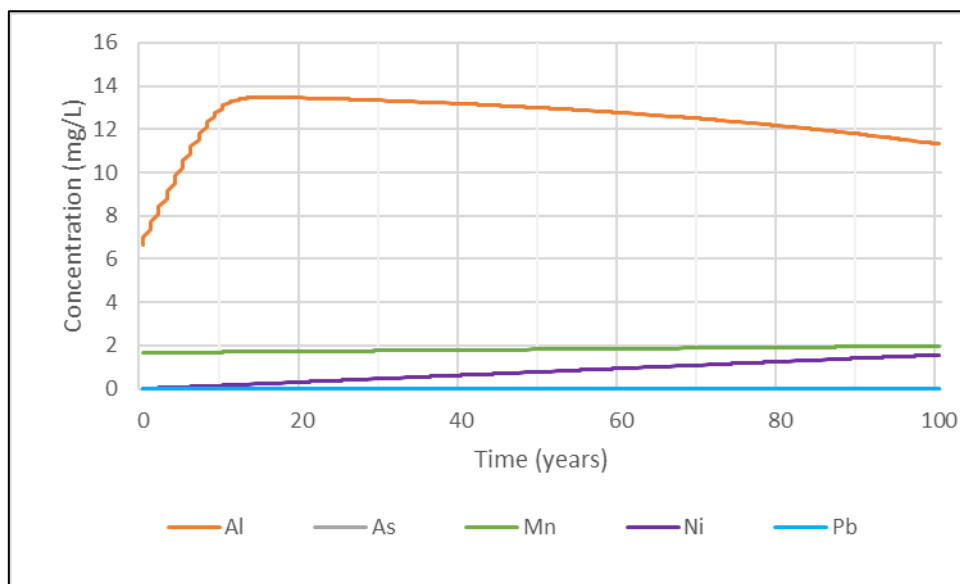
Figure 8-11: Fluid metal(loid) composition after weathering over a period of 100 years subjected to a steadily decreasing oxygen fugacity in Scenario 2 for the western operation system.
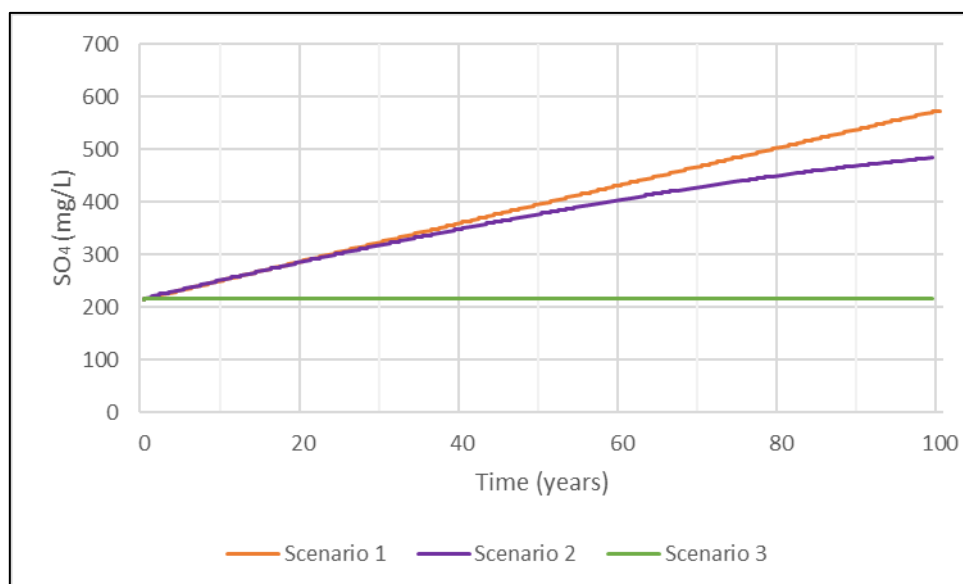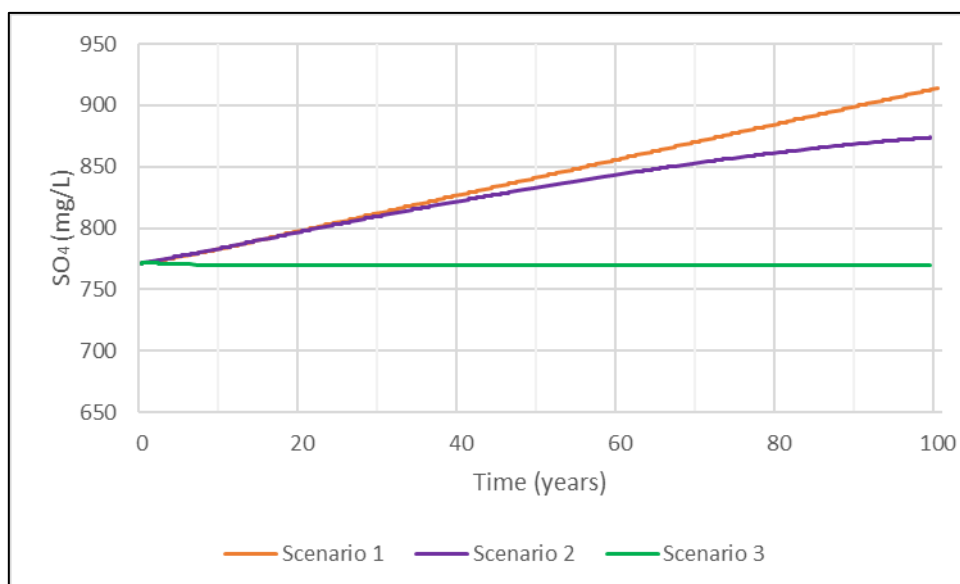

Figure 8-12: Fluid composition in terms of sulphate [SO₄] after weathering over a period of 100 years under the different fugacity scenarios for the western operation system.

Pyrite oxidation is the main influence on the chemical species concentrations and the system parameters. The models support the assumption that no neutralisation capacity is provided by carbonate minerals. It can be assumed that carbonate minerals were present in the system and depleted over time. It is also possible that all buffering capacity is consumed along the flow path to eventual decant. The pH thus decreased until equilibrium was reached with most soluble secondary hydroxides such as aluminium -and iron hydroxides which allowed for steady increase and decrease of the pH in the 100-year transient simulations as indicated in Figure 8-9. During the simulations, the pH rises from 3.46 to a maximum of 3.68 where after it gradually decreases and stabilises at 3.64 in Scenario 2. During the simulations, various other chemical species also reacted and dissolved to be present in various concentrations as shown in Table 8-7 (refer to Figure 8-10 and Figure 8-11).

Ferric iron concentrations increased at the lower pH values and ferric hydroxide minerals are present in saturated states.

As with previous weathering models, the weathering/dissolution rate of especially pyrite, as well as the fugacity of oxygen is most sensitive and controls the outcome of both the resultant mine decant water chemistry and the pH of the system after reactions has reached a state close to equilibrium.

8.4 CONCLUDING SUMMARY

The following conclusions can be summarised from Chapter 8:

- The purpose of the geochemical modelling exercises was mainly to reduce uncertainty through constant sensitivity analyses, and to facilitate understanding of the interaction of geochemical processes with a focus on metal(loid) mobility to a level at which potential liability can be quantified.

- Weathering models were respectively simulated for the coal discard dump system and the eastern -and western underground operations. Sensitivity analyses focused on the pyrite reaction rate, and oxygen fugcity leading to the evaluation of calibrated systems. This allowed for interpretation and investigation of processes involved in the evolution of the groundwater and mine decant water as observed in the monitoring data set.

- Risks associated with the contamination of soil, surface water and groundwater resources by metal(loid)s from all geological mine waste, i.e. coal discard dumps and underground extraction areas, are significant.

- The final calibrated coal discard dump model indicated a Ca-SO$_4$ water type with a pH between 7.87 and 8.26 and a TDS between 532 and 668 mg/L, correlating with monitoring data.

- The contamination of shallow groundwater by sulphate, manganese and selenium from the coal discard material in the post operational phase are significant and further mitigation measures should be considered as this can pose a problem for future groundwater users.

- The final calibrated eastern operation model indicated a Ca-SO$_4$ water type with a pH between 7.17 and 7.62 and a TDS of 1 340 to 1 493 mg/L, correlating well with monitoring data.

- Contamination of groundwater and surface water by sulphate, iron, manganese and selenium, which remain mobile within the decant water emanating from the eastern operations, is significant and mitigation measures should be implemented as the receiving streams are considered as sensitive receptors.

- The final calibrated western operation model indicated a Ca-SO$_4$ water type with a pH value between 3.61 and 3.64 and a TDS of 1 361 to 1 423 mg/L, agreeing with monitoring data.

- Contamination of groundwater and surface water by sulphate, iron, manganese, aluminium, lead, nickel, and selenium, which remain mobile within the western operation decant water, is significant and mitigation measures should be implemented as the receiving streams are considered as sensitive receptors.

CHAPTER 9:
HYDROGEOCHEMICAL ASSESSMENT AND MODEL DISCUSSION

This chapter is dedicated to the discussion of the modelling results and serves as a conclusion and summary of this dissertation with the final objectives addressed. All model results as discussed in the next sections are presented in Appendix D: Model Results and are available on request.

9.1   SYSTEM COMPONENT MODELS

Nordstrom and Alpers (1999) identified the most important factors affecting the generation of acid mine waters as the amount, concentration, grain size, and distribution of pyrite present in the mine waste. As discussed in Chapter 2 and Chapter 7 of this dissertation, the rate at which pyrite oxidises may vary depending on the accessibility of air, moisture, and microbes to the pyrite reactive surfaces. The generation and persistence of acidity as a product of pyrite oxidation, are further influenced by available buffering materials. Kinetic principles were used to model these complex geochemical processes to evaluate the result of pyrite oxidation, carbonate buffering, soluble hydroxide buffering, and silicate hydrolysis.

Laboratory test results as discussed in Chapter 6 contributed to the mineralogical data and proportions used in the forward reaction path models to conclude with a system understanding of geochemical processes and satisfy the specific objectives of the study.

9.1.1   Coal discard dumps model

Three weathering scenarios, as discussed in section 8.2.5 of this dissertation, were simulated following an analytical calibration path. Significant changes in terms of dissolved species concentration were observed between the three simulated scenarios. However, the resultant water type remained unchanged. During the simulation of Scenario 1 the system was allowed to react for 100 years at a fixed fugacity. Constant calibration and sensitivity analyses were performed by adjusting, especially, the mineral weathering rates until more realistic results in line with the monitoring data were obtained. Based on the first weathering model scenario, it was clear that to allow for a simulation with results closer to the monitoring data, the fugacity of the system had to be adjusted. It has been concluded by numerous studies that the rate of sulphide oxidation in mining waste is controlled by the supply of oxidant to the mineral surface (Davis & Ritchie, 1986; Nicholson *et al.*, 1990; Blowes *et al.*, 1994).

The parameters with the most realistic results that agreed with conceptual understanding of the hydrogeochemical environment were used to simulate the system in a state closest to that observed in the downstream groundwater monitoring data. The modelled water composition from the calibrated system will

not necessarily have the same chemical concentrations as observed in the monitoring data set but needs to be proportionally in the same ionic distribution range and the water type should show the same facies (Van Coller, 2013). Following the three scenarios, with evaluations of the system dynamics as well as the sensitivity of the system to certain parameter changes, the knowledge of the calibration path accumulated to calibrated simulations of the system in Scenarios 2 and 3. The model parameters for the scenarios are described in section 8.2 of this dissertation.

Scenarios 2 and 3 resulted in a chemical sample with a pH between ~7.87 and 8.26 for a transient simulation of 100 years. Dissolution of calcite allow for neutralisation reactions to occur as illustrated in Figure 8-1 where circum-neutral to alkaline conditions is maintained throughout the simulation period. The pH of the system increased to a maximum of 9.85 within the first few days of simulation (Figure 8-1). It is unlikely that calcite will buffer the system to a pH of 9.85, and it is therefore assumed that OH^-, contributed by the initial dissolution of silicate minerals, allowed for the pH to show the sharp increase. Buffering by means of calcite dissolution is thought dominant after this sharp increase. Blowes *et al.* (1994) explained that the principal mechanisms in inactive mine wastes are carbonate mineral dissolution, hydroxide mineral dissolution and aluminosilicate mineral dissolution. Many acid-neutralising reactions are independent of gas-phase oxygen concentration, which is distinct from pyrite oxidation reactions. As H^+ is released by pyrite oxidation reactions, the coal discard pore water becomes undersaturated with respect to calcite, leading to calcite dissolution buffering the pore and groundwater. It is suggested by the models that H^+ generated by pyrite oxidation is less than the acid consumed by carbonate-mineral dissolution. The pore and groundwater pH are controlled completely by carbonate mineral dissolution, limiting the development of other pH buffering zones (refer to sections 2.1.2.1, 2.1.2.2, and 7.3.4.2). Similar observations were made by Blowes (1990) and Jambor and Blowes (1991). According to White *et al.* (1993) carbonates are quite reactive and if present in large amounts can delay propagation of acid.

Allowing for the analogue values used in Scenarios 2 and 3, the resultant simulated sample displayed a Ca-SO_4 (Figure 9-1) water facie with a TDS between ~532 and 668 mg/L. Note that only the water quality evolution following Scenario 3 is shown in Figure 9-1. The calcium dominated water system does not corelate entirely with the region groundwater as sodium and magnesium is typically the predominant cations in the downstream monitoring data set. However, Ca-SO_4 water facies have been observed in upstream groundwater monitoring data (refer to section 5.3.1.2). The analysis of the resultant water as it progresses shows that the final fluid is saturated with secondary minerals similar to those observed in the XRD laboratory analyses. Calcium [Ca^{2+}], magnesium [Mg^{2+}], sodium [Na^+], potassium [K^+], chloride [Cl^-], sulphate [SO_4^{2-}], bicarbonate [HCO_3^-], aluminium [Al], iron [Fe], manganese [Mn], and selenium [Se] were present in the simulated sample with concentrations resembling those observed in the monitoring data set. The presence of these constituents can be explained due to dissolution of especially silicates, oxides and sulphides associated with the coal layers and country rocks (Campaner *et al.*, 2014). The lower levels of magnesium, potassium and sodium may be attributed to the formation of secondary mineral precipitates caused by predicted relatively high sulphate levels (may include formation of gypsum, magnesium sulphate, potassium -and sodium jarosites) (Swart *et al.,* 1998). The high calcium levels are related to the equilibrium-controlled dissolution of calcite.

Nitrate [NO$_3^-$] is a compound readily found in fertilisers and explosives used in the regional area for agriculture and mining related activities (Van Coller, 2013). Thus, for the purpose of all the models, nitrate, nitrite [NO$_2^-$] and other nitrogen containing aqueous species were not of concern.
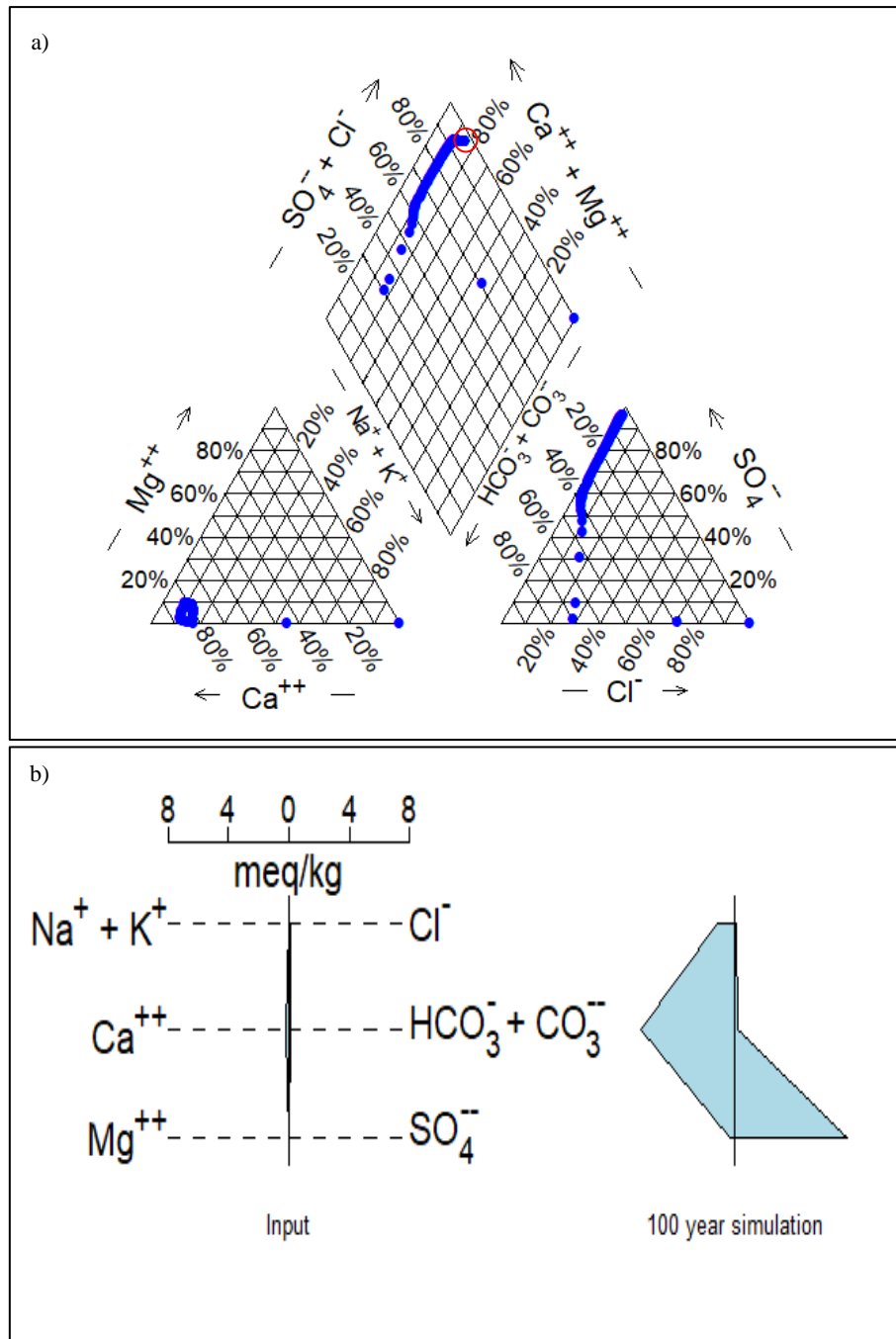
Figure 9-1: Piper (a) and Stiff (b) diagram indicating the water type as well as the evolution of the water over the 100-year period following the Scenario 3 simulation for the coal discard dump system.

The Piper diagram in Figure 9-1 indicates the evolution path of the water sample with the initial Na-Cl facies of the distilled water as it follows a reaction path subjected to weathering and precipitation of various minerals. Calcium increases very quickly (equilibrium-controlled dissolution) as well as sulphate as the saturated species precipitates out of solution to end at a Ca-SO$_4$ water facie (position indicated in red in the Piper diagram). A

water sample with a strong calcium and sulphate ion distribution may be described as groundwater in gypsum-bearing sedimentary aquifers and groundwaters affected by oxidation of pyrite (Younger, 2007).

According to Smith (1999) for surface binding reactions of metal(loid)s on oxide minerals, the pH of solution is a master variable (refer to section 7.3.4.4). Anion adsorption is the mirror image of cation adsorption in that anion adsorption tends to decrease with increasing pH (Szlachta & Chubar, 2013). Therefore, the pH at which metal(loid) sorption becomes significant varies with the particular metal(loid) cation/anion, the particular sorbent, the solid: solution ratio, the specific surface area of the sorbent, the total metal-cation concentration, and the concentration of other competing or interacting species. The importance of sorption reactions in controlling trace-element concentrations in natural systems is partly due to the initial rapid equilibration of most sorption reactions (Smith, 1999). Precipitation reactions typically require longer periods of time. Studies performed by Hachiya *et al*. (1984), and Hayes and Leckie (1986) showed that it generally takes seconds to minutes for metals to sorb to external surface sites and rapidly equilibrate with the surrounding solution.

Results following Scenario 3 indicated that manganese and selenium remain mobile under more reducing, alkaline conditions. Therefore, it can be ascertained when considering the model results and the monitoring data that manganese is mobile in the groundwater regime. The solubility of manganese is controlled by the redox potential and pH of the system (Nadaska *et al*., 2012) where low pH or low redox potential favour the reduction of insoluble manganese oxides resulting in increased manganese mobility (refer to section 2.1.2.3.3). According to Nadaska *et al*. (2012) the solubility of manganese is high in anaerobic conditions at pH above 6.0, as well as in aerobic conditions at pH below 5.5. As water infiltrates downwards through soils and sediments and percolates to the groundwater table, the soil environment becomes more anaerobic and hence more reducing. The reduction reactions follow a sequence in which oxygen is removed first, followed by nitrate and manganese. Progressively more reducing conditions result in the reduction of iron followed by sulphate. In these anaerobic conditions, manganese is mobilised (released from minerals) and reduced to its more soluble form, Mn^{2+} (Nadaska *et al*., 2012). Manganese concentrations are however controlled by the precipitation of pyrolusite.

As with manganese, the chemical form and mobility of selenium is largely controlled by the redox potential and pH of the water (refer to section 2.1.2.3.7). It has been shown by various studies that selenium is highly mobile under oxidising, acidic, neutral and alkaline conditions (Brookins, 1988; Gondi *et al*., 1992; Fadlelmawla *et al*., 1994). Its mobility however decreases with decreasing pH, and it is generally less mobile to immobile under reducing conditions (Gondi *et al.,* 1992). However, under the specific redox potential (refer to Appendix D: Model Results) and pH of the modelled system following Scenario 3, selenium mainly occurs as selenite [SeO_3^{2-}] which is stable under alkaline conditions. A study by Fadlelmawla *et al*. (1994) indicated that total selenium concentrations in groundwater were found to increase with depth and then decrease near the groundwater table. Samples collected near surface contained low concentrations of selenium. Studies by Bar-Yosef and Meek (1987) showed that selenium solubility is governed by adsorption between pH 4.0 and 8.0. Sorption of selenium generally decreases with increasing pH (Mayland *et al*., 1991). Neal *et al*. (1987) reported that under neutral to alkaline conditions, adsorption of selenium can be low and leaching into

groundwater or drainage water is possible. Kabata-Pendias and Pendias (2001) explained that adsorption of selenium by clay minerals becomes negligible above pH of 8.0.

Table 9-1: Range of measured field observations together with model water quality concentrations for the coal discard dump system.

Parameter	Units	Baseline range in unmined areas	Downstream boreholes		Scenario 2	Scenario 3
			5th Percentile	95th Percentile		
		Value	Value	Value	Value	Value
pH	pH units	6.87-8.59	6.84	8.64	7.87	8.26
TDS	mg/L	145.0-354.0	231.60	1016.22	668	532
Ca	mg/L	9.20-25.43	15.66	89.53	153	124
Mg	mg/L	2.50-11.81	10.14	102.66	11	4
Na	mg/L	10.92-90.40	33.58	79.51	23	23
K	mg/L	2.54-6.70	3.69	18.99	5	5
Cl	mg/L	4.58-20.64	5.61	37.11	2	2
HCO$_3$	mg/L	90.70-213.0	53.61	182.10	28	13
SO$_4$	mg/L	3.80-38.15	14.74	644.05	440	357
Fe	mg/L	0.01-0.25	0.03	5.72	0.44	0.22
Al	mg/L	0.03-0.19	0.02	0.275	<0.001	<0.001
Mn	mg/L	0.01-0.02	0.02	0.49	<0.001	0.038
Se	mg/L	0.01	0.02	0.029	0.034	0.069

The modelled water quality following Scenario 3 shows elemental concentration content close to that observed in the monitoring data set (Table 9-1) with only sodium, magnesium and bicarbonate below the downstream groundwater lower limit (5th percentile) and calcium above the groundwater 95th percentile limit. Manganese concentrations predicted by the models is much lower than that observed in the monitoring data set, however it confirms the mobility of manganese in reducing, alkaline conditions. As mentioned before, manganese concentration is controlled by the precipitation of pyrolusite. Selenium concentrations, however, are higher than that observed in the monitoring data. Nonetheless it suggests that selenium is mobile under more reducing, alkaline conditions of the groundwater.

The evolution of the water as indicated in Figure 8-2 and Figure 8-3 corelates with saturation levels and development of minerals both in solution and precipitated states in the resultant simulated water. The saturated minerals within the system include the following:

- Calcite   Carbonate $CaCO_3$

- Chamosite-7A   7A-Clay $Fe_2Al_2SiO_5(OH)_4$

- Kaolinite   7A-Clay $Al_2Si_2O_5(OH)_4$

- Pyrolusite   Oxide MnO_2

- Saponite-Ca   Smectite $Ca.165Mg_3Al.33Si_3.67O_{10}(OH)_2$

- Nontronit-Ca   Smectite $Ca.165Fe_2Al.33Si_3.67O_{10}(OH)_2$

- Goethite   Hydroxide $FeOOH$

- Siderite   Carbonate $FeCO_3$

- Tridymite   Silica SiO_2

The above list of saturated minerals within the final fluid are mostly clay type minerals containing different proportions of sodium, calcium, magnesium, iron, aluminium and bicarbonate/carbonate. The calibrated model indicated that these minerals are all in saturated states. During the development of the water over the 100-year simulation period these minerals developed to super saturated states allowing for the precipitation of some minerals lowering the concentrations of some of the elemental concentrations. The hydroxide and clay mineral development within the system is confirmed by the laboratory XRD observations with hydroxide and clay minerals being abundant (refer to section 6.2).

Based on the path followed during all scenarios, the following system observations and model conclusions can be made upon the development and investigation of the calibrated models:

1. The weathering and dissolution reactions of the carbonate and mafic minerals within the Ecca geology allows for pH values ranging between ~7.87 and 8.26 with buffering reactions, mainly from calcite, not allowing any acidic environments to develop within the regional groundwater. Thus, although the acid-base accounting (ABA) assessment suggested acidic drainage from the coal discard material, sufficient neutralisation capacity is contributed by the waste material and regional geology along the flow path of infiltrated water as it migrates through the coal discard pores until it percolates to the shallow water table.

2. The system is most sensitive to alterations in the oxygen fugacity as the availability of oxygen drives pyrite oxidation. Simulations suggest that available oxygen tends to deplete in the natural groundwater system. The more reducing environment allows for the mobilisation of especially manganese.

3. Field solid samples as well as modelled results indicate saturation of carbonate, clay and hydroxide minerals with the development of secondary minerals most likely to be kaolinite and smectite-type clays.

4. Due to the alkaline environment of the groundwater, adsorption of selenium to hydrous ferric oxides (HFO) is negligible and therefore remain mobile.

5. Manganese and selenium may reach concentrations within the groundwater above the recommended guideline for drinking water which may pose health risks to groundwater users.

9.1.2   Eastern operations' model

The mineral phases and abundances used in the different scenarios were deduced based on XRD and XRF results with a lower proportion of calcite allowed to react. Mineralogical data were limited, therefore certain assumptions were made regarding the abundance of calcite during the calibration process.

Three weathering scenarios, as discussed in section 8.2.5, were simulated following an analytical calibration path. Significant changes in terms of dissolved species concentration were observed between the three

scenarios which resulted in the simulation of different water type. During the simulation of Scenario 1 the system was allowed to react for 100 years at a fixed fugacity and constant calibration and sensitivity analyses were performed. The sensitivity analyses included alterations of the abundance of calcite, and mineral weathering rates (especially that of pyrite) until more realistic results that compared well with the monitoring data set were obtained. Based on the first scenario simulation, it was clear that to allow for simulation with results closer to that observed in the monitoring data set, the fugacity of the system should be adjusted as slight water level fluctuations within the underground voids are expected to occur (refer to Chapter 7). Consequently, Scenario 2 was simulated with the oxygen fugacity linearly changing over a 100-year period as illustrated in Figure 9-2. The oxygen fugacity slides from 0.18 to 0.0021, to simulate an environment with readily reduced atmospheric influence. This conceptually represent water level rise within the compartments.
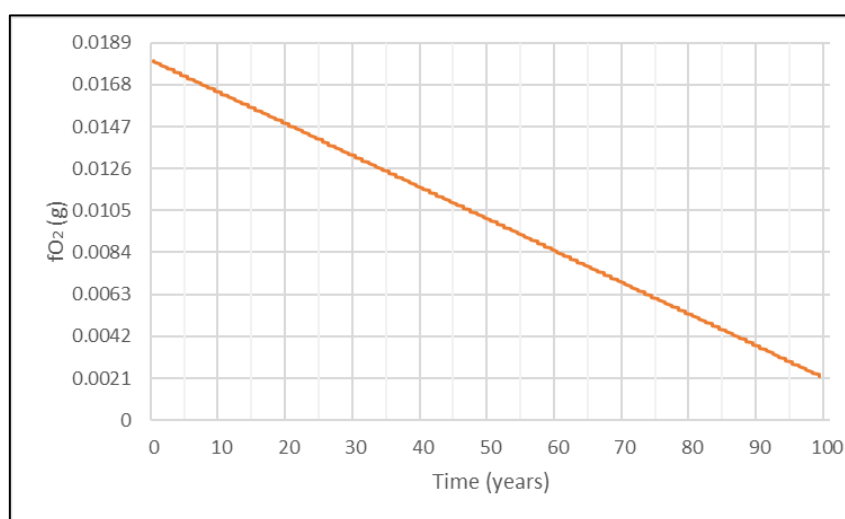
Figure 9-2: Linear decrease of oxygen fugacity [fO_2] over the simulation period.

The parameters with the most realistic results that were in line with conceptual understanding of the hydrogeochemical environment were used to simulate the system in a state closest to that observed in the decant monitoring data. Following the different scenarios with evaluations of the system dynamics as well as the sensitivity of the system to certain parameter changes, the knowledge of the calibration path accumulated in calibrated simulations of the system in Scenarios 1 and 2. Refer to section 8.2 for descriptions of the model parameters.

Scenarios 1 and 2 simulated a chemical sample with a pH between ~7.17 and 7.62 for a transient simulation of 100 years. Calcite dissolution allowed for buffering reactions to occur as illustrated Figure 8-5 with the pH of the system increasing to a maximum of 7.62. These neutralisation reactions occurred due to a system in disequilibrium within the rate at which reactions took place (Van Coller, 2013). Allowing for the analogue values used in Scenarios 1 and 2, simulated water quality displayed a Ca-SO_4 (Figure 9-3) water type with a TDS between ~1 340 and 1 493 mg/L. The calcium and sulphate dominated water system agrees well with that observed in the monitoring data set. Calcium, magnesium, sodium, potassium, chloride, sulphate, bicarbonate, aluminium, iron, manganese, nickel and selenium were present in the simulations with concentrations resembling those observed in the monitoring data. Most of the above-mentioned ions are released by the

dissolution of mainly silicate, oxide and sulphide minerals associated with the coal layers and host rocks within the system (Campaner *et al.*, 2014).
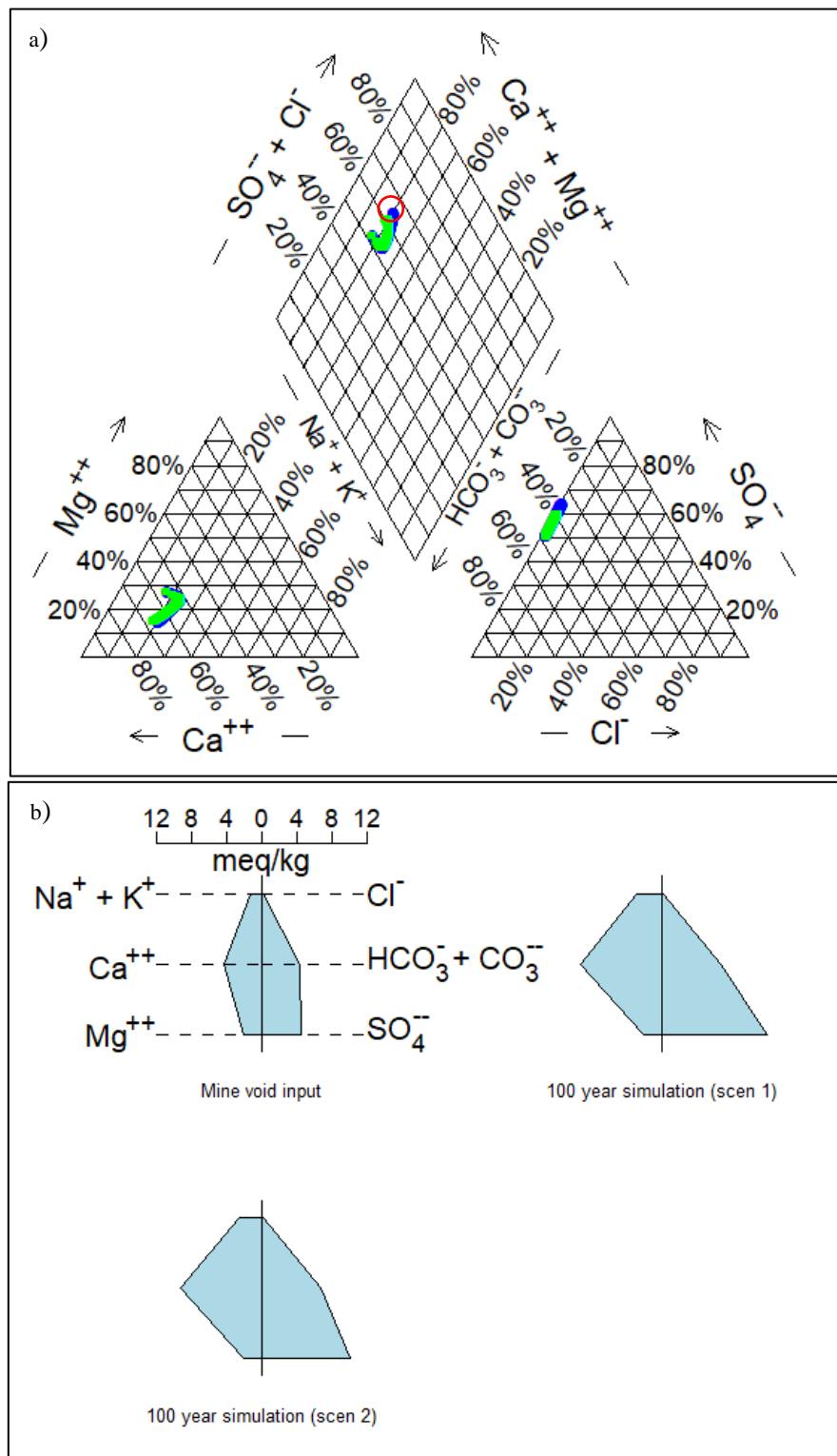
Figure 9-3: Piper (a) and Stiff (b) diagram indicating the water type as well as the evolution of the water over the 100-year period following simulations for Scenarios 1 (blue) and 2 (green) for the eastern operation system.

The Piper diagram shown in Figure 9-3 reflects the evolution path of the weathering water sample with initial Ca-SO$_4$ facies of the mine void water as it follows a reaction path with magnesium and sulphate increasing as

the saturated species precipitates out of solution to remain at a Ca-SO$_4$ water facies (position indicated in red in the Piper diagram). The main difference in the evolution paths between the two scenarios is that Scenario 1 is more enriched in sulphate. This suggest that more oxygen is available to mediate pyrite oxidation to release more sulphate in the water. Considering water level fluctuation and decreased oxygen fugacity, the rate at which pyrite oxidises is lowered and hence lower sulphate concentrations are simulated in Scenario 2. As mentioned before, Younger (2007) describes a water sample with a strong calcium and sulphate ion distribution to be product of groundwaters affected by oxidation of pyrite.

Model results following Scenarios 1 and 2 show that manganese and selenium are mobile under circum-neutral and oxidising to slightly less oxidising conditions, with nickel only partially mobile. Under the specific redox state (refer to Appendix D: Model Results) and pH of the modelled systems, manganese mainly occurs as Mn^{2+} and thus remain in solution. However a decrease in manganese concentration occurs as the pH rises between Scenario 1 and Scenario 2 and may indicate that a raise in pH of the system would very much likely precipitate manganese. The concentration of dissolved nickel is also strongly dependant on the pH of the system, showing a general decrease as the pH increases. Blowes *et al.* (1994) reported nickel concentrations from >250 mg/L to <10 mg/L as the pH increased to above 5.8 within the siderite buffering zone. It is therefore inferred that nickel is removed from solution through adsorption or coprecipitation with the secondary ferric oxyhydroxide precipitates.

Table 9-2: Range of measured field decant observations together with simulated water quality concentrations for the eastern operations system.

| Parameter | Units | Baseline range in unmined areas | Decant | | Scenario 1 | Scenario 2 |
| | | | 5th Percentile | 95th Percentile | | |
		Value	Value	Value	Value	Value
pH	pH units	6.87-8.59	7.02	8.27	7.17	7.62
TDS	mg/L	145.0-354.0	742.40	2761.60	1493	1340
Ca	mg/L	9.20-25.43	141.97	514.40	189	189
Mg	mg/L	2.50-11.81	59.84	180.20	26	26
Na	mg/L	10.92-90.40	17.41	63.20	69	60
K	mg/L	2.54-6.70	2.92	7.56	0.14	0.12
Cl	mg/L	4.58-20.64	4.85	9.92	5	5
HCO$_3$	mg/L	90.70-213.0	159.60	423.40	410	410
SO$_4$	mg/L	3.80-38.15	397.20	1643.0	574	484
Fe	mg/L	0.01-0.25	0.03	4.86	105	78
Al	mg/L	0.03-0.19	0.01	0.14	<0.001	<0.001
Mn	mg/L	0.01-0.02	0.01	2.22	0.53	0.43
Se	mg/L	0.01	0.024	0.039	0.057	0.057
Ni	mg/L	0.01	0.013	0.36	0.015	0.007

According to Campaner *et al.* (2014), in areas where pyrite weathering occurs in the presence of carbonate rocks, calcite and dolomite will dissolve when in contact with strong acids. In general, the pH of the system tends to neutral conditions due to the consumption of H$^+$-ions followed by the dissociation of carbonic acid [H$_2$CO$_3$] and the stability of bicarbonate ions in solution (Webb & Sasowsky, 1994). Despite the fact that the relationship between carbonate species is controlled by pH, the alkalinity in water systems may be strongly controlled by the dissolution of carbonate minerals (Campaner *et al.*, 2014). This may explain the relatively

high bicarbonate levels simulated, where the pyrite weathering influence is confirmed by the high sulphate concentrations.

The resultant water shows elemental concentration content close to that observed in the monitoring data set (Table 9-2) with only magnesium and potassium below the lower limit (5th percentile) of the decant water quality. As mentioned before, at neutral to alkaline conditions, cationic trace metals tend to be adsorbed by surface negative charges, whereas oxyanions tend to be adsorbed by surface positive charges under low pH conditions (Stumm & Morgan, 1996; Cravotta, 2008; Campaner *et al*., 2014). Selenium concentrations are higher than that observed in the monitoring data but nonetheless suggest that selenium is mobile under the oxidising to less oxidising, alkaline conditions of the mine water. Nickel, however, show concentrations lower than that observed in the monitoring data and suggest that nickel is less mobile under alkaline conditions. It further suggests that Ni may be removed through adsorption to HFO surfaces under the alkaline, oxidising to slightly less oxidising conditions. Physico-chemical conditions frequently favour chemical equilibrium and precipitation of metals, like nickel, a few metres downstream from discharge points, removing chemical species in solution (Campaner *et al*., 2014).

Based on the simulation paths followed during the different scenarios the following system observations and model conclusions can be made upon the development and investigation of the calibrated models:

1. The weathering and dissolution reactions of the carbonate minerals within the Ecca geology and coal seams allows for pH values ranging between ~7.17 and 7.62 with buffering reactions not allowing any acidic environments to develop within the mine water discharging at the specific decant positions.

2. The system is most sensitive to changes in oxygen fugacity as the availability of oxygen drives pyrite oxidation. The simulated values suggest that the oxygen fugacity tends to decrease, however constant oxygen fluctuation is expected within the underground voids mimicking the dynamic seasonal fluctuation of water levels.

3. Field solid samples as well as modelled results indicate saturation of ferric hydroxide minerals.

4. Due to the near neutral to alkaline environment of the mine decant water it is inferred that nickel concentrations may be lowered through adsorption; however, selenium and manganese are less influenced.

5. Manganese, selenium, and to a lesser extent nickel, may reach concentrations within the mine void and decant water that pose risks to the environment.

9.1.3   Western operations' model

The mineral phases and abundances used in the different scenarios were based on XRD and XRF results and water chemical analysis data observed in the monitoring data set. The specific mineralogy of the western underground operations could not be collected and analysed, therefore assumptions were made regarding the

presence of carbonate mineral phases in the mine waste material. The monitoring data suggested that no alkalinity is present in the decant water and thus calcite was omitted as a simple reactant.

As with previous models, three weathering scenarios were simulated following an analytical calibration path. Significant changes in terms of dissolved species concentration was observed between the three scenarios, however the water type remained unchanged. During the simulation of Scenario 1, the system was allowed to react for 100 years at a fixed fugacity and constant calibration and sensitivity analyses were performed by adjusting the mineral weathering rates, especially that of pyrite, until more realistic results were obtained. Based on the first scenario, it was clear that to allow for a simulation with results closer to that of the monitoring data, the fugacity of the system had to be adjusted. Slight water level fluctuations within the underground voids are expected to occur as discussed in the conceptual model and thus support alterations of the oxygen fugacity within the system (refer to Figure 9-2). Following the different scenarios with evaluations of the system dynamics as well as the sensitivity of the system to certain parameter changes, the knowledge of the calibration path accumulated to a calibrated system in Scenarios 1 and 2 (refer to section 8.2 for model parameters).

Scenarios 1 and 2 simulated a chemical sample with a pH between ~3.61 and 3.64 for a transient simulation of 100 years. Due to the low pH of the system, buffering capacity is provided by soluble hydroxides which includes aluminium -and iron hydroxides (refer to Figure 8-9).

Allowing for the analogue values used in Scenarios 1 and 2 the modelled sample displayed a Ca-SO$_4$ (Figure 9-4) water type with a TDS between ~1 361 and 1 423 mg/L. The calcium and sulphate dominated system agrees well with that observed in the monitoring data set. Calcium, magnesium, sodium, potassium, chloride, sulphate, bicarbonate, aluminium, iron, manganese, nickel, lead and selenium were present in the simulations with concentrations resembling mine decant monitoring data.
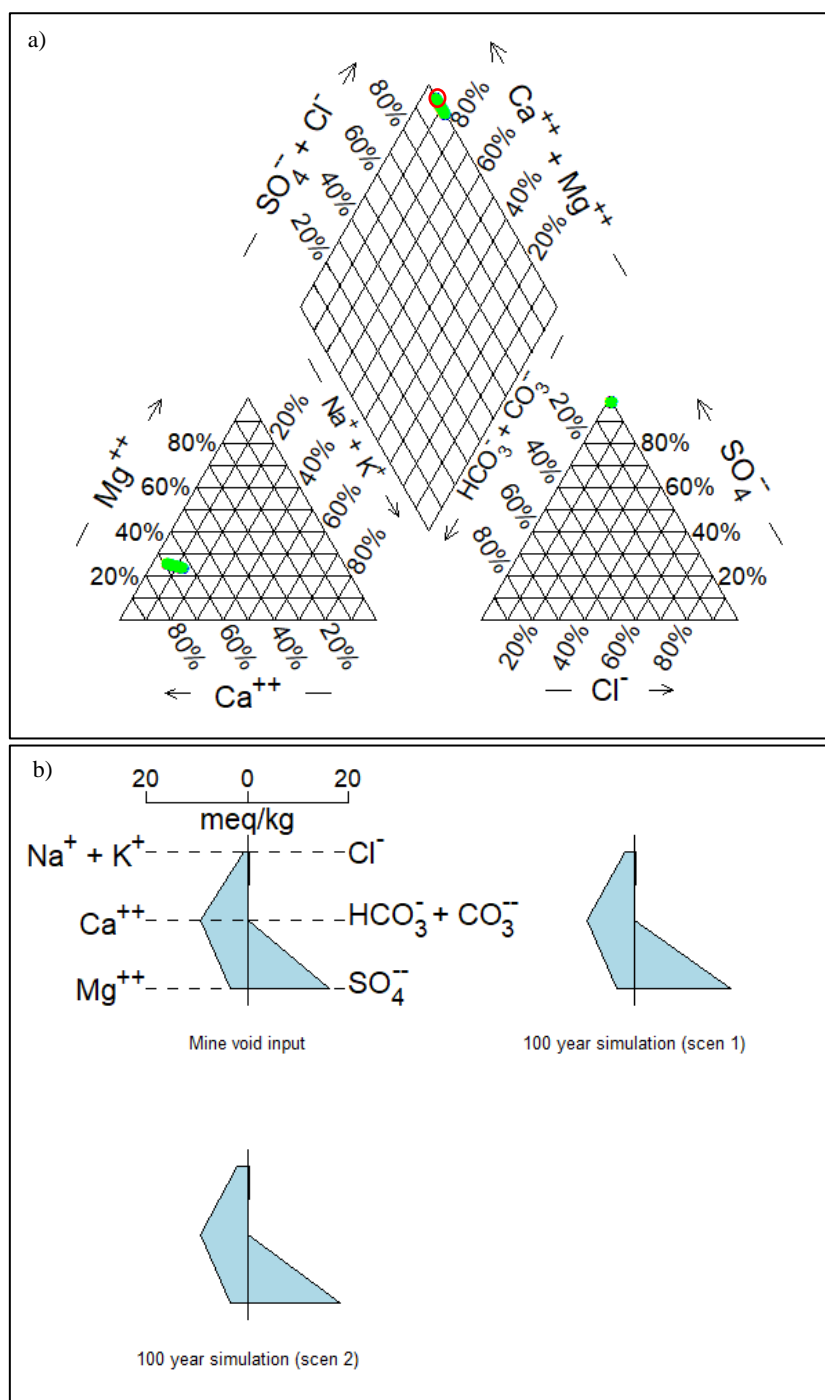
Figure 9-4: Piper (a) and Stiff (b) diagram indicating the water type as well as the evolution of the water over the 100-year period following simulations for Scanrios 1 (blue) and 2 (green) for the western operations system.

The Piper diagram in Figure 9-4 indicates the evolution path of the weathering simulations with initial Ca-SO_4 facie where after calcium slightly increases to remain at a Ca-SO_4 facie (position indicated in red in the Piper diagram). The evolution paths followed by Scenarios 1 and 2 appears to be exactly the same. Water samples with strong calcium and sulphate ion distributions may be the product of groundwaters affected by oxidation of pyrite (Younger, 2007).

Ferric iron [Fe^{3+}] becomes more mobile in acidic mine waters and precipitate as ferric hydroxides [$Fe(OH)_3$] under oxidising conditions due to its lower mobility (Figure 9-5). Generally, when the levels of dissolved

oxygen are higher, iron predominantly occurs in its ferric oxidation state, while at lower dissolved oxygen levels, iron occur as ferrous iron.
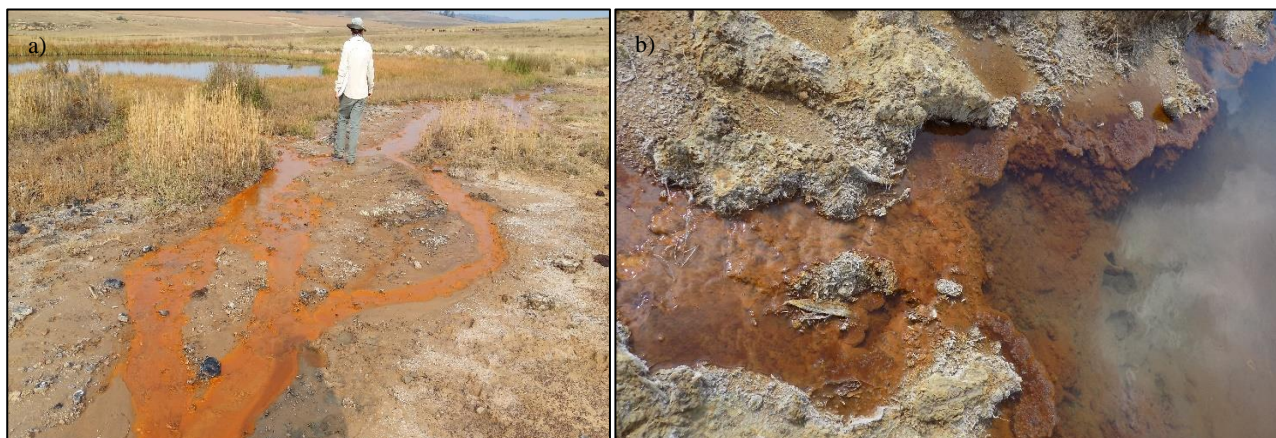
Figure 9-5: Fe(OH)₃ precipitates at Butter Adit Decant (a) and W1 Decant (b).

The model results following Scenarios 1 and 2 suggest that aluminium, manganese, lead, selenium, and nickel are mobile under the acidic conditions of the mine decant water. Aluminium becomes more mobile with a decreasing pH (Smith, 2007). This is supported by Waters and Webster-Brown (2013) who evaluated the effects of acid mine drainage (AMD) on the water quality and ecology of streams in New Zealand and found that the mobility and toxicity of dissolved aluminium is dependent on speciation. The speciation of aluminium is dependent on the pH of the system which affects aluminium hydrolysis, and organic carbon and sulphate complexation with aluminium. They found that dissolved aluminium $[Al^{3+}]$ concentrations dominated in water of pH 3.8 to 4.8, while aluminium organic and -hydroxide complexes dominated in higher pH systems. Moreover, manganese is highly mobile under the acidic conditions of the mine decant water.

As pyrite oxidises, the pH of the system decreases and concentration of dissolved sulphate increases. Such conditions significantly modify the chemical speciation and relative distribution of chemical forms of lead in solution. According to a study by Reddy *et al.* (1995) the availability and mobility of Pb^{2+} increased at a decreased pH due to the chemical form in which the metal ion is present in solution. Nickel is also more mobile due to the acidic nature of the water. Adsorption of lead and nickel in acidic system conditions is not very significant as the sorption of cations generally decrease with decreasing pH (Smith, 1999). Kinniburgh and Jackson (1981) described the critical pH ranges for sorption of divalent metal cations on hydrous iron and aluminium oxides and suggested that the critical pH range for lead, nickel, and manganese are 3.0-5.0, 5.0-6.5, and 6.5-7.5, respectively. According to Smith (1999) nickel are difficult to self-mitigate in mine waters due to their relatively weak sorption on hydrous iron oxides. Consequently, nickel tend to remain mobile in waters discharging from mined lands.

According to Howard (1977) selenium is likely to be strongly adsorbed by hydrated surfaces of ferric oxides. It is clear when comparing the selenium concentrations simulated for the eastern and western operations that lower selenium concentrations are predicted for the western operations (Table 9-3). The lower concentrations may be ascribed to the more acidic environment that favours selenium adsorption (Dhillon & Dhillon, 1999).

Selinite may also be readily reduced to insoluble elemental selenium under the acidic conditions (Liu & Narasimhan, 1994). However, selenium is not removed completely and remain mobile within the system. A study by Rait *et al.* (2010), and Pauwels *et al.* (2010) confirmed that dissolved arsenic can strongly be adsorbed to fine grained ferric iron minerals such as hydroxides, oxyhydroxides and hydroxy sulphates, which is further accelerated under acidic conditions (Smith, 1999).

Table 9-3: Range of measured field decant observations together with simulated water quality concentrations for the western operation system.

Parameter	Units	Baseline range in unmined areas	Decant		Scenario 1	Scenario 2
			5th Percentile	95th Percentile		
		Value	Value	Value	Value	Value
pH	pH units	6.87-8.59	2.91	3.32	3.61	3.64
TDS	mg/L	145.0-354.0	881.40	2850.60	1423	1361
Ca	mg/L	9.20-25.43	134.15	393.34	185	185
Mg	mg/L	2.50-11.81	36.14	43.51	41	41
Na	mg/L	10.92-90.40	10.28	16.42	20	20
K	mg/L	2.54-6.70	4.99	8.48	41	41
Cl	mg/L	4.58-20.64	3.97	6.70	10	10
HCO_3	mg/L	90.70-213.0	2.50	2.50	2	2
SO_4	mg/L	3.80-38.15	598.95	2053.97	914	874
Fe	mg/L	0.01-0.25	13.90	120.16	59	48
Al	mg/L	0.03-0.19	12.0	71.66	14	11
Mn	mg/L	0.01-0.02	1.12	6.88	1.98	1.98
As	mg/L	0.005	0.021	0.021	0.005	0.005
Pb	mg/L	0.0075	0.035	0.035	0.033	0.033
Se	mg/L	0.01	0.01	0.01	0.034	0.034
Ni	mg/L	0.01	0.322	2.472	1.57	1.57

The system is characterised by prevailing acidic conditions which may, according to Vermeulen and Usher (2006b), be ascribed to mining under shallow conditions. In this zone most of the neutralisation potential has been leached through circulating water prior to mining. High calcium and magnesium concentrations found in the decant mine water may be due to dissolution of carbonate and silicate rocks present in the local stratigraphic sequence. Similar observations were made by Vermeulen and Usher (2006b) during a study at Schoongezicht Colliery. Neutralisation through carbonate dissolution is not demonstrated by the water quality and implies that the amount of carbonate minerals is too low to neutralise the acid water at sufficiently high rates to prevent acidic conditions (Vermeulen & Usher, 2006b). The acidic pH of the decant water thus indicates that available carbonates (mainly calcite) have been depleted to a large degree (Banwart *et al.*, 2002). Carbonate minerals are therefore no longer reacting sufficiently to release significant amounts of calcium [Ca^{2+}]. Hence, plagioclase is considered as the source of calcium (Banwart *et al.*, 2002). The acidic nature and higher rate of pyrite oxidation when compared to carbonate neutralisation reactions within this system have led to very high sulphate loadings, which are not always constrained by secondary mineral saturation (Vermeulen & Usher, 2006b). The elevated concentrations of aluminium further indicate faster weathering of aluminosilicates under the acidic conditions (Backstrom & Sartz, 2016).

The simulations show elemental concentration content close to that observed in the monitoring data set (Table 9-3) with only potassium and chloride exceeding the upper range (95th percentile) mine decant water limits. Again, selenium concentrations are higher than that observed in the monitoring data but suggest that selenium is mobile under the oxidising to slightly less oxidising, acidic conditions of the mine decant water.

Based on the simulation paths followed during the weathering scenarios the following system observations and model conclusions can be made upon the development and investigation of the calibrated models:

1. Due to the absence of carbonate minerals, oxidation of pyrite allowed for pH values ranging between ~3.61 to 3.64. The reactions allow acidic environments to develop within the mine decant water systems. Dynamic equilibrium between dissolution and precipitation of aluminium -and iron hydroxides therefore allows the pH to demonstrate minor fluctuations over the simulation period.

2. Field solid samples as well as modelled results indicate saturation of ferric hydroxide minerals.

3. Due to the acidic nature of the mine decant water it is inferred that selenium and arsenic concentrations may be lowered through adsorption. However, manganese, lead, and nickel are less influenced.

4. Manganese, aluminium, lead, nickel and selenium may reach concentrations within the mine void and decant water that may have detrimental effects on freshwater ecosystems.

9.2 MODELLED GROUNDWATER AND MINE WATER

Groundwater in the area is mainly used for domestic purposes and small-scale irrigation and livestock watering. As the mine decant water affects non-perennial streams in the area, inflowing water will impact on aquatic ecosystems. The following sub-sections compares and summarises the main chemical constituents in the modelled groundwater and mine waters to the national water quality standards as set out by SABS and DWA to augment identification of risks to potential water users and the environment. It is important to mention once again that the simulated concentrations for the different component models do not reflect true concentrations measured in the field or monitoring data sets and simply indicate where constituents may create potential risks.

9.2.1 Standards for domestic water supply

The model water quality of groundwater downstream of the coal discard dumps was classified according to the SANS drinking water standards 241:2015 to evaluate the water for human use and consumption.

Table 9-4: Domestic water use quality classification of the simulated groundwater quality downstream of the coal discard dumps.

Parameter	Units	Standard guideline	Risk	Coal discard dump system	
				Scenario 2	Scenario 3
				Value	Value
pH	pH units	5-9.7	Operational	7.87	8.26
TDS	mg/L	<1200	Aesthetic	668	532
Ca	mg/L	_b	-	153	124
Mg	mg/L	_b	-	11	4
Na	mg/L	<200	Aesthetic	23	23
K	mg/L	_b	-	5	5
Cl	mg/L	<300	Aesthetic	2	2
HCO$_3$	mg/L	_b	-	28	13
SO$_4$	mg/L	<500	Chronic health	440	357
Fe	mg/L	<2	Chronic health	0.44	0.22
Al	mg/L	<0.3	Operational	<0.001	<0.001
Mn	mg/L	<0.4	Chronic health	<0.001	0.038
Se	mg/L	<0.01	Chronic health	0.034	0.069

b – No established guideline value

Based on the standards for drinking water, Scenarios 2 and 3, which represent potential water quality of groundwater downstream of the coal discard dumps, display elevated levels of selenium (Table 9-4). Model selenium concentrations were above the allowed limits for drinking water and may reach concentrations that may not be suitable for consumption and can potentially cause chronic health effects. Case reports have shown that chronic exposure to selenium compounds is associated with several adverse health effects in humans. Early toxic effects may impair endocrine function on the synthesis of thyroid hormones and on the metabolism of growth hormones. Other adverse effects of selenium exposure include the impairment of natural killer cells activity and at higher levels, hepatoxicity and gastrointestinal disturbances. After exposure of high levels of selenium, dermatologic effects, such as nail and hair loss and dermatitis may follow (Vinceti *et al*., 2001).

It is unlikely that groundwater directly downstream of the coal discard dumps will be exploited for domestic use, however due to the growth of rural communities in the local area, groundwater may increasingly be depended on for domestic use in the future. Based on the summary and classification given above, the groundwaters will be suitable with minor treatment and water management practices in place.

9.2.2　Standards for irrigation water supply

The model water quality of the groundwater and mine decant water has been classified according to the DWA water quality guidelines for agricultural use in irrigation (DWAF, 1996a).

Table 9-5: Irrigation water use quality classification of the simulated groundwater and mine decant water chemistry.

Parameter	Units	Max acceptable	Risk	Coal discard dump system		Eastern operation system		Western operation system	
				Scenario 2	Scenario 3	Scenario 1	Scenario 2	Scenario 1	Scenario 2
				Value	Value	Value	Value	Value	Value
pH	pH units	6.5-8.4	<6.5 or >8.4	7.87	8.26	7.17	7.62	3.61	3.64
TDS	mg/L	540	>540	668	532	1493	1340	1423	1361
Ca	mg/L	_b	-	153	124	189	189	185	185
Mg	mg/L	_b	-	11	4	26	26	41	41
Na	mg/L	70	>70	23	23	69	60	20	20
K	mg/L	_b	-	5	5	0.14	0.12	41	41
Cl	mg/L	350	>350	2	2	5	5	10	10
HCO_3	mg/L	_b	-	28	13	410	410	2	2
SO_4	mg/L	_b	-	440	357	574	484	914	874
Fe	mg/L	20	>20	0.44	0.22	105	78	59	48
Al	mg/L	20	>20	<0.001	<0.001	<0.001	<0.001	14	11
Mn	mg/L	10	>10	<0.001	0.038	0.53	0.43	1.98	1.98
Se	mg/L	0.05	>0.05	0.034	0.069	0.057	0.057	0.034	0.034
Ni	mg/L	2	>2	-	-	0.015	0.007	1.57	1.57
As	mg/L	_b	-	-	-	-	-	0.005	0.005
Pb	mg/L	2	>2	-	-	-	-	0.033	0.033

b – No established guideline value

Based on the classification of the modelled groundwater and mine decant water quality for the different systems to its suitability for irrigation (Table 9-5), the following summary of conclusions can be derived:

- Sample Scenario 2 for the groundwater downstream of the coal discard dumps reflects water quality that is suitable for irrigation use.

- Sample Scenario 3 for the groundwater downstream of the coal discard dumps show elevated levels of selenium. The mobility of selenium under more reduced conditions may limit its use for irrigation.

- Samples Scenario 1 and 2 for the mine decant water in the eastern operations display elevated levels of TDS, iron and selenium. These constituents may reach concentrations that may be harmful to moderately and highly sensitive crops.

- Samples Scenario 1 and 2 for the mine decant water in the western operations display acidic pH and elevated levels of TDS and selenium which may pose potential risks to moderately and highly sensitive crops.

Although some constituents remain in solution and hence are problematic, the suitability of water quality for crop irrigation depends on the specific plant species and cultivars as well as the irrigation management methods.

9.2.3   Standards for livestock water supply

The model water quality of the groundwater and mine decant water has been classified according to the DWA water quality guidelines for agricultural use in livestock watering (DWAF, 1996b).

Table 9-6: Livestock water use quality classification of the simulated groundwater and mine decant water quality.

Parameter	Units	TWQR	Coal discard dump system		Eastern operation system		Western operation system	
			Scenario 2	Scenario 3	Scenario 1	Scenario 2	Scenario 1	Scenario 2
			Value	Value	Value	Value	Value	Value
pH	pH units	_[b]	7.87	8.26	7.17	7.62	3.61	3.64
TDS	mg/L	0-1000	668	532	1493	1340	1423	1361
Ca	mg/L	0-1000	153	124	189	189	185	185
Mg	mg/L	0-500	11	4	26	26	41	41
Na	mg/L	0-2000	23	23	69	60	20	20
K	mg/L	_[b]	5	5	0.14	0.12	41	41
Cl	mg/L	0-1500	2	2	5	5	10	10
HCO_3	mg/L	_[b]	28	13	410	410	2	2
SO_4	mg/L	0-1000	440	357	574	484	914	874
Fe	mg/L	0-10	0.44	0.22	105	78	59	48
Al	mg/L	0-5	<0.001	<0.001	<0.001	<0.001	14	11
Mn	mg/L	0-10	<0.001	0.038	0.53	0.43	1.98	1.98
Se	mg/L	0-50	0.034	0.069	0.057	0.057	0.034	0.034
Ni	mg/L	0-1	-	-	0.015	0.007	1.57	1.57
As	mg/L	_[b]	-	-	-	-	0.005	0.005
Pb	mg/L	0-0.1	-	-	-	-	0.033	0.033

[b] – No established guideline value

Based on the classification of the modelled groundwater and mine decant water quality for the different systems to its suitability for livestock watering (Table 9-6), the following summary of conclusions can be made:

- The groundwater simulated downstream of the discard dumps is suitable for livestock watering and can be consumed safely with no adverse effects by all livestock;

- TDS and iron concentrations in samples Scenarios 1 and 2, representing mine decant water quality of the eastern operations, is above the recommended Target Water Quality Range (TWQR) and thus decant water will not be suitable for livestock watering.

- Concentrations of TDS, iron, aluminium, and nickel in samples Scenarios 1 and 2, representing mine decant water quality for the western operations, is above the recommended TWQR guidelines and are therefore not suitable for livestock watering.

The mine decant water are not used for livestock watering, however due to the rural community and extensive farmlands in the local area it is important to assess whether the water is safe to livestock if consumed accidently.

9.2.4 Standards for aquatic ecosystems

The model water quality of the mine decant water has been classified according to the DWA water quality guidelines for aquatic ecosystems (DWAF, 1996c).

Table 9-7: Aquatic ecosystems water quality classification of the simulated mine decant water chemistry.

Parameter	Units	TWQR	Chronic effect value	Acute effect value	Eastern operation system		Western operation system	
					Scenario 1	Scenario 2	Scenario 1	Scenario 2
					Value	Value	Value	Value
Fe	mg/L	_b	-	-	105	78	59	48
Al	mg/L	0-0.01	0.02-0.15	>0.15	<0.001	<0.001	14	11
Mn	mg/L	0-0.18	0.37-1.3	>1.3	0.53	0.43	1.98	1.98
Se	mg/L	0-0.002	0.005-0.03	>0.03	0.057	0.057	0.034	0.034
Ni	mg/L	_b	-	-	0.015	0.007	1.57	1.57
As	mg/L	_b	-	-	-	-	0.005	0.005
Pb	mg/L	0-0.0012	0.0024-0.016	>0.016	-	-	0.033	0.033

[b] – No established guideline value

Based on the classification of specific constituents simulated in the mine decant water in terms of risk to aquatic ecosystems (Table 9-7), the following conclusion summary can be derived:

- The eastern operations simulated mine decant water show concentrations of selenium above the TWQR and above the acute effect value (AEV).

- The western operations simulated mine decant water display concentrations of aluminium, manganese, selenium and lead above the TWQR and above the AEV.

The mine decant water emanating from the eastern -and western operations are classified within the AEV class, which means that metal concentrations in the water may reach concentrations that could induce toxic effects in aquaic organisms, disturbing organisms' growth, metabolism, or reporoduction with consequences to the entire trophic chain, including on humans. High levels of metals in the environment could be a hazard for function of natural ecosystems and human health, due to their toxic effects, long persistence, bioaccumulatice properties, and biomagnificaton in the food chain (Gheorghe *et al*., 2017). Due to mixing and dilution processes that occur as the decant water flows into the surface water bodies, some constituents may precipitate out of solution or may be adsorbed to HFO. Due to the adaptability of some species to these levels, organisms may be able to live and reproduce in these waters. However, due to the desorption and remobilisation processes of metals, the sediments constitute a long-term source of contamination to the food chain (Gheorghe *et al*., 2017).

9.3 FINAL CONCEPTUAL MODEL SUMMARIES

Based on the literature study and conceptual models, various scenarios of forward reaction path models specifically subjected to alterations in oxygen fugacity, were simulated. The main aim of the modelling

exercises was to study the current groundwater and mine water hydrochemistry and summarise and understand the geochemical processes currently dominant in the systems as well as those expected to influence the water qualities in the future.

During the forward reaction path models, various processes were identified that lead to the formation of the groundwater and mine water currently observed in the monitoring data sets. When considering the coal discard dump system, as rainwater (represented by distilled water in the models) with a neutral pH infiltrates into the coal discard dumps and regional soils and geology, the fluid-rock interaction does not only cause physical weathering, but the chemical reactions taking place allow for geochemical weathering of the primary minerals (refer to Chapter 7). This leads to the evolution of the water from a diluted atmospheric signature towards the groundwater chemistry observed. The model groundwater reflects a Ca-SO$_4$ water type with a pH between 7.48 and 8.26 due to various dissolution/weathering reactions of the primary minerals and precipitation of secondary minerals as discussed in Chapter 7. The calcium, sodium, potassium, iron, magnesium, aluminium and silicate rich minerals react and contribute to the observed groundwater signature. Groundwaters may become super saturated with respect to secondary mineral phases over time which may then be precipitated, given minimal dilution processes and atmospheric conditions prevail. However, ideal conditions of no dilution and atmospheric influences are rarely the case. The weathering of the system allowing groundwater to chemically evolve occurs with reducing and eventual depleting oxygen fugacity.

When considering the eastern -and western operation models, as the mine void water migrates along the flow paths to final discharge (decant), the primary minerals in the coal roof and floor materials as well as exposed mineral surfaces within the coal boards and pillars are subjected to geochemical weathering. This leads to the evolution of the mine void water from Ca-SO$_4$ water types to more enriched mine decant water quality as observed in the monitoring data sets. The mine decant water simulated for the eastern operation system is a Ca-SO$_4$ type with a pH between 7.17 and 7.62 and is formed through various dissolution/weathering reactions of the main primary minerals (refer to Chapter 7). The mine decant water simulated for the western operation system is a Ca-SO$_4$ type with a pH between 3.61 and 3.64 formed through various dynamic equilibrium dissolution and precipitation reactions. Over time, without dilution, the systems can become super saturated with respect to secondary mineral phases. The weathering of the systems allowing the mine water to evolve to the mine decant water qualities occur with decreasing oxygen fugacity to accommodate water level fluctuation and rise within the voids. Oxidising conditions are however expected to be reestablished at the discharge point allowing certain metals to precipitate.

Discussions of chemical processes and chemical mineral weathering and precipitation reactions dominant in the evolution of potential water type chemistry as concluded by the forward reaction path models are presented in Chapter 7 with additional discussions presented in previous sections of Chapter 9. Simplified summaries of the model findings for the different hydrogeochemical systems or components are illustrated in Figure 9-6 and Figure 9-7.
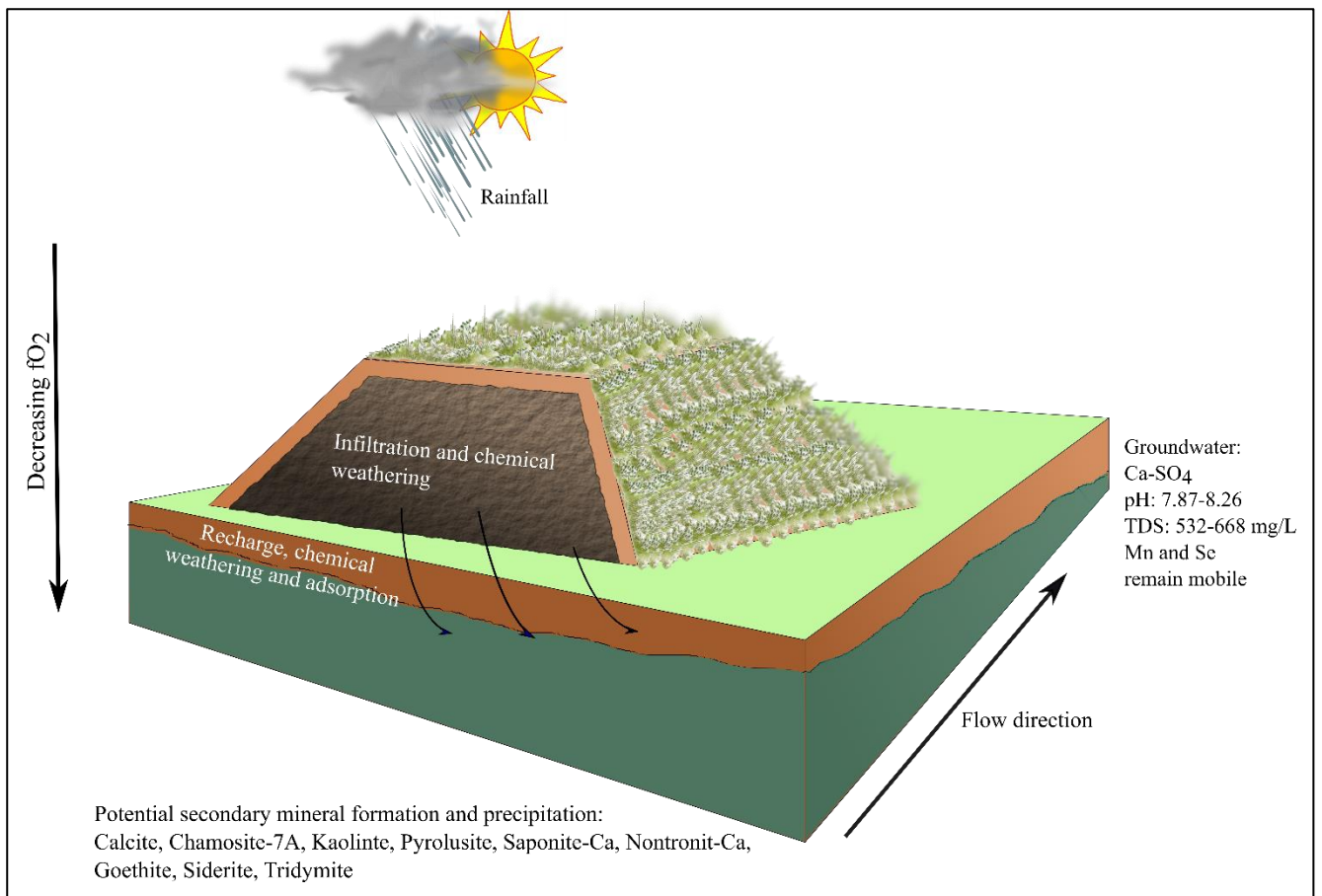
Figure 9-6: Final simplified conceptual model for the hydrogeochemical coal discard dump model.
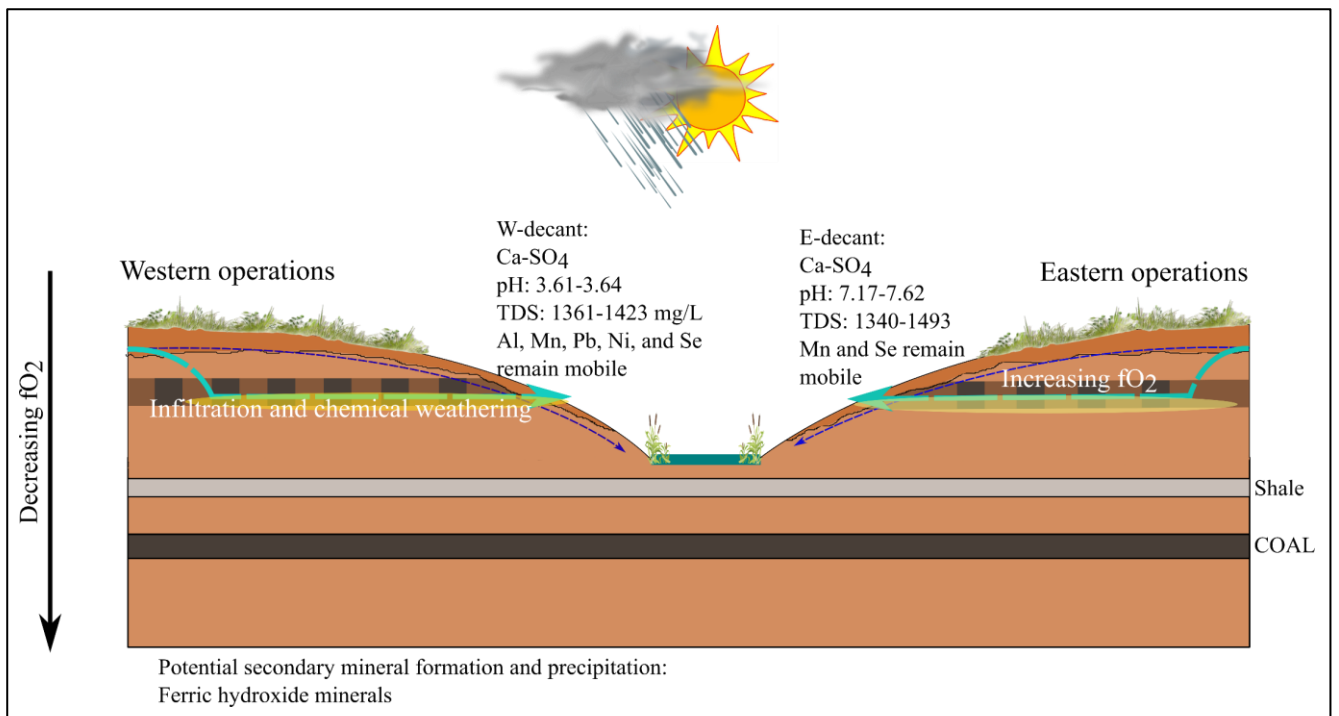
Figure 9-7: Final simplified conceptual model for the hydrogeochemical underground operation models.

9.4 IDENTIFIED RISKS AND RECOMMENDED MITIGATION METHODS

9.4.1 Appraisal of risks

The full appraisal of risks identified in previous chapters are summarised in the following section. The risks owing to coal discard deposited on coal discard facilities, flooding of the mine voids and decant of water at surface discharge points are briefly discussed below. The sequence in which they are listed does not imply any prioritisation of the risks.

9.4.1.1 Risks owing to coal discard deposited on coal discard facilities and flooding of the mine voids

9.4.1.1.1 *Contamination of shallow groundwater resources*

As already established, leaching from the coal discard dumps to shallow groundwater resources may lead to contamination of groundwater which serves as a source of potable water in the area. The SANS 241:2015 are given in the Chapter 5 discussions and suggest that constituents may reach concentrations above the recommended maximum guideline for drinking water. Furthermore, rising mine affected waters within the mine voids will not only come into contact with surface water resources but will also tend to flow into down-gradient areas via groundwater conduits. The extent and effects of mine water seeping to the groundwater regime is illustrated in Figure 3-16. Contamination of groundwater by metals, specifically iron and manganese, is highly probable in the long-term and pose a moderate risk. Selenium contamination further poses a definite, long-term, highly significant risk. Contamination of groundwater and soil by sulphate further pose a high-level risk to groundwater users. The extent of subsurface seepage of the mining-influenced waters (MIW) to the groundwater regime can unfortunately not be confirmed as no monitoring boreholes are available along the perimeter of the mine.

9.4.1.2 Risks owing to decant of water at the surface

9.4.1.2.1 *Ecological impacts*

The decant of MIW in the eastern and western operations that is characterised by neutral mine drainage and AMD, respectively, could result in ecological impacts within surface streams. These impacts are expected to be most significant directly downstream of a decant. The persistence of AMD conditions at the western operations is a definite, long-term, highly significant risk. Furthermore, the contamination of groundwater, soil and surface water by metals (Fe, Mn, Al, Ni, and Pb), metalloids (Se) and sulphate are definite, long-term highly significant risks (refer to section 9.2.4). The acidic water increases the solubility of aluminium and other metals which may be present in the affected region. The overall effect is to render the water toxic to varying degrees. Ultimately, the water becomes neutralised by a combination of dilution processes and reactions with the river sediment or various soil minerals. Certain constituents, particularly sulphate, have relatively high

solubilities and remain in solution (McCarthy, 2011). These effects will persist downstream until enough water is added to the stream to have a significant dilution effect. The ecological effects as a result of AMD and mine influenced waters elevated in metal(loid)s can be sourced from DeNicola and Stapleton (2002), Hogsden and Harding (2012), and He *et al*. (2015).

9.4.1.2.2 *Regional impacts on major river systems*

One of the pervasive messages regarding coal mining and associated AMD and elevated metal(loid) loadings in Mpumalanga is that it has a major impact on South Africa's major river systems. AMD has become a serious environmental concern in South Africa, particularly for the long-term sustainability of the country's fresh water supply (Annandale *et al.,* 2007; McCarthy & Humphries, 2013). Decanting mine water from the Union Colliery is important contributors to recurrent low-quality water in the Vaalwater -and Boesmanspruit which are significant due to their location within the Komati River catchment that includes Nooitgedacht Dam. The Boesmanspruit flows into the Boesmanspruit Dam which is a source of raw water supply for Carolina and on to the Nooitgedacht Dam. The Vaalwaterspruit directly discharges into the Nooitgedacht Dam. McCarthy and Humphries (2013) highlighted such concerns when water in the Boesmanspruit Dam, underwent rapid deterioration following a large rainstorm event in January 2012. The water displayed a sudden drop in pH and was accompanied by elevated levels of iron, aluminium and manganese and sulphate that rendered the water toxic and unsuitable for use for approximately seven months. In the long-term, pollution of these dams is likely to proceed gradually, as is currently also occurring at the Middelburg and Witbank Dams. The contamination from the mine discharges, especially that of the western operations, represent areas where mitigation or management strategies should be focused.

9.4.2 Management strategies

Different management strategies aimed to minimise the risks associated with MIW and AMD, especially within the Mpumalanga Coalfields, have been reviewed and described by various authors (Grobbelaar *et al.,* 2004; McCarthy & Pretorius, 2009; Coleman *et al*., 2011). Therefore, the purpose of the following sections is to comment on the most executable and feasible management options in the Union Colliery context, and not necessarily to describe the process and mechanics behind the different techniques and technologies.

According to RoyChowdhury *et al*. (2015) abandoned and decommissioned mine sites often accelerate the process of acid generation and may necessitate decades of proper management practices to reclaim. Management strategies reviewed were identified based on the water management hierarchy preferred by South African legislation (DWAF, 2007) which includes pollution prevention and minimization, the re-use of contaminated water and water treatment. The assessment process was further directed towards the evaluation of various common management options adopted at many Mpumalanga collieries. Remediation and mitigation techniques generally focus on the treatment of already produced AMD before their discharge into water bodies (RoyChowdhury *et al*., 2015).

It is clear from preceding discussions that efforts and available funds should be focused on implementing mitigation measures to minimise the contamination caused by the surface discharges and subsurface seepage from the underground complexes. Based on application of the pollution prevention and minimization principle, the primary management options that were evaluated related to underground mine void flooding and water treatment (active, passive and in situ treatments). Given the variability in water quality between the different operations (East and West) and the possibility that the water quality in the mine voids may change over time, it is likely that a suite of different technologies will be required.

The physical constraints of the terrain and the fact that the underground mine workings cannot be accessed, limits potential pollution minimisation management strategies for the underground workings to the following:

1. Underground mine void flooding

2. Control of the point discharges or diverting the flow to more accessible and manageable areas

3. Passive treatment of certain discharges that poses risk in terms of acidity and metal(loids) loadings

4. Active treatment through lime dosing and desalination plants

5. Unconventional methods

9.4.2.1 Mine void flooding

Flooding of the mine voids will create an oxygen poor environment where acid generating reactions will slow down significantly (Vermeulen & Usher, 2006b). According to McCarthy and Pretorius (2009) limiting oxygen ingress into mine workings have been implemented to try to mitigate the deteriorating water quality in the Olifants River. Essentially, continued production of acidity in mine water is dependent on the steady supply of oxygen, thus suggesting that if oxygen can be excluded, acid generation will eventually cease. McCarthy and Pretorius (2009) observed that in view of deeper mines, rapid flooding after closure will ensure consumption of the oxygen and provided that there are no additional inflows, acid generation will cease. This will lead to stratification of mine water with water of better quality near surface, whereas contaminated water will stratify at greater depths.

In the event that complete flooding of the mine voids is possible, as simulated in Scenario 3 of the eastern and western operations' models (refer to sections 8.3.2 and 8.3.3), sulphate concentrations decrease dramatically especially for the eastern operation component (Table 8-6). The effects of exhausting the oxygen supply over time on the sulphate concentration within the western operation system is less pronounced (Table 8-7). The model results following these scenarios indicate decreased metal(loid) concentrations (do not include all modelled metals), however these constituents remain in solution. This suggests that complete flooding of the mine voids will not resolve all risks posed by elevated metal(loid) concentrations.

Unfortunately, the topography of the Union Colliery mining areas will also not allow complete flooding as decant elevations will tend to control the water level at the lowest topographic level within each compartment. Above this level an unsaturated zone exists in the shallower portions of the underground workings. Thus, water emerges at adits and drainage pipes, thereby setting up groundwater circulation within the mine voids ensuring

a continued oxygen supply and acid generation in the mining level (McCarthy & Pretorius, 2009). The mixing of air, water, and exposed sulphides in this zone will continue to form acid and neutral mine drainage.

9.4.2.2 Control of point discharges and reuse of water

Various mines in the Olifants River catchment collectively manage and control the release of polluted water to minimise the levels of pollution (McCarthy & Pretorius, 2009). Stored mine water within the mine workings are released in a controlled manner at times corresponding to events associated with sufficient runoff to dilute contaminants to acceptable levels. However, managing point discharges is very difficult at decommissioned mines where water is emanating from mine wastes uncontrollably and may only be possible while mines are in production (McCarthy & Pretorius, 2009).

As the Union Colliery is located on a regional high, the closing of drainage pipes may only lead to other discharges at weak geological structures or at shallow subsidence areas. This is therefore not a long-term solution. Diverting the contaminated water to more accessible and manageable areas where the water can be easily treated by means of conventional and unconventional active and passive systems is therefore a more executable option.

Many mines faced with the problem of uncontrollable discharges or excess water may curtail the discharging mine water to evaporation and pollution control dams. These dams are generally shallow, and the water is allowed to evaporate. According to McCarthy and Pretorius (2009) such dams have to comply to certain measures such as liners which can be very expensive. Long-term maintenance costs for the removal and disposal of accumulated salts and repairing leaks also need to be kept in mind. The Union Colliery constructed a series of pollution control dams to curtail decant water at the Butter Adit from entering surface streams, however, from recent inspection it was observed that the curtailing of the decant water to the dams are not very effective as most of the water flows past the control dams (Figure 9-5a).

The use of contaminated and gypsiferous mine water for irrigation have been discussed by Annandale *et al.* (2002), Vermeulen *et al.* (2007) and Coleman *et al.* (2011). According to McCarthy and Pretorius (2009) a number of programmes are underway to examine the use of acid neutralisation, sulphate-contaminated water for crop irrigation. According to Jovanovic *et al.* (2002) the commercial production of crops under irrigation of gypsiferous mine water is feasible and the resulting environmental impact is limited. Results have been promising; however some studies have determined that sulphate are accumulating in the soil (McCarty & Pretorius, 2009; Coleman *et al.*, 2011). McCarthy and Pretorius (2009) concluded that this method of mitigation is not feasible in the long-term due to sulphate accumulation in the soil which may form hard gypcrete cement that may have severe long-term impacts on agricultural productivity.

Section 9.2.2 of this dissertation indicate that model mine decant water is not suitable for irrigation. However, although some elements are problematic, the suitability of water quality for crop irrigation depends on the specific plant species and cultivars as well as the irrigation management methods.

9.4.2.3   Active and passive treatment options

The western operation discharges are characterised by a low pH and management decisions should be directed towards the treatment of discharges using active processes (lime dosing) while the vestigial acidity is being depleted, followed by long-term passive treatment (constructed wetlands technology) for the juvenile acidity (Gandy & Evans, 2002). Active treatment can be successful, it however necessitates a long-term and continuous commitment to treatment. The most common methods employed for active treatment of mine water are lime neutralisation, ion exchange and carbonate neutralisation. These methods are quite demanding in chemical use, energy input and mechanical parts as well as skilled manpower (Blowes *et al*., 2003).

According to Barton (1978) amphoterism is exhibited by most divalent and trivalent metals which refers to these metals' solubility minimum in the circum-neutral pH range and enhanced solubilities under both acidic and basic conditions. Different metals display solubility minimums at different pH values which provides the basis for the removal of metals during rapid neutralisation of AMD by active treatment in the form of lime or any other carbonate or hydroxide treatment. Barium carbonate [$BaCO_3$] processes for sulphate and metal removal from MIW can be sourced from Hlabela *et al*. (2006), and Castillo *et al.* (2015). During these methods, $BaCO_3$ dispersed alkaline substrates are used in the remediation or at least partial remediation of mine drainage (Van Heerden *et al*., n.d.). Such attempts have been made at the Union Colliery in the form of a small pilot treatment plant.

According to a report to the inter-ministerial committee on AMD (Coetzee *et al*., 2010), neutralisation of mine water and subsequent discharge to the environment may produce conditions similar to the status quo during periods of active mining. However, this approach may not be sustainable in the medium to long-term as it could result in excessive salt loads in the receiving water bodies, which will require the release of clean water for dilution or extra desalination plants. The water quality is not expected to improve in the near future as suggested by the geochemical models. Options of direct consumptive use of neutralised mine water or desalination and sale of the water to local users should be investigated.

McCarthy and Pretorius (2009) referred to contamination in the Brugspruit tributary of the Olifants River caused by acidic discharge from abandoned mines located northwest of Witbank. Mitigation strategies included a system to collect water and divert it to a treatment plant where sodium hydroxide [NaOH] was added to neutralise the acid. The Brugspruit Water Pollution Control Works was commissioned in 1997 at a cost of R26.5 million. The treatment approach solved the acid problem, however, the sulphate problem remained. Furthermore, mining companies located in the Witbank coalfield addressed the problem of acidic drainage by constructing a treatment plant to convert contaminated water to such a quality water suitable for drinking where after the water is then disposed. The Emalahleni Water Reclamation Plant was commissioned in 2007 at a cost of R300 million. This plant generates 20 ML of water per day at a cost of R10 per cubic meter and the design life is approximately 20 years. Compared to this, Vaal River water delivered to the area costs R3 per cubic meter. Water purification plants are the only systems that is capable of producing water of a quality equivalent to that which existed prior to mining. However, the cost of treatment is extremely high. It is expected that acid generation will decline as pyrite oxidation nears completion, however it is unclear how

long this will take. Acid and sulphate production are likely to persist for hundreds of years (McCarthy & Pretorius, 2009). It is clear that active treatment is usually prohibitively expensive at decommissioned mine sites that could continue to discharge acidic and metal(loid) contaminated water for centuries post closure.

Passive treatment refers to the development of a self-operating system that can treat the effluent without constant human intervention. The foundation of passive treatment is to allow nature to purify itself over time. Linked ponds or artificial constructed wetlands allows organic matter, bacteria and algae to filter, adsorb, absorb and precipitate out the ecotoxic metal ions and to further reduce the acidity of the water (Blowes *et al*., 2003). These systems, upon construction, can treat mine decant water for 15 to 25 years with minimal routine maintenance cost. The surface area required for these systems is however significant, demanding well into the hundred-hectare range for effective treatment. As the eastern operations are characterised by circum-neutral discharge, passive treatment using constructed wetland technologies may be an option. Conventional passive treatment technologies are reviewed by RoyChowdhury *et al*. (2015). Grobbelaar *et al.* (2004) however pointed out that the use of wetlands for the treatment of mine water has been a failure under South African conditions. After more than 25 years of research in passive treatment systems, wetlands of any significance in terms of mine water treatment does not exist anywhere in Mpumalanga. Wetlands are described in literature as well-constructed structures that is kept under anaerobic conditions and harvested periodically to remove metal(loid) build-up. However, in the South African context, if not well maintained, wetlands are nothing but toxic waste sites (Grobbelaar *et al.,* 2004). Pitfalls and challenges of passive remediation for MIW treatment were also described by Johnson and Hallberg (2002).

9.4.2.4   Unconventional methods

Alternative unconventional methods, such as in situ bioremediation and inorganic reduction are potential methods to consider as these methods allow contaminants to be treated within the mine voids, thus reducing exposure risks on surface (Van Heerden *et al.,* n.d.). Bioremediation refers to the use of living micro-organisms to degrade environmental contaminants to less toxic forms. Organic or inorganic compounds to cause indigenous organisms to effect remediation of the environment may be added, e.g. biostimulation, or contaminant degrading bacteria may be injected directly into the contaminant zone, e.g. bioaugmentation. Bioremediation techniques are also more economical than traditional methods and since bioremediation is based on natural processes, the public considers it more acceptable than other technologies where high proportion waste is generated. The groundwater flow and transport model (refer to section 3.7) confirms that water within the underground voids moves very slowly within and between compartments and towards discharge points, which is desirable for in situ remediation. However, very few examples exist in South Africa where classic, efficient bioremediation principles have been applied at a site (Van Heerden *et al.,* n.d.).

9.5   CONCLUDING SUMMARY

Although predictive modelling is by nature uncertain, it is an invaluable tool for helping to understand and describe the physical and chemical changes that can occur in environments affected by mining activities. It is highlighted that modelling calculations are well-educated guesses and there will always be inadequate data and contentious ambiguities in the conclusions. Nevertheless, the advantage of modelling is that it can consider some of the complex interaction between hydrology, geochemistry, geology and other site characteristics which is a major step beyond various static and kinetic tests for which comparison, evaluation and agreement is lacking.

Chapter 9 accumulated and gathered the information and results from literature studies, field monitoring data and model results into in-depth discussions and interpretations, with the final objectives addressed.

The forward reaction path models and simulations led to a systematic pathway to calibrated systems with certain parameters yielding results closest to that observed in the monitoring data sets. The simulations allowed for conceptualised summaries and visual representation to the main processes and chemical reactions involved in the hydrogeochemical fluid-rock interactions forming the groundwater and mine decant water as observed in the field monitoring data sets.

The different hydrogeochemical systems were modelled with results for each system measured against various water use guidelines to determine the suitability of the water for different uses to evaluate potential risks to water users and aquatic environments. The main observations during the model simulations include the following:

Coal discard dump weathering models:

- The weathering reactions of the carbonate and mafic minerals within the Ecca geology allows for pH values ranging between ~7.87 and 8.26 with buffering reactions not allowing any acidic environments to develop within the regional groundwater. Thus, although the ABA assessment suggested acidic drainage from the coal discard material, sufficient neutralisation capacity is contributed by the coal discard material and regional geology along the flow path of infiltrated water as it migrates through the discard pores until it percolates to the shallow groundwater table.

- The system is most sensitive to alterations in oxygen fugacity as the availability of oxygen drives pyrite oxidation. The simulated values suggest that oxygen tends to deplete in the natural groundwater system. The reducing environment allows for the mobilisation of especially manganese.

- Field solid samples as well as modelled results indicate saturation of carbonate, clay and hydroxide minerals with the development of secondary minerals most likely to be kaolinite and smectite-type clays.

- Due to the alkaline environment of the groundwater, adsorption of selenium to hydrous ferric oxides (HFO) is negligible and therefore remain mobile.

- Manganese and selenium remain mobile in the groundwater system and selenium, specifically, may reach concentrations above the recommended guidelines for drinking water which may pose major health risks to groundwater users.

Eastern operations' weathering models:

- The weathering reactions of the carbonate minerals within the Ecca geology and coal seams allow for pH values ranging between ~7.17 and 7.62 with buffering reactions not allowing any acidic environments to develop within the mine water discharging at the specific decant points.

- The system is most sensitive to changes in the oxygen fugacity as the availability of oxygen drives pyrite oxidation. The simulated values suggest that oxygen fugacity tends to fluctuate and imitates water level rise within the underground voids.

- Field solid samples as well as modelled results indicate saturation of ferric hydroxide minerals.

- Due to the alkaline environment of the mine water it is inferred that nickel concentrations may be lowered through adsorption; however, selenium and manganese concentrations are less influenced.

- Manganese and especially selenium may reach concentrations within the mine void and decant water that pose risks to the environment and local aquatic ecosystems.

Western operations' weathering models:

- Due to the depletion of carbonate minerals, weathering reactions and oxidation of pyrite allows for pH values ranging between ~3.61 to 3.64. Reactions thus allow acidic environments to develop within the mine water discharging at the specific decant points.

- Field solid samples as well as modelled results indicate saturation of ferric hydroxide minerals.

- Due to the acidic nature of the mine water it is inferred that selenium and arsenic concentrations may be lowered through adsorption. However, manganese, lead, and nickel are less influenced.

- Manganese, aluminium, lead, nickel, and selenium may reach concentrations within the mine void and decant water that pose risks to the environment and local aquatic environments.

Risks and management strategies:

- The main risks identified include contamination of shallow groundwater resources owing to coal discard deposited on coal discard dumps and the flooding of the underground mine voids. Decant of MIW at the surface are associated with ecological impacts and regional impacts on some major river systems.

- The most feasible mitigation and management options for the MIW include unconventional remediation methods such as in situ bioremediation and inorganic reduction. Regarding the western operations, active drainage treatment in the form of lime dosing coupled with unconventional

remediation methods such as in situ bioremediation and inorganic reduction serve as potential management strategies.

The main research conclusions discussed in this chapter will be listed and given in condensed form within Chapter 10.

CHAPTER 10:
CONCLUSIONS AND RECOMMENDATIONS

This document is a written dissertation for research done to evaluate changes in mine waste drainage quality from a geochemical approach with the aim to identify current and anticipated risks to sensitive receptors through geochemical modelling.

Each chapter of this dissertation was a written representation and discussion of various elements within the research framework to evaluate and address the objectives of the study. Each chapter was shortly summarised within the document; however the following integrated summary gives the main conclusions from Chapters 5 to 9 as these chapters addressed the specific key objectives of the study.

Chapter 5: Baseline Hydrogeochemical Conditions

- The determination of baseline hydrogeochemical conditions is vital to determine the current situation and provides understanding of the dominant controls on the water chemistry within the area.

- Baseline conditions for the respective hydrogeochemical areas/components were reflected by the 5th and 95th percentile range. This range reflects typical concentrations for each hydrogeochemical area as it is resilient to outlier values.

- A comparison between observations and hydrogeochemical areas indicate that there is no dominant cation type in most areas. Exceptions included the groundwater regime which is dominated by sodium, and the mining-influenced waters (MIW) of both the eastern and western operations, which is dominated by calcium. In terms of the major anions, bicarbonate is a significant anion along with sulphate in the groundwater, surface water and eastern operations. Sulphate is the dominant anion in the western operations. There is a distinct trend in all areas, except for groundwater in the unmined land, to be or to become sulphate dominated which is expected in the mining-influenced area.

- The pH reflects a bimodal distribution. The western operations decant water are characterised by acidic pH, whereas the other hydrogeochemical areas indicate circum-neutral to alkaline conditions. Relatively few samples display pH values between 4.0 and 6.0 since the pH will be driven towards one mode or the other depending on the relative abundance and extent of pyrite weathering and carbonate mineral neutralisation.

- The groundwater hydrogeochemical areas displayed elevated concentration fluxes in the dry as well as in the wetter months. Acidity, as well as sulphate and metal concentrations tend to increase in the dry season with lower values and concentrations observed in the wetter months from October to March. The latter may be ascribed to increased percolation of infiltrated water to the groundwater table during prolonged precipitation events and therefore increased mixing and dilution may occur along the flow paths. The higher concentrations observed in the wetter months may be indicative of the flushing out of built up oxidation products within the coal discard dumps after the first rain. Hereafter

concentrations decrease due to mixing and dilution processes driven by further precipitation events and the circulation of shallow groundwater.

- The underground operations display increased concentration fluxes of especially sulphate, iron and manganese predominantly in the wetter months. This may indicate the flushing out of accumulated oxidation products within the mine voids due to increased infiltrated rainwater as well as shallow groundwater. When dry conditions are re-established, contaminant loads are generally lower in comparison to the wetter seasons due to reduced flow within the mine voids. This trend is mimicked in the downstream sampling stations within the Vaalwaterspruit and Boesmanspruit tributaries.

Chapter 6: Geochemical Assessment Results and Discussion

Although it is not recommended to make conclusions based solely on static test data without cognisance of the hydrogeochemical conceptual model and encountered environmental conditions, conclusions presented were based on the results presented and discussed in the chapter.

- The mine waste comprised varying proportions of primary minerals, quartz, K-feldspar, albite, muscovite, enstatite, pargasite/tremolite, pyrite and calcite, and secondary minerals including, gypsum, hematite and goethite. The main clay minerals included kaolinite and smectite-type clays.

- The mine waste consisted of varying proportions of two major oxides, SiO_2 and Al_2O_3. In addition, Fe_2O_3, TiO_2, MgO, CaO, MnO, K_2O, P_2O_5, and Na_2O were present in minor concentrations. MnO, P_2O_5 and Na_2O were barely present in the Susanna coal sample material. Numerous trace elements were also detected in the waste material and when compared to the water quality data, nickel, cobalt, and lead are potential contaminants.

- According to the ABA results, all samples had initial pH levels at or above 6.43. This suggests that the material does not contain readily available acidity, but alkalinity that may be readily released over time.

- Material from the coal discard dumps acidified under oxidising conditions. The Susanna coal sample was an exception. This implies that the coal discard material has excess AP over NP. However, in a laboratory scenario the milling and crushing of rock samples to a fine powder increases surface area and thus increases reaction tempos.

- The NNP values together with the NPR values, suggested that the coal discard material have a high likelihood to produce acid. This was supported by the relatively high sulphide-sulphur concentrations in the samples which implies long-term acid generation.

- The Susanna coal sample material can, according to the NNP and NPR ratios, be regarded as highly likely to maintain neutral conditions, although the sulphide-sulphur concentration of this sample suggests potential long-term acidification.

Chapter 7: Conceptual Models

- The development of site conceptual models is a vital step in predicting water quality at mine sites. In order to create a well-defined and representative conceptual model, the collection and interpretation of hydrogeologic and geochemical data from the mine is a necessity.

- The discussions presented in this chapter were highly simplified descriptions of the basic chemistry of sulphide oxidation, AMD generation and associated neutralisation, secondary mineral formation and adsorption processes. The chemistry and reactions of processes that take place in true mine water systems are extremely complex.

- Rainfall and evaporation serve as the drivers of water availability within the coal discard dumps. Rainwater infiltration and percolation to the underground voids influence the water levels within the workings. Subsidence areas along the perimeter of the mined compartments may be associated with higher infiltration rates. Water serves a necessity for geochemical reactions and is a crucial transport mechanism of dissolved components.

- Shallow groundwater infiltration to the underground mine voids further influence the water levels and allow mixing of infiltrated groundwater with built up oxidation products. The increased water flux leads to mine decant at adits and sinkholes.

- Adits (most of which have been sealed and fitted with drainage pipes), subsidence areas as well as boreholes intersecting the mine voids provide pathways for oxygen diffusion. The coal discard dumps system as well as the underground voids are therefore assumed to represent open systems as the mine wastes are in contact with a gas phase.

- Mining has created a new water table within the mine voids with new flow vectors, allowing oxygen and water to mix with pyrite resulting in drainage characterised by either circum-neutral or acidic pH, and elevated sulphate and metal(loid)s which then discharge at the surface.

- Reactions assumed dominant within the coal discard dumps and along flow paths within the eastern operations include pyrite oxidation, carbonate neutralisation, secondary mineral precipitation and adsorption. The reactions assumed to be dominant along flow paths within the western underground operations include pyrite oxidation, hydroxide dissolution and neutralisation, secondary mineral precipitation and dissolution, and adsorption.

- Ultimately, the rate of oxidation and acid generation varies depending on the accessibility of air, moisture, and microbes to the pyrite surfaces and the neutralisation capacity of available buffering materials.

- The mine discharges contaminated water into two important river catchments and is expected to continue discharging water into these rivers in perpetuity. Apart from seeps, seven significant discharge points in well-defined flow channels affects two primary river systems, namely the Vaalwaterspruit and the Boesmanspruit. Apart from the aquifer systems affected through leaching

from the coal discard dumps and subsurface seepage from the underground operations, three tributaries of the Vaalwaterspruit and one Boesmanspruit tributary were identified as sensitive receptors.

- Conceptual models are not unique and can change over time. It is therefore necessary to revisit conceptual models and modify predictive models based on new site-specific information. However, for the purposes of this study and due to time constraints, water quality monitoring data only up to June 2017 were considered in the conceptual models and subsequent selection of input water chemistries for the geochemical models.

Chapter 8: Numeric Geochemical Models

- The purpose of the geochemical modelling exercises was mainly to reduce uncertainty through constant sensitivity analyses, and to facilitate understanding of the interaction of geochemical processes with a focus on metal(loid) mobility to a level at which potential liability can be quantified.

- Weathering models were respectively simulated for the coal discard dump system and the eastern -and western underground operations. Sensitivity analyses focused on the pyrite reaction rate, and oxygen fugcity leading to the evaluation of calibrated systems. This allowed for interpretation and investigation of processes involved in the evolution of the groundwater and mine decant water as observed in the monitoring data set.

- Risks associated with the contamination of soil, surface water and groundwater resources by metal(loid)s from all geological mine waste, i.e. coal discard dumps and underground extraction areas, are significant.

- The final calibrated coal discard dump model indicated a Ca-SO$_4$ water type with a pH between 7.87 and 8.26 and a TDS between 532 and 668 mg/L, agreeing with monitoring data.

- The contamination of shallow groundwater by sulphate, manganese and selenium from the coal discard material in the post operational phase are significant and further mitigation measures should be considered as this can pose a problem for future groundwater users.

- The final calibrated eastern operation model indicated a Ca-SO$_4$ water type with a pH between 7.17 and 7.62 and a TDS of 1 340 to 1 493 mg/L, correlating well with monitoring data.

- Contamination of groundwater and surface water by sulphate, iron, manganese and selenium, which remain mobile within the decant water emanating from the eastern operations, is significant and mitigation measures should be implemented as the receiving streams are considered as sensitive receptors.

- The final calibrated western operation model indicated a Ca-SO$_4$ water type with a pH value between 3.61 and 3.64 and a TDS of 1 361 to 1 423 mg/L, agreeing with monitoring data.

- Contamination of groundwater and surface water by sulphate, iron, manganese, aluminium, lead, nickel, and selenium, which remain mobile within the western operation decant water, is significant and mitigation measures should be investigated.

Chapter 9: Hydrogeochemical Assessment and Model Discussion

- Although predictive modelling is by nature uncertain, it is an invaluable tool for helping to understand and describe the physical and chemical changes that can occur in environments affected by mining activities.

- Chapter 9 accumulated and gathered the information and results from literature studies, field monitoring data and model results into an in-depth discussion and interpretation, with the final objectives addressed.

- The forward reaction path models and simulations led to a systematic pathway to calibrated systems with certain parameters yielding results closest to that observed in the monitoring data sets. The simulations allowed for conceptualised summaries and visual representation to the main processes and chemical reactions involved in the hydrogeochemical fluid-rock interactions forming the groundwater and mine decant water as observed in the field monitoring data sets.

- The different hydrogeochemical systems were modelled with results for each system measured against various water use guidelines to determine the suitability of the water for different uses and to highlight potential risks. The main observations during the model simulations included the following:

Coal discard dump weathering models:

- The weathering reactions of the carbonate and mafic minerals within the Ecca geology allows for pH values ranging between ~7.87 and 8.26 with buffering reactions not allowing any acidic environments to develop within the regional groundwater. Thus, although the ABA assessment suggested acidic drainage from the coal discard material, sufficient neutralisation capacity is contributed by the coal discard material and regional geology along the flow path of infiltrated water as it migrates through the discard pores until it percolates to the shallow groundwater table.

- The system is most sensitive to alterations in oxygen fugacity as the availability of oxygen drives pyrite oxidation. The simulated values suggest that oxygen tends to deplete in the natural groundwater system. The more reducing environment allows for the mobilisation of especially manganese.

- Field solid samples as well as modelled results indicated saturation of carbonate, clay and hydroxide minerals with the development of secondary minerals most likely to be kaolinite and smectite-type clays.

- Due to the alkaline environment of the groundwater, adsorption of selenium to hydrous ferric oxides is negligible and therefore remain mobile.

- Manganese and selenium remain mobile in the groundwater system and selenium, specifically, may reach concentrations above the recommended guidelines for drinking water which may pose adverse health risks to groundwater users.

Eastern operations' weathering models:

- The weathering reactions of the carbonate minerals within the Ecca geology and coal seams allow for pH values ranging between ~7.17 and 7.62 with buffering reactions not allowing any acidic environments to develop within the mine water discharging at the specific decant points.

- The system is most sensitive to changes in the oxygen fugacity as the availability of oxygen drives pyrite oxidation. The simulated values suggest that oxygen fugacity tends to fluctuate and imitates water level rise within the underground voids.

- Field solid samples as well as modelled results indicated saturation of ferric hydroxide minerals.

- Due to the alkaline environment of the mine water it is inferred that nickel concentrations may be lowered through adsorption; however, selenium and manganese concentrations are less influenced.

- Manganese and especially selenium may reach concentrations within the mine void and decant water that may induce toxic effects in aquatic organisms. High levels of metals in the environment could be a hazard for function of natural ecosystems and human health, due to their toxic effects, long persistence, bioaccumulative properties, and biomagnificaton in the food chain.

Western operations' weathering models:

- Due to the depletion of carbonate minerals, weathering reactions and oxidation of pyrite allows for pH values ranging between ~3.61 to 3.64. Reactions thus allow acidic environments to develop within the mine water discharging at the specific decant points.

- Field solid samples as well as modelled results indicate saturation of ferric hydroxide minerals.

- Due to the acidic nature of the mine water it is inferred that selenium and arsenic concentrations may be lowered through adsorption. However, manganese, lead, and nickel are less influenced.

- Manganese, aluminium, lead, nickel, and selenium may reach concentrations within the mine void and decant water that pose high level risks to the environment and local aquatic environments.

Risks and management strategies:

- The main risks identified included contamination of shallow groundwater resources owing to coal discard deposited on coal discard dumps and the flooding of the underground mine voids. Decant of MIW at the surface are associated with ecological impacts and regional impacts on some major river systems.

- The most feasible mitigation and management options for the MIW include unconventional remediation methods such as in situ bioremediation and inorganic reduction. Regarding the western operations, active drainage treatment in the form of lime dosing coupled with unconventional remediation methods including in situ bioremediation and inorganic reduction serve as potential management strategies.

Recommendations:

Although enlightening results have been achieved with the specific research framework, further refinement are needed, and the following future improvements and research are recommended for the respective mine:

- Extensive solid waste sampling of floor and roof lithologies for the respective eastern and western compartments to better characterise the waste material and obtain possible mineralogical property differences (especially between the eastern and western operations) in order to better define the modelled systems.

- Collect and evaluate seepage water from the coal discard dumps to contextualise the ABA and NAG results. As conventional active and passive treatment methods may not be feasible over the long-term, the evaluation of the effectiveness of in situ bioremediation and its effect on the discharging mine water may provide a better option for mitigation.

It is further recommended that the process of mine drainage chemistry prediction and assessment, risk appraisal and the recommendation of remedial measures be revisited and continued with ongoing assessments. Predictions made for the mine drainage chemistry should be constantly checked and updated as new monitoring data is made available. Mitigation needs will also become more clearly defined as prediction testing proceeds.

As a final remark, Price (2009) should be kept in mind:

"Our understanding of the properties and processes determining drainage chemistry is far from complete. However, the available prediction tools combined with a comprehensive, well-informed approach and cautious interpretation of the results should allow mines with sulphidic geologic materials to meet receiving environment objectives and minimise the liability and risk."

REFERENCE LIST

Ahanger, F.A., Sharma, H.K., Rather, M.A. & Rao, R.J. 2014. Impact of mining activities on various environmental attributes with specific reference to health impacts in Shatabdipuram, Gwalior, India. *International Research Journal of Environment Sciences*, 3(6)81-87.

Allwright, A.J. 2018. Union Colliery geohydrology investigation: Modelling. Report to South 32, Report No. 02/2017/AA. Institute for Groundwater Studies, University of the Free State, Bloemfontein, South Africa. (Unpublished Report).

Alpers, C.N. & Nordstrom, D.K. 1999. Geochemical modelling of water-rock interactions in mining environments. In: Plumlee, G.S. & Logsdon, M.J. (eds.), *The Environmental Geochemistry of Mineral Deposits.* Reviews in Economic Geology, Vol. 6A. Society of Economic Geologists, Chelsea, USA. Pages 289-323.

Ammann, A.A., Michalke, B. & Schramel, P. 2002. Speciation of heavy metals in environmental water by ion chromatography coupled to ICP-MS. *Analytical and Bioanalytical Chemistry*, 372(3)448-452.

Annandale, J.G., Beletse, Y.G., De Jager, P.C., Jovanovic, N.Z., Steyn, J.M., Benade, N., Lorentz, S.A., Hodgson, F.D.I., Usher, B. & Vermeulen, D. 2007. Predicting the environmental impact and sustainability of irrigation with coal mine water. Report to the Water Research Commission, Report No. 1149/01/07. Water Research Commission, Pretoria, South Africa.

Annandale, J.G., Jovanovic, N.Z. & Claassens, A.S. 2002. The influence of irrigation with gypsiferous mine water on soil properties and drainage water. Report to the Water Research Commission, Report No. 858/1/02, ISBN No: 1-86845-952-7. Water Research Commission, Pretoria, South Africa.

Anon. 2011. Special report on acid mine drainage. Available at: http://mg.co.za/specialreport/acid-mine-drainage.

Aphane, V. & Vermeulen, P.D. 2011. Acid mine drainage and its potential impact on the water resources in the Waterberg coalfield. Available at: http://gwd.org.za/sites/gwd.org.za/files/05_V%20Aphane_Acid%20Mine%20drainage%20and%20its%20potential%20impact.pdf.

Appelo, C.A.J. & Postma, D. 1993. *Geochemistry, Groundwater and Pollution*. A.A. Balkema Publishers, Rotterdam. 536 pages.

Appelo, C.A.J. & Postma, D. 2005. *Geochemistry, Groundwater and Pollution*, 2nd Ed. A.A. Balkema Publishers, Leiden.

Auditor-General South Africa (ed.). 2009. Performance audit of the rehabilitation of abandoned mines at the Department of Minerals and Energy. Report of the Auditor-General to Parliament. Pretoria, South Africa.

Azzie, B.A.M. 2002. Coal mine water in South Africa: Their geochemistry, quality and classification. University of Cape Town, Cape Town, South Africa. (DPhil Thesis).

Backstrom, M. & Sartz, L. 2016. Use of multivariate statistics in order to understand the flow of acid rock drainage from an abandoned mining site. *Journal of Environmental Protection*, 7, 358-371.

Bailey, R.T., Cody, B.M. & Gates, T.K. 2009. Mobilization and reactive transport of selenium in a stream-aquifer system: From field monitoring toward remediation modelling. In: Proceedings of Hydrology Days. March 25-27, Colorado State University. Pages 1-13.

Baker, B.J. & Banfield, J.F. 2003. Microbial communities in acid mine drainage. *FEMS Microbiology Ecology,* 44, 139-152.

Banister, S., Van Biljon, M. & Pulles, W. 2002. Development of appropriate procedures for water management when planning underground mine closure - a regional approach using gold mining as a case study in. In: Proceedings of the WISA Mine Water Division - Mine Closure Conference. October 23-24, Randfontein, South Africa. Pages 23-24.

Banks, D. 1994. The abandonment of the Killingdal Sulphide Mine, Norway: A saga of acid mine drainage and radioactive waste disposal. *Mine Water and the Environment*, 13, 35-48.

Banks, D., Burke, S.P. & Gray, C.G. 1997a. Hydrogeochemistry of coal mine drainage and other ferruginous waters in north Derbyshire and south Yorkshire, UK. *Quarterly Journal of Engineering Geology and Hydrogeology*, 30, 257-280.

Banks, D., Parnachev, V.P., Frengstad, B., Holden, W., Vedernikov, A.A. & Karnachuk, O.V. 2002. Alkaline mine drainage from metal sulphide and coal mines: Examples from Svalbard and Siberia. In: Younger, P.L. & Robins, N.S. (eds.), *Mine Water Hydrogeology and Geochemistry*. Special Publications No. 198. Geological Society, London. Pages 187-296.

Banks, D., Younger, P.L., Arnesen, R-T., Iversen, E.R. & Banks, S.D. 1997b. Mine-water chemistry: the good, the bad and the ugly. *Environmental Geology*, 32(1)157-174.

Banwart, S., Evans, K. & Croxford, S. 2002. Predicting mineral weathering rates at field scale for mine water risk assessment. In: Younger, P.L. & Robins, N.S. (eds.), *Mine Water Hydrogeology and Geochemistry*. Special Publications No. 198. Geological Society, London. Pages 137-157.

Barton, P. 1978. The acid mine drainage. In: Nriagu, I.O. (ed.), *Sulphur in the Environment, Part II, Ecological Impacts*. John Wiley & Sons, New York. Pages 313-358.

Bar-Yosef, B. & Meek, D. 1987. Selenium sorption by kaolinite and montmorillonite. *Soil Science*, 144, 11-19.

Bell, F.G. & Bullock, S.E.T. 1996. The problem of acid mine drainage, with an illustrative case history. *Environmental Engineering Geoscience,* 2, 369-392.

Bell, F.G., Bullock, S.E.T., Hiilbich, T.F.J. & Lindsay, P. 2001. Environmental impacts associated with an abandoned mine in the Witbank coalfield, South Africa. *International Journal of Coal Geology,* 45(2-3)195-216.

Benjamin, M.M. 1983. Adsorption and surface precipitation of metals of amorphous iron oxyhydroxide. *Environmental Science and Technology*, 17, 686-692.

Bennett, K. 2016. Abandoned mines - environmental, social and economic challenges. In: Fourie, A.B. & Tibbett, M. (eds.), Proceedings of the 11th International Conference on Mine Closure. Perth. Pages 241-252.

Benoit, G. 1995. Evidence of the particle concentration-effect for lead and other etals in fresh-waters based on ultraclean techniques analyses. *Geochimica et Cosmochimica Acta*, 59(13)2677-2687.

Bester, M. & Vermeulen, P.D. 2010. Investigation of potential water quality and quantity impacts associated with mining of the shallow Waterberg coal reserves, west of the Daarby Fault, Limpopo Province, South Africa. *Water SA*, 36(5)531-542.

Bethke, C.M. & Yeakel, S. 2016a. The Geochemist's Workbench Essentials Guide Release 11.0. Department of Geology, University of Illinois.

Bethke, C.M. & Yeakel, S. 2016b. The Geochemist's Workbench Reaction Modeling Guide Release 11.0. Department of Geology, University of Illinois.

Bethke, C.M. & Yeakel, S. 2016c. The Geochemist's Workbench Reactive Transport Modeling Guide Release 11.0. Department of Geology, University of Illinois.

Bethke, C.M. 1996. *Geochemical Reaction Modelling - Concepts and Applications*. Oxford University Press, Oxford, United Kingdom.

Bethke, C.M. 2008. *Geochemical and Biogeochemical Reaction Modelling*, 2nd Ed. Cambridge University Press, Cambridge.

Bigham, I.M. 1994. Mineralogy of ochre deposits formed by sulphide oxidation. In: Jambor, J.L. & Blowes, D.W. (eds.), *The Environmental Geochemistry of Sulfide Mine-Wastes*. Short Course Handbook, Vol. 22. Mineralogical Association of Canada, Nepean, Ontario. Pages·103-132.

Bigham, J.M. & Nordstrom, D.K. 2000. Iron and aluminium hydroxysulphates from acid sulphate waters. In: Alpers, C.N., Jambor, J.L. & Nordstrom, D.K. (eds.), *Sulphate Minerals: Crystallography, Geochemistry and Environmental Significance*. Reviews in Mineralogy and Geochemistry, Vol. 40. Mineralogical Society of America and Geochemical Society, Washington D.C. Pages 351-403.

Blowes, D.W. & Jambor, J.L. 1990. The pore-water geochemistry and the mineralogy of the vadose zone of sulfide tailings, Waite Amulet, Quebec, Canada. *Applied Geochemistry,* 5, 327-346.

Blowes, D.W. & Ptacek, C.J. 1994. Acid-neutralization mechanisms in inactive mine tailings. In: Jambor, J.L. & Blowes, D.W. (eds.), *The Environmental Geochemistry of Sulfide Mine-Wastes*. Short Course Handbook, Vol. 22. Mineralogical Association of Canada, Nepean, Ontario. Pages 271-292.

Blowes, D.W. 1990. The geochemistry, hydrogeology and mineralogy of decommissioned sulfide tailings: A comparative study. University of Waterloo, Waterloo, Canada. (DPhil Thesis).

Blowes, D.W., Ptacek, C.J., Frind, E.O., Johnson, R.H., Robertson, W.D. & Molson, J.W. 1994. Acid neutralization reactions in inactive mine tailings impoundments and their effect on the transport of dissolved metals. In: Proceedings of the International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, Vol. 1: Mine drainage. Pages 429-438. DOI: 10.21000/JASMR94010429.

Blowes, D.W., Ptacek, C.J., Jambor, J.L. & Weisener, C.G. 2003. The geochemistry of acid mine drainage. In: Holland, H.D. & Turekian, K.K. (eds.), *Treatise on Geochemistry*, Vol. 9. Elsevier, Oxford. Pages 149-204. Available at: http://dx.doi.org/10.1016/B0- 08-043751-6/09137-4.

Blowes, D.W., Ptacek, C.J., Jambor, J.L., Weisener, C.G., Paktunc, D., Gould, W.D. & Johnson, D.B. 2014. The geochemistry of acid mine drainage. In: Holland, H.D. & Turekian, K.K. (eds.), *Treatise on Geochemistry*, 2nd Ed., Vol. 11. Elsevier, Oxford. Pages 131-190. Available at: https://doi.org/10.1016/B978-0-08- 095975-7.00905-0.

Blowes, D.W., Smith, L., Sego, D., Smith, L., Neuner, M., Gupton, M., Moncur, M., Moore, M., Klassen, R., Deans, T., Ptacek, C., Garvie, A. & Reinson, J. 2007. Prediction of effluent water quality from waste rock piles in a continuous permafrost region. In: Cidu, R. & Frau, F. (eds.), IMWA Symposium 2007: Water in Mining Environments. May 27-31, Cagliari, Italy. Pages 3-9. Available at: https://www.imwa.info/docs/ imwa_2007/IMWA2007_Blowes.

Bowell, R.J. 2002. The hydrogeochemical dynamics of mine pit lakes. In: Younger, P.L. & Robins, N.S. (eds.), *Mine Water Hydrogeology and Geochemistry*. Special Publications No. 198. Geological Society, London. Pages 159-185.

Brady, K.B. & Hornberger, R.H. 1990. The prediction of mine drainage quality in Pennsylvania. In: *Mine Drainage and Surface Mine Reclamation*, Vol. 1. USBM IC 9183. Pages 33-43.

Brady, K.B.C., Perry, E.F., Beam, R.L., Bisko, D.C., Gardner, M.D. & Tarantino, J.M. 1994. Evaluation of acid-base accounting to predict the quality of drainage at surface coal mines in Pennsylvania, USA. In: Proceedings of the International Land Reclamation and Mine Drainage Conference. April 24-29, Pittsburgh.

Brady, K.B.C., Rose, A.W., Cravotta, C.A. & Hellier, W.W. 1997. Bimodal distribution of pH in coal-mine drainage (abs.). Geological Society of America, GSA Abstracts with Programs, 29(1)32.

Brady, K.B.C., Rose, A.W., Hawkins, J.W. & DiMatteo, M.R. 1996. Shallow ground water flow in unmined regions of the northern Appalachian Plateau - Part 2: Geochemical characteristics. In: Proceedings of the 13th Annual Meeting American Society for Surface Mining and Reclamation. American Society for Surface Mining and Reclamation. May 18-23, Princeton. Pages 52-62.

Brady, K.B.C., Smith, M.W. & Schueck, J. (eds.). 1998. *Coal mine drainage prediction and pollution prevention in Pennsylvania*. The Pennsylvania Department of Environmental Protection, Harrisburg, Pennsylvania.

Bredehoeft, J. 2005. The conceptualization model problem - surprise. *Hydrogeology Journal*, 13, 37-46.

Bricker, O.P. 1965. Some stability relations in the system $Mn-O_2-H_2O$ at 25°C and one atmosphere total pressure. *American Mineralogist*, 50, 1296-1354.

Brookins, D.G. 1988. *Eh-pH Diagrams for Geochemistry*. Springer, Berlin-Heidelberg.

Brough, C.P., Warrender, R., Bowell, R.J., Barnes, A. & Parbhakar-Fox, A. 2013. The process mineralogy of mine wastes. *Minerals Engineering*, 52, 125-135.

Broughton, L.M. & Robertson, A.M. 1992. Acid rock drainage from mines - where we are now. In: Proceedings of the IMM Minerals, Metals and Environment Conference. February 4-6, Manchester, United Kingdom.

Broughton, L.M., Chambers, R.W. & Roberston, A.M. 1992. Mine rock guidelines: Design and control of drainage water quality. Report No. 93301. (Unpublished Report)

Bullock, S.E.T. & Bell, F.G. 1997. Some problems associated with past mining at a mine in the Witbank coalfield, South Africa. *Environmental Geology,* 33(1)61-71.

Bullock, S.E.T., Bell, F.G. & Marsh, C.A. 1997. The environmental impacts associated with a coal mine in the Witbank coalfield, Republic of South Africa. In: Marinos, P.G., Koukis, G.C., Tsiambaos, G.C. & Stournaras, G.C. (eds.), *Engineering Geology and the Environment*. Proceedings of the International Symposium on Engineering Geology and the Environment. June 23-27, Athens, Greece. A.A. Balkema, Rotterdam. Pages 2327-2333.

Bureau for Food and Agricultural Policy (BFAP). 2012. Evaluating the impact of coal mining on agriculture in the Delmas, Ogies and Leandra districts - with a specific focus on maize production. A report by BFAP, compiled for the Maize Trust.

Camden-Smith, B., Johnson, R.H., Camden-Smith, P. & Tutu, H. 2015. Geochemical modelling of water quality and solutes transport from mining environments. In: Lee, T.S. (ed.), *Research and Practices in Water Quality*. INTECH. Pages 39-63. DOI: 10.5772/59234.

Campaner, V.P., Luiz-Silva, W. & Machado, W. 2014. Geochemistry of acid mine drainage from a coal mining area and processes controlling metal attenuation in stream waters, southern Brazil. *Annals of the Brazilian Academy of Science*, 82(2)539-554.

Carreras, H.A., Wannaz, E.D. & Pignata, M.L. 2009. Assessment of human health risk related to metals by the use of biomonitors in the province of Cordoba, Argentina. *Environmental Pollution*, 157(1)117-122. DOI: 10.1016/j.envpol.2008.07.018.

Castillo, J., Gomez-Arias, A., Posthumus, J., Welman-Purchase, M. & Van Heerden, E. 2015. Geochemical study of the interaction of acid and alkaline mine drainage with $BaCO_3$. In: Proceedings of the 10th International Conference on Acid Rock Drainage & IMWA Annual Conference. April 21-24, Santiago, Chile.

Chon, H-T., Kim, J-Y. & Choi, S-Y. 1999. Hydrogeochemical characteristics of acid mine drainage around the abandoned Youngdong coal mine. *Resource Geology*, 49(2)113-120.

Cidu, R., Biddau, R. & Fanfani, L. 2009. Impact of past mining activity on the quality of groundwater in SW Sardinia (Italy). *Journal of Geochemical Exploration*, 100, 125-132.

Coetzee, H. n.d. Mining legacies and sustainability: Reflections on quarter of a century spent looking at abandoned mines in South Africa. Council for Geoscience, Pretoria, South Africa.

Coetzee, H., Hobbs, P.J., Burgess, J.E., Thomas, A., Keet, M., Yibas, B., Van Tonder, D., Netili, F., Rust, U., Wade, P. & Maree, J. 2010. Mine water management in the Witwatersrand gold fields with special emphasis on acid mine drainage. Report to the inter-ministerial committee on acid mine drainage.

Coetzee, H., Horstmann, U., Ntsume, G. & Croukamp, L. 2003. The potential environmental impact of the decant of water from Witwatersrand. In: Proceedings of the Eighth International Congress on Mine Water and the Environment. Johannesburg, South Africa.

Coleman, T.J., Usher, B., Vermeulen, D., Scholtz, N. & Lorentz, S. 2011. Prediction of how different management options will affect drainage water quality and quantity in the Mpumalanga coal mines up to 2080. Report to the Water Research Commission, Report No. 1628/1/11. Water Research Commission, Pretoria, South Africa.

Cravotta, C.A. 2007. Passive aerobic treatment of net-alkaline, iron-laden drainage from a flooded underground anthracite mine, Pennsylvania, USA. *Mine Water and the Environment*, 26(3)128-149. DOI: 10.1007/s10230-007-0002-8.

Cravotta, C.A. 2008. Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. *Applied Geochemistry*, 23(2)203-226.

Cravotta, C.A., Brady, K.B.C., Gustafson-Minnich, L.C. & DiMatteo, M.R. 1994. Geochemical and geohydrological characteristics of bedrock and mine spoil from two methods of mining at a reclaimed surface coal mine in Clarion County, Pennsylvania, USA. U.S. Bureau of Mines Special Publication SP-06B. Pages 242-249.

Cravotta, C.A., Brady, K.B.C., Rose, A.W. & Douds, J.B. 1999. Frequency distribution of the pH of coal mine drainage in Pennsylvania. In: Morganwalp, D.W., & Buxton, H. (eds.), *Contamination from Hardrock Mining,* Vol. 1. Water-Resources Investigations Report 99-4018A, USGS.

Crawford, J. 1999. Geochemical modelling - A review of current capabilities and future directions. SNV Report 262. Swedish Environmental Protection Agency, Stockholm, Sweden.

Cruywagen, L-M. 2017. Personal communication. Institute for Groundwater Studies, University of the Free State, Bloemfontein, South Africa.

Darnley, A.G., Bjo¨rklund, A., Bblviken, B., Gustavsson, N., Koval, P.V., Plant, J.A. & Xuejing, X. with contributions by Garrett, R.G. & Hall, G.E.M. 1995. A global geochemical database for environmental and resource management. Earth Science Series, Vol. 19. Paris, France.

Davies, T. 2014. *Mpumalanga crisis: why is nobody listening?* Opinion: A desperate battle is raging across vast tracts of Mpumalanga between coal mining on the one hand and water preservation, food security and tourism on the other. Centre of Environmental rights. Available at: https://www.groundup.org.za/media/features/mpumalanga/mpumalanga_0002.html.

Davis, G.B. & Ritchie, A.I.M. 1986. A model of oxidation in pyritic mine wastes. Equations and approximate solution. *Applied Mathematical Modelling,* 10, 314-322.

Davis, J.A. & Kent, D.B. 1990. Surface complexation modeling in aqueous geochemistry. In: Hochella, M.F. & White, A.F. (eds.), *Mineral-Water Interface Geochemistry*. Reviews in Mineralogy, Vol. 23. Mineralogical Society of America, Washington D.C. Pages 177-260.

Declercq, J., Charles, J., Bowell, R., Warrender, R. & Barnes, A. 2017. Comparison of thermodynamic equilibrium and kinetic approach in the predictive evaluation of waste rock seepage quality in Northern Finland. In: Wolkersdorfer, C., Sartz, L., Sillanpää, M. & Häkkinen, A. (eds.), Proceedings of International Mine Water Association, Mine Water and Circular Economy. Lappeenranta, Finland. Pages 664-671.

DeNicola, D.M. & Stapleton, M.G. 2002. Impact of acid mine drainage on benthic communities in streams: the relative roles of substratum vs. aqueous effects. *Environmental Pollution*, 119, 303-315.

Department of Environmental Affairs and Tourism (DEAT). 2006. South African Environmental Outlook: A report on the state of environment. Department of Environmental Affairs and Tourism, Pretoria, South Africa.

Venter, A. 2000. Quality of domestic water supplies, Vol. 2: Sampling guide. Department of Water Affairs and Forestry (DWAF).

Department of Water Affairs and Forestry (DWAF). 1996a. South African Water Quality Guidelines. Volume 4: Agricultural Use: Irrigation 2nd Edition. Holmes, S. (ed.). Department of Water Affairs and Forestry.

Department of Water Affairs and Forestry (DWAF). 1996b. South African Water Quality Guidelines: Volume 5: Agricultural Use: Livestock Watering 2nd Edition. Holmes, S. (ed.). Department of Water Affairs and Forestry.

Department of Water Affairs and Forestry (DWAF). 1996c. South African Water Quality Guidelines. Volume 7: Aquatic Ecosystems 2nd Edition. Holmes, S. (ed.). Department of Water Affairs and Forestry.

Department of Water Affairs and Forestry (DWAF). 2007. Best Practice Guideline H4: Water Treatment. Department of Water Affairs and Forestry, Pretoria, South Africa.

Dhillon, K.S. & Dhillon, S.K. 1999. Adsorption - desorption reactions of selenium in some soils of India. *Geoderma*, 93, 19-31.

Dills, G. & Rogers Jr., D.T. 1974. Macroinvertebrate community structure as an indicator of acid mine pollution. *Environmental Pollution*, 6, 239-262.

Dold, B. 2010. Basic concepts in environmental geochemistry of sulfidic mine-waste management. In: Kumar, S.E. (ed.), *Waste Management*. INTECH. Pages 173-198. Available at:

https://www.intechopen.com/books/wastemanagement/basic-concepts-in-environmental-geochemistry- of-sulfidic-mine-waste-management.

Donovan, J.J., Fletcher, J., Strager, M. & Werner, E. 1999. Hydrogeological and geochemical response to mine flooding in the Pittsburgh coal basin, Southern Monongahela River Basin. National Mined Land Reclamation Centre Project WV-132, West Virginia University. Final report to US Environmental Protection Agency.

Drever, J.I. 1997. *The Geochemistry of Natural Waters, Surface and Groundwater Environments*. Prentice Hall, New York.

Duker, A.A., Carranza, E.J.M. & Hale, M. 2005. Arsenic geochemistry and health. *Environment International,* 31, 631-641.

Durand, J. 2012. The impact of gold mining on the Witwatersrand on the rivers and karst system of Gauteng and North West Province, South Africa. *Journal of African Earth Sciences*, 68, 24-43.

Durkin, T.V. & Herrmann, J.G. 1996. Introduction: Focusing on the problem of mining wastes. EPA Seminar Publication 625/R-95/007 on Managing Environmental Problems at Inactive and Abandoned Metals Mine Sites.

Durkin, T.V. 1995. Acid mine drainage: Reclamation at the Richmond Hill and Gilt Edge mines, South Dakota. EPA Seminar Publication 625/R-95/007 on Managing Environmental Problems at Inactive and Abandoned Metals Mine Sites.

Einstein, A. & Infeld, L. 1938. *The Evolution of Physics*. Simon & Schuster, NewYork.

ERMITE-Consortium. 2004. Younger, P.L. & Wolkersdorfer, C. (eds.). Mining impacts on the fresh water environment: Technical and managerial guidelines for catchment scale management. *Mine Water and the Environment,* 23, 2-80. DOI: 10.1007/s10230-004-0028-0.

Evangelou, V.P. & Zhang, Y.L. 1995. A review: Pyrite oxidation mechanisms and acid mine drainage prevention. *Environmental Science and Technology,* 25(2)141-199.

Evangelou, V.P. 1995. *Pyrite Oxidation and Its Control*. CRC Press, Boca Raton.

Evangelou, V.P. 1998. Pyrite chemistry: The key for abatement of acid mine drainage. In: Geller, W. (ed.), *Acidic Mining Lakes*. Springer Verlag, Berlin, Heidelberg.

Fadlelmawla, A.A., Reddy, K.J. & Vance, G.F. 1994. Geochemical processes affecting the mobility of dissolved selenium in surface coal mine backfill environments. In: Proceedings of the Effects of Human-Induced Changes on Hydrologic Systems. American Water Resources Association. June 26-29, Jackson Hole, Wyoming.

Farnham, I.M., Singh, A.K., Stetzenbach, K.J. & Johannsesson, K.H. 2002. Treatment of non-detects in multivariate analysis of groundwater chemistry data. *Chemometrics and Intelligent Laboratory Systems*, 60(1-2)265-281.

Fashola, M.O., Ngole-Jeme, V.M. & Babalola, O.O. 2016. Heavy metal pollution from gold mines: Environmental effects and bacterial strategies for resistance. *International Journal of Environmental Research and Public Health*, 13, 1047.

Feris, L. & Kotze, L.J. 2014. The regulation of acid mine drainage in South Africa: Law and governance perspectives. *Potchefstroom Electronic Law Journal*, 17(5).

Foos, A. 1997. Geochemical modeling of coal mine drainage, Summit County, Ohio. *Environmental Geology*, 31(3/4)205-210.

Gandy, C.J. & Evans, K.A. 2002. Laboratory and numerical modelling studies of iron release from a spoil heap in County Durham. In: Younger, P.L. & Robins, N.S. (eds.), *Mine Water Hydrogeology and Geochemistry*. Special Publications No. 198. Geological Society, London. Pages 205-214.

Garrels, R.M. & Thompson, M.E. 1960. Oxidation of pyrite by iron sulphate solutions. *American Journal of Science,* 258(A)57-67.

Geldenhuis, S. & Bell, F.G. 1998. Acid mine drainage at a coal mine in the Eastern Transvaal, South Africa. *Environmental Geology,* 34(2/3)234-242.

Gheroghe, S., Stoica, C., Vasile, G.G., Nita-Lazar, M., Stanescu, E. & Lucaciu, I.E. 2017. Metals toxic effects in aquatic ecosystems: Modulators of Water Quality. In: Tutu, H. (ed.), *Water Quality*. DOI: 10.5772/62562.

Goerke-Mallet, P., Melchers, C. & Kretschmann, J. 2016. Global post-mining challenges - experiences gained from the German hard coal mining industry. In: Proceedings of the 16th International Congress for Mine Surveying. September 12-16, Brisbane, Australia.

Golder Associates. 2016a. Geochemistry aspects of related mine closure planning of Union and related collieries - Phase 2. Report to South 32, Report No. 1531132-298586-1. (Unpublished Report).

Golder Associates. 2016b. Surface water impacts and related closure planning of Union Colliery - Phase 2: Catchment water quality model. Report to South 32, Report No. 1527383-299439-1. (Unpublished Report).

Goldich, S.S. 1938. A study in rock weathering. *Journal of Geology*, 46, 17-58.

Gomo, M. & Vermeulen, D. 2014. Hydrogeochemical characteristic of a flooded underground coal mine groundwater system. *Journal of African Earth Sciences*, 92, 68-75.

Gondi, F., Panto, G., Feher, J., Bogye, G. & Alfthan, G. 1992. Selenium in Hungary. The rock-soil-human system. *Biological Trace Element Research*, 35(3)299-306.

Gray, N.F. 1997. Environmental impact and remediation of acid mine drainage: A management problem. *Environmental Geology,* 30(1/2)62-71.

Griffin, N.J., Palmer, C.G. & Scherman, P-A. 2014. Critical analysis of environmental water quality in South Africa: historic and current trends. Report to the Water Research Commission, WRC Report No. 2184/1/14. Water Research Commission, Pretoria, South Africa.

Grobbelaar, R. 2001. The long-term impact of intermine flow from collieries in the Mpumalanga Coalfields. University of the Free State, Bloemfontein, South Africa. (M.Sc. Dissertation).

Grobbelaar, R., Usher, B., Cruywagen, L-M., De Necker, E. & Hodgson, F.D.I. 2004. Long-term impact of intermine flow from collieries in the Mpumalanga coalfields. Report to the Water Research Commission, Report No. 1056/1/04. Water Research Commission, Pretoria, South Africa.

Guler, C., Thyne, G.D., Mccray, J.E. & Turner, A.K. 2002. Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. *Hydrogeology Journal*, 10(1)455-474.

Gunther, P., Mey, W. & Van Niekerk, A. 2006. A sustainable mine water treatment initiative to provide potable water for a South African city - a public private partnership. Paper presented at the Water in mining Conference. November14-16, Brisbane.

Gupta, S.K. & Nikhil, K. 2016. Ground water contamination in coal mining areas: A critical review. *International Journal of Engineering and Applied Sciences*, 3(2)69-74.

Gzyl, G. & Banks, D. 2007. Verification of the "first flush" phenomenon in mine water from coal mines in the Upper Silesian Coal Basin, Poland. *Journal of Contaminant Hydrology*, 92, 66-86.

Hachiya, K., Sasaki, M., Saruta, Y., Mikami, N. & Yasanuga, T. 1984. Static and kinetic studies of adsorption-desorption of metal ions on the γ-Al_2O_3 surface. *The Journal of Physical Chemistry*, 88, 23-31.

Hancox, P.J. & Gotz, A.E. 2014. South Africa's coalfields - A 2014 perspective. *International Journal of Coal Geology*, 132, 170-254.

Hansen, R.N. 2018. Environmental Geochemistry Module Dictate, GLGY 6873. Department of Geology, University of the Free State, Bloemfontein, South Africa.

Hattingh, R.P., Pulles, W., Krantz, R., Pretorius, C. & Swart, S. 2002. Assessment, prediction and management of long-term post-closure water quality: a case study - Hlobane Colliery, South Africa. In: Younger, P.L. & Robins, N.S. (eds.), *Mine Water Hydrogeology and Geochemistry*. Special Publications No. 198. Geological Society, London. Pages 297-314.

Haunch, S. 2013. The legacy of historic mining and water quality in a heavily mined Scottish river catchment. College of Science and Engineering, University of Edinburgh, Edinburgh. (DPhil Thesis).

Hawkes, H.E. & Webb, J.S. 1962. *Geochemistry in Mineral Exploration*. Harper & Row, New York.

Hayes, K.F. & Leckie, J.O. 1986. Mechanism of lead ion adsorption at the goethite-water interface. In: Davis, J.A. & Hayes, K.F. (eds.), *Geochemical Processes at Mineral Surfaces*, ACS Symposium Series 323. American Chemical Society, Washington D.C. Pages 114-141.

He, F., Jiang, W., Tang, T. & Cai, Q. 2015. Assessing impact of acid mine drainage on benthic macroinvertebrates: can functional diversity metrics be used as indicators? *Journal of Freshwater Ecology*, 30(4)513-524. DOI: 10.1080/02705060.2014.998730.

Hem, J.D. 1985. *Study and Interpretation of the Chemical Characteristics of Natural Water*, 3rd Ed. U.S Geological Survey Water-supply Paper 2254.

Hlabela, P., Maree, J. & Bruinsma, D. 2006. Barium carbonate process for sulfate and metal removal from mine water. *Mine Water and the Environment*, 26(1)14-22.

Hobbs, P., Oelofse, S.H.H. & Rascher, J. 2008. Management of environmental impacts from coal mining in the upper Olifants catchment as a function of age and scale. International Journal of Water Resources Development, CSIR Natural Resources and the Environment, Pretoria, South Africa.

Hobbs, P.J. 1998. A preliminary assessment of acid generation in the flooding Sigma Colliery underground mine. VSA Geo-Consultants, Internal Report. 5 pages.

Hodgson, F. & Vermeulen, D. 2002a. Union Colliery: Mine water qualities and quantities. Report to South 32. Institute for Groundwater Studies, University of the Free State, Bloemfontein, South Africa. (Unpublished Report).

Hodgson, F. & Vermeulen, D. 2002b. Union Colliery: An investigation into the groundwater pollution potential from the Union and Black Diamond coal discard dumps. Report to South 32. Institute for Groundwater Studies, University of the Free State, Bloemfontein, South Africa. (Unpublished Report).

Hodgson, F. & Vermeulen, D. 2008. Follow-up geohydrological and hydrochemical studies for Union Colliery. Report to South 32, Report number 2008/01/FDIH. Institute for Groundwater Studies, University of the Free State, Bloemfontein, South Africa. (Unpublished Report).

Hodgson, F.D.I. & Krantz, R.M. 1998. Groundwater quality deterioration in the Olifants River Catchment above Loskop Dam with specialised investigations in the Witbank Dam Sub-Catchment. Report to the Water Research Commission, WRC Report No. 291/1/98. Water Research Commission, Pretoria, South Africa.

Hodgson, F.D.I. 2001. Underground storage of water from pit 5 and 6, at Kriel Colliery. Report to Kriel Colliery. (Unpublished Report).

Hodgson, F.D.I., Vermeulen, P.D., Cruywagen, L-M. & De Necker, E. 2007. Investigation of water decant from the underground collieries in Mpumalanga. Report to the Water Research Commission, Report No: 1263/1/07. University of the Free State, Bloemfontein, South Africa.

Hogsden, K.L. & Harding, J.S. 2012. Consequences of acid mine drainage for the structure and function of benthic stream communities: a review. *Freshwater Science*, 31, 108-120.

Horowitz, A.J. & Elrick, K.A. 1988. Interpretation of bed sediment trace metal data: methods for dealing with grain size effect. In: Lichtenberg, J.J., Winter, J.A., Weber, C.I. & Fradkin, L. (eds.), *Chemical and biological characterization of sludges, sediments, dredge spoils and drilling muds*, Vol. STP 976. ASTM, Philadelphia. 114 pages.

Howard, J.H. 1977. Geochemistry of selenium: Formation of ferroselite and selenium behaviour in the vicinity of oxidizing sulphide and uranium deposits. *Geochimica et Cosmochimica Acta*, 41(11)1665-1678.

Huisamen, A. & Wolkersdorfer, C. 2016. Modelling the hydrogeochemical evolution of mine water in a decommissioned opencast coal mine. *International Journal of Coal Geology*, 164(1)3-12.

Hydrogeological Map Series of the Republic of South Africa, 2003.

Institute for Groundwater Studies (IGS). 2017. Union Colliery geohydrology investigation: Volume calculations. Report to South32. Institute for Groundwater Studies, University of the Free State, Bloemfontein, South Africa. (Unpublished Report).

Iribar, V. 2004. Origin of neutral mine water in flooded underground mines: an appraisal using geochemical and hydrogeological methodologies. University of the Basque Country, Geodynamics Department. International Mine Water Association.

Jambor, J.L. & Blowes, D.W. 1991. Mineralogical study of low-sulphide, high-carbonate, arsenic-bearing tailings from the Delnite minesite, Timmins, Ontario. In: Proceedings of the Second International Conference on the Abatement of Acidic Drainage. September 16-18, Montreal, Quebec.

Jambor, J.L., Dutrizac, J.E. & Chen, T.T. 2000a. Contributions of specific minerals to the neutralisation potential in static tests. In: Proceedings of the Fifth International Conference on Acid Rock Drainage. Denver, Colorado.

Jambor, J.L., Nordstrom, D.K. & Alpers, C.N. 2000b. Metal-sulphate salts from sulphide mineral oxidation. In: Alpers, C.N., Jambor, J.L. & Nordstrom, D.K. (eds.), *Sulphate Minerals: Crystallography,*

Geochemistry and Environmental Significance. Reviews in Mineralogy and Geochemistry, Vol. 40. Pages 303-350.

Jarvis, A.P. & Gandy, C.J. 2010. A case study of long-term geochemical evolution of coal waste rock drainage and its remediation. In: Proceedings of the International Mine Water Association. Sydney. Pages 241-244.

Jarvis, A.P. & Younger, P.L. 1997. Dominating chemical factors in mine water induced impoverishment of the invertebrate fauna of two streams in the Durham coalfield, UK. *Journal of Chemical Ecology*, 13, 249-270.

Jaynes, D.B., Rogowski, A.S. & Pionke, H.B. 1984. Acid mine drainage from reclaimed coal strip mines. Model description. *Water Research Resources*, 20, 233.

Jeffrey, L.S. 2005. Characterization of the coal resources of South Africa. *The Journal of The South African Institute of Mining and Metallurgy*, 105(2)95-102.

Johnson, C.A. 1986. The regulation of trace element concentrations in river and estuarine waters contaminated with acid mine drainage: the adsorption of Cu and Zn on amorphous Fe oxyhydroxides. *Geochimica et Cosmochimica Acta*, 50, 2433-2438.

Johnson, D.B. & Hallberg, K.B. 2002. Pitfalls of passive mine water treatment. *Reviews in Environmental Science and Biotechnology*, 1, 335-343.

Johnson, D.B. & Hallberg, K.B. 2003. The microbiology of acidic mine waters. *Research in Microbiology*, 154, 466-73.

Johnson, D.B. & Hallberg, K.B. 2005a. Biogeochemistry of the compost bioreactor components of a composite acid mine drainage passive remediation system. *Science of the Total Environment,* 338, 81-93.

Johnson, D.B. & Hallberg, K.B. 2005b. Acid mine drainage remediation options: a review. *Science of the Total Environment*, 338, 3-14.

Jovanovic, N.Z., Annandale, J.G., Claassens, A.S., Lorentz, S.A., Tanner, P.D., Aken, M.E. & Hodgson, F.D.I. 2002. Commercial production of crops irrigated with gypsiferous mine water. *Water SA*, 28(4)413-422.

Jurjovec, J., Ptacek, C.J. & Blowes, D.W. 2000. Mechanisms controlling metal release in mill tailings. In: Proceedings of the International Conference on Acid Rock Drainage (ICARD). May 21-24, Denver, Colorado.

Kabata-Pendias, A. & Pendias, H. 2001. *Trace Elements in Soils and Plants*. CRC Press, Boca Raton, Florida, USA.

Kania, T. 1998. Application of the principles of postmining water quality prediction in coal mine drainage prediction and pollution prevention in Pennsylvania. The Pennsylvania Department of Environmental Protection, Report No. 5600-Bk-DEP2256.

Karbassi, A.R., Monavari, S.M., Nabi Bidhendi, G.R., Nouri, J. & Nematpour, K. 2008. Metal pollution assessment of sediment and water in the Shur River. *Environmental Monitoring and Assessment*, 147, 107-116.

Kennedy, V.C., Jones, B.F. & Zellweger, G.W. 1974. Filter pore-size effects on the analysis of Al, Fe, Mn and Ti in water. *Water Resources Research*, 10, 785-790.

Kinniburgh, D.G. & Jackson, M.L. 1981. Cation adsorption by hydrous metal oxides and clay. In: Anderson, M.A. & Rubin, A.J. (eds.), *Adsorption of inorganics at solid-liquid interfaces*. Ann Arbor Science, Ann Arbor, Michigan. Pages 91-160.

Kleinmann, R.L.P., Crerar, D.A. & Pacelli, R.R. 1981. Biogeochemistry of acid mine drainage and a method to control acid formation. *Mining Engineering*, 33(3)300-304.

Kwong, Y.T.J. 1993. Prediction and prevention of acid rock drainage from a geological and mineralogical perspective. MEND Project 1.32.1. 47 pages.

Langmuir, D. & Mahoney, J.J. 1984. Chemical equilibrium and kinetics of geochemical processes in ground water studies. In: Hitchon, B. & Wallick, E. (eds.), *Practical Applications of Ground Water Geochemistry*. National Water Well Association, Dublin, Ohio. Pages 69-95.

Lapakko, K. 2002. Metal mine rock and waste characterization tools: An overview. International Institute for Environment and Development Report, No. 67. Minnesota Department of Natural Resources, United States. 31 pages.

Lapakko, K.A. 1994. Evaluation of neutralisation potential determinations for metal mine waste and a proposed alternative. In: Proceedings of the International Land Reclamation and Mine Drainage Conference, Vol. 1. April 24-29, Pittsburgh, Pennsylvania. Pages 129-137.

Lawrence, R.W. & Day, S. 1997. Chemical prediction techniques for ARD. Short Course, No. 2. In: Proceedings of the Fourth International Conference on Acid Rock Drainage. May 31 - June 6, Vancouver, British Columbia. Available at: http://mend-nedem.org/wpcontent/ uploads/IW-02.pdf.

Lee, J.Y., Cheon, J.Y., Lee, K.K., Lee, S.Y. & Lee, M.H. 2001. Statistical evaluation of geochemical parameters distribution in a groundwater system contaminated with petroleum hydrocarbons. *Journal of Environmental Quality*, 35(5)1548-1563.

Letterman, R.D. & Mitsch, W.J. 1978. Impact of mine drainage on a mountain stream in Pennsylvania. *Environmental Pollution,* 17, 53-73.

Li, M. 2000. Acid rock drainage prediction for low sulphide, low-neutralisation potential mine wastes. In: Proceedings of the Fifth International Conference on Acid Rock Drainage, Vol. 1. Denver, Colorado.

Lichtner, P.C. 1996. Continuum formulation of multicomponent-multiphase reactive transport. In: Lichtner, P.C., Steefel, C.I. & Oelkers, E.H. (eds.), *Reactive Transport in Porous Media*. Reviews in Mineralogy, Vol. 34. Pages 1-81.

Liu, C.W. & Narasimhan, T.N. 1994. Modelling of selenium transport at the Kesterson reservoir, California, USA. *Journal of Contaminant Hydrology*, 15, 345-366.

Lottermoser, B. 2007. *Mine Wastes: Characterization, Treatment and Environmental Impacts*, 2nd Ed. Springer, Heidelberg, Germany.

Lottermoser, B.G., Ashley, P.M. & Lawie, D.C. 1999. Environmental geochemistry of the Gulf Creek copper mine area, north-eastern New South Wales, Australia. *Environmental Geology*, 39, 61-74.

Lovett, R.J. n.d. Removal of manganese from acid mine drainage. West Virginia University, Department of Chemistry. Available at: https://wvmdtaskforce.files.wordpress.com/2015/12/92-lovett.pdf.

Luis, A.T., Teixeira, P., Almeida, S.F.P., Ector, L., Matos, J.X. & Ferreira da Silva, E.A. 2009. Impact of acid mine drainage (AMD) on water quality, stream sediments and periphytic diatom communities in the surrounding streams of Aljustrel mining area (Portugal). *Water, Air and Soil Pollution*, 200(1)147-167.

Lupankwa, K., Naicker, K., Bezuidenhout, N. & Ochieng, L. n.d. Contaminant source-term model development for a backfilled opencast coal mine in the Karoo Basin. Golder Associates Africa, Groundwater and Geochemistry Division, Environmental Technology Business Unit, Johannesburg, South Africa.

Mack, B., McDonald, L.M. & Skousen, J. 2010. Acidity decay of above-drainage underground mines in West Virginia. *Journal of Environmental Quality*, 39(1)1043-1050.

Maest, A.S., Kuipers, J.R., Travers, C.L. & Atkins, D.A. 2005. Predicting Water Quality at Hardrock Mines: Methods and Models, Uncertainties and State-of-the-art. Kuipers & Associates and Buka Environmental, Washington D.C.

Magombedze, C. 2006. Geochemical processes controlling the generation and environmental impacts of acid mine drainage in semi-arid conditions. Norweigian University of Science and Technology, Faculty of

Engineering Science and Technology, Department of Geology and Mineral Resources Engineering. (DPhil Thesis).

Majzlan, J., Drahota, P. & Filippi, M. 2015. Parageneses and crystal chemistry of arsenic minerals. In: Bowell, R.J., Alpers, C.N., Jamieson, H.E., Nordstrom, D.K. & Majzlan, J. (eds.), *Arsenic, Environmental Geochemistry, Mineralogy, and Microbiology*. Reviews in Mineralogy and Geochemistry, Vol. 79. Mineralogical Society of America and Geochemical Society, De Gruyter, Chantilly, Virginia.

Mayer, K.U., Blowes, D.W. & Frind, E.O. 2003. Advances in reactive-transport modeling of contaminant release and attenuation from mine-waste deposits. In: Jambor, J.L., Blowes, D.W. & Ritchie, A.I.M. (eds.), *Environmental Aspects of Mine Wastes*. MAC Mineralogical Reviews, Vol. 31, Mineralogical Association of Canada. Pages 283-302.

Mayland, H.F., Gough, L.P. & Stewart, K.C. 1991. Selenium mobility in soils and its absorption, translocation, and metabolism in plants. USGS Circular No. 1064. Pages 57-64.

McCarthy, T. 2010. The decanting of acid mine water in the Gauteng city-region: Analysis, prognosis and solutions. School of Geosciences, University of the Witwatersrand, Johannesburg, South Africa.

McCarthy, T.S. & Humphries, M.S. 2013. Contamination of the water supply to the town of Carolina, Mpumalanga, January 2012. *South African Journal of Science*, 109(9/10)1-10.

McCarthy, T.S. & Pretorius, J.P. 2009. Coal mining on the Highveld and its implications for future water quality in the Vaal River system. In: Proceedings of the International Mine Water Conference. Pretoria, South Africa. Pages 56-65.

McCarthy, T.S. 2011. The impact of acid mine drainage in South Africa. *South African Journal of Science,*107(5/6)1-7. Available at: http://dx.doi.org/10.4102/sajs. v107i5/6.712.

McKeown, M., Christensen, D., Mueller, S., O'Kane, M., Weber, P. & Bird, B. 2017. Forecasting long-term water quality after closure: Boliden Aitik Cu mine. In: Proceedings of Mine Water and Circular Economy, International Mine Water Association. Lappeenranta, Finland.

McKibben, M.A. & Barnes, H.L. 1986. Oxidation of pyrite in low temperature acidic solutions. Rate laws and surface textures. *Geochimica et Cosmochimica Acta,* 50, 1509-1520.

Mey, W.S. & Van Niekerk, A.M. 2009. Evolution of mine water management in the Highveld Coalfields. In: Proceedings of the International Mine Water Conference. October 19-23, Pretoria, South Africa.

Miller, S., Robertson, A. & Donahue, T. 1997. Advances in acid drainage prediction using the net acid-generating (NAG) test. In: Proceedings of the Fourth International Conference on Acid Rock Drainage. May 31 - June 6, Vancouver.

Miller, S.D. 1979. Chemistry of a pyritic strip-mine spoil. Yale University, New Haven. 189 pages. (DPhil Thesis).

Mills, C. 1998a. An introduction to acid rock drainage. Available at: http: //www. enviromine. com/ard/Eduardpage/ARD. htm.

Mills, C. 1998b. The role of micro-organisms in acid rock drainage. Available at: http: //www. enviromine. com/ard/Midroorganisms/roleof. htm.

Mohanty, J.K., Mishra, S.K. & Nayak, B.B. 2001. Sequential leaching of trace elements in coal: A case study from Talcher coalfield, Orissa. *Journal of the Geological Society of India*, 58(5)441-447.

Montero, I.C., Brimhall, G.H., Alpers, C.N. & Swayze, G.A. 2005. Characterization of waste rock associated with acid drainage at the Penn Mine, California, by ground based visible to short-wave infrared reflectance spectroscopy assisted by digital mapping. *USGS Staff - Published Research*, 491. Available at: http://digitalcommons.unl.edu/usgsstaffpub/491.

Monterroso, C., Alvarez, E., Fernande-Marcos, M.L. & Macias, F. 1999. Geochemistry of aluminium and iron in mine soils from As Pontes, Galcicia (N.W. Spain). *Water, Air and Soil Pollution*, 110, 81-102.

Morin, K.A. & Hutt, N.M. 1994a. An empirical technique for predicting the chemistry of water seeping from mine-rock piles. In: Proceedings of America Society of Mining and Reclamation. Pages 12-19. Available at: https://www.asmr.us/Portals/0/Documents/Conference-Proceedings/1994-Volume-1/0012-Morin.pdf.

Morin, K.A. & Hutt, N.M. 1994b. Observed preferential depletion of neutralisation potential over sulphide minerals in kinetic tests: site-specific criteria for safe NP/AP ratios. In: Proceedings of the International Land Reclamation and Mine Drainage Conference. April 24-29, Pittsburgh.

Morin, K.A. 1983. Prediction of subsurface contaminant transport in acidic seepage from uranium tailings impoundments. University of Waterloo, Waterloo, Ontario, Canada. (DPhil Thesis).

Morin, K.A., Gerencher, E., Jones, C.E. & Konasewich, D.E. 1991. Critical literature review of acid drainage form waste rock. Canadian Centre for Mineral and Energy Technology, MEND/NEDEM Report No. 1.11.1. 182 pages.

Mosely, L.M., Daly, R., Palmer, D., Yeates, P., Dallimore, C., Biswas, T. & Simpson, S.L. 2015. Predictive modelling of pH and dissolved metal concentrations and speciation following mixing of acid drainage with river water. *Applied Geochemistry*, 59, 1-10.

Mosley, L.M., Palmer, D., Leyden, E., Fitzpatrick, R. & Shand, P. 2014. Changes in acidity and metal geochemistry in soils, groundwater, drain and river water in the lower Murray River after a severe drought. *Science of the Total Environment*, 485-486, 281-291.

Muniruzzaman, M., Kauppila, P.M. & Karlsson, T. 2018. Water quality prediction of mining waste facilities based on predictive models. GTK Open File Research Report 16/2018. Geological Survey of Finland.

Mylona, E., Xenidis, A. & Paspaliaris, I. 2000. Inhibition of acid generation from sulphidic wastes by the addition of small amounts of limestone. *Minerals Engineering*, 13(10)1161-1175.

Nadaska, G., Lesny, J. & Michalik, I. 2012. Environmental aspect of manganese chemistry. Department of Biotechnology, University of SS, Slovakia. Available at: http://heja.szif.hu/ENV/ENV-100702-A/env100702a.pdf.

Naicker, K., Cukrowska, E. & McCarthy, T.S. 2003. Acid mine drainage from gold mining activities in Johannesburg, South Africa and environs. *Environmental Pollution*, 122(1)29-40.

Neal, R.H., Sposito, G., Holtzclaw, K.M. & Traina, S.J. 1987. Selenite adsorption on alluvial soils. Soil composition and pH effects. *Soil Science Society of America Journal*, 51, 1161-1165.

Newbrough, P. & Gammons, C.H. 2002. An experimental study of water-rock interaction and acid rock drainage in the Butte mining district, Montana. *Environmental Geology*, 41, 705-719.

Nicholson, R.V., Gillham, R.W. & Reardon, E.J. 1990. Pyrite oxidation in carbonate-buffered solution: 2. Rate control by oxide coatings. *Geochimica et Cosmochimica Acta*, 54, 395-402.

Nordstrom, D.K. & Alpers, C.N. 1999. Geochemistry of acid mine waters. In. Plumlee, G.S. & Logsdon, M.J. (eds.), *The Environmental Geochemistry of Mineral Deposits*. Reviews in Economic Geology, Vol. 6A. Society of Economic Geologists, Inc., Littleton, Colorado.

Nordstrom, D.K. & Ball, J.W. 1986. The geochemical behaviour of aluminium in acidified surface waters. *Science*, 232, 54-56.

Nordstrom, D.K. & Southam, G. 1997. Geomicrobiology of sulfide mineral oxidation. In: Banfield, J.F. & Nealson, K.H. (eds.), *Geomicrobiology*. Reviews in Mineralogy. Mineralogical Society of America. Pages 361-390.

Nordstrom, D.K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary minerals. In: Kittrick, J.A., Fanning, D.S. & Hosner, L.R. (eds.), *Acid Sulfate Weathering*. Soil Science Society of America, Madison, Wisconsin. Pages 37-58.

Nordstrom, D.K. 1999. Some fundamentals of aqueous geochemistry. In: Plumlee, G.S. & Logsdon, M.J. (eds.), *The Environmental Geochemistry of Mineral Deposits - Part A: Processes, Techniques, and*

Health Issues. Reviews in Economic Geology, Vol. 6A. Society of Economic Geologists, Inc., Chelsea, Michigan. Pages 117-123.

Nordstrom, D.K. 2000. Advances in the hydrochemistry and microbiology of acid mine waters. *International Geology Review*, 42(6)499-515. Available at: http://dx.doi.org/10.1080/00206810009465095.

Nordstrom, D.K. 2011. Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters. *Applied Geochemistry*, 26, 1777-1791.

Nordstrom, D.K. 2012. Models, validation, and applied geochemistry: Issues in science, communication and philosophy. *Applied Geochemistry*, 27, 1899-1919.

Nordstrom, D.K. 2015. Baseline and pre-mining geochemical characterisation of mined sites. *Applied Geochemistry*, 57, 17-34.

Nordstrom, D.K., Alpers, C.N., Ptacek, C.J. & Blowes, D.W. 2000. Negative pH in extremely acidic mine waters from Iron Mountain, California. *Environmental Science and Technology,* 34, 254-258.

Nordstrom, D.K., Blowes, D.W. & Ptacek, C.J. 2015. Hydrogeochemistry and microbiology of mine drainage: An update. *Applied Geochemistry,* 57, 3-16. Available at: https://doi.org/10.1016/j.apgeochem.2015.02.008.

Nouri, J., Mahvi, A.H., Jahed, G.R. & Babaei, A.A. 2008. Regional distribution pattern of groundwater heavy metals resulting from agricultural activities. *Environmental Geology*, 55(6)1337-1343.

Nyarko, B.J.B., Dampare, S.B., Serfor-Armah, Y., Osae, S., Adotey, D. & Adomako, D. 2008. Biomonitoring in the forest zone of Ghana: the primary results obtained using neutron activation analysis and lichens. *International Journal of Environment and Pollution*, 32. 467 pages.

Ochieng, G.M., Seanego, E.S. & Nkwonta, O.I. 2010. Impacts of mining on water resources in South Africa: A review. *Scientific Research and Essays*, 5(22)3351-3357.

Oelofse, S.H.H. 2008. Emerging issues paper: Mine water pollution. Report prepared for the Department of Environmental Affairs and Tourism (DEAT). CSIR Natural Resources and the Environment. Pretoria, South Africa.

Oelofse, S.H.H., Hobbs, P.J., Rascher, J. & Cobbing, J.E. 2007. The pollution and destruction threat of gold mining waste on the Witwatersrand - A West Rand case study. CSIR Natural Resources and the Environment Department. Pretoria, South Africa.

Oreskes, N. & Belitz, K. 2001. Philosophical issues in model assessment. In: Anderson, M.G. & Bates, P.D. (eds.), *Model Validation in the Hydrological Sciences*. John Wiley & Sons. 500 pages.

Oreskes, N., Shrader-Frechette, K. & Belitz, L. 1994. Verification, validation, and confirmation of numerical models in the Earth sciences. *Science*, 263, 641-646.

Pabalari, R. & Sabido, L.M. 2007. Software validation plan and report for Geochemist's Workbench version 6.0. San Antonio.

Paktunc, A.D. 1999. Mineralogical constraints on the determination of neutralization potential and prediction of acid mine drainage. *Environmental Geology*, 39(2)103-112.

Palandri, J.L. & Kharaka, Y.K. 2004. A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modelling. Open File Report 2004-1068, U.S. Geological Survey. Prepared in cooperation with the National Energy Technology Laboratory - United States Department of Energy. Menlo Park, California.

Parbhakar-Fox, A. & Lottermoser, B.G. 2015. A critical review of acid rock drainage prediction methods and practices. *Minerals Engineering,* 82, 197-124.

Pauwels, H., Pettenati, M. & Greffie, C. 2010. The combined effect of abandoned mines and agriculture on groundwater chemistry. *Journal of Contaminant Hydrology*, 115, 64-78.

Pearce, J., Weber, P., Pearce, S. & Scott, P. 2016. Acid and metalliferous drainage contaminant load prediction for operational or legacy mines at closure. In: Fourie, A.B. & Tibbett, M. (eds.), *Mine Closure,* Proceedings of the 11th International Conference on Mine Closure. 2016 Australian Centre for Geomechanics, Perth. Pages 663-676.

Perkins, E.H., Gunter, W.D., Nesbitt, H.W. & St-Arnaud, L.C. 1997. Critical review of classes of geochemical computer models adaptable for prediction of acidic drainage from mine waste rock. In: Proceedings of the Fourth International Conference on Acid Rock Drainage, Vol. 2. May 31- June 6, Vancouver, British Columbia. Pages 587-601.

Perry, E.F. 2001. Modelling water-rock interactions in flooded underground coal mines, Northern Appalachian Basin. *Geochemistry: Exploration, Environment, Analysis*, 1(1)61-70.

Pinetown, K.L., Ward, C.R. & Van der Westhuizen, W.A. 2007. Quantitative evaluation of minerals in coal deposits in the Witbank and Highveld Coalfields, and the potential impact on acid mine drainage. *International Journal of Coal Geology*, 70, 166-183.

Pitkanen, P., Partamies, S. & Luukkonen, A. 2004. Hydrogeochemical interpretation of baseline groundwater conditions at the Olkiluoto Site. Posiva Report. Olkiluoto, Finland.

Plumlee, G.S. & Logsdon, M.J. (eds.) 1999. *The Environmental Geochemistry of Mineral Deposits*. Reviews in Economic Geology, Vol. 6A.

Plumlee, G.S., Smith, K.S., Montour, M., Ficklin, W.H. & Mosier, E.L. 1999. Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types. In: Filipek, L.H. & Plumlee, G.S. (eds.), *The Environmental Geochemistry of Mineral Deposits - Part B: Case Studies and Research Topics*. Reviews in Economic Geology, Vol. 6A. Society of Economic Geologists. Pages 373-432.

Postma, B. & Schwab, R. 2002. Mine closure: the way forward from DWAF'S perspective. WISA workshop on mine closure, Randfontein.

Price, W.A. 1997. Draft: Guidelines and recommended methods for the prediction of metal leaching and acid rock drainage at minesites in British Colombia. British Colombia Mine Reclamation section (MRS). British Colombia Ministry of Employment and Investment, Energy and Minerals Division. Smithers, British Colombia. 143 pages.

Price, W.A. 2009. Prediction manual for drainage chemistry from sulfidic geologic materials. MEND Report 1.20.1. Natural Resources Canada. 579 pages.

Price, W.A., Errington, J. & Koyanagi, V. 1997a. Guidelines for the prediction of acid rock drainage and metal leaching for mines in British Columbia: Part 1. General procedures and information requirements. In: Proceedings of the Fourth International Conference on Acid Rock Drainage, Vol. 1. May 31 - June 6, Vancouver, British Colombia. Pages 1-14.

Price, W.A., Morin, K. & Hutt, N. 1997b. Guidelines for the prediction of acid rock drainage and metal leaching for mines in British Columbia: Part 2. Recommended procedures for static and kinetic testing. In: Proceedings of the Fourth International Conference on Acid Rock Drainage, Vol. 1. May 31 - June 6, Vancouver, British Columbia. Pages 15-30.

Ptacek, C.J. & Blowes, D.W. 1994. Influence of siderite on the pore-water chemistry of inactive mine-tailings impoundment. In: Alpers C.N. & Blowes, D.W. (eds.), *Environmental Geochemistry of Sulfide Oxidation*. ACS Symposium Series 550. Pages 172-189.

Pulles, W., Banister, S. & Van Biljon, M. 2005. The Development of appropriate procedures towards and after closure of underground gold mines from a water management perspective. Report to the Water Research Commission, Report No 1215/1/05. Water Research Commission, Pretoria, South Africa.

Pulles, W., Howie, D., Otto, D. & Easton, J. 1995. A manual on mine water treatment and management in South Africa. Report to the Water Research Commission. Water Research Commission, Pretoria, South Africa.

Qian, G., Schuman, R.C., Li, J., Short, M.D., Fan, R., Li, Y., Kawashima, N., Zhou, Y., Smart, R.S.C. & Gerson, A.R. 2017. Strategies for reduced acid and metalliferous drainage by pyrite surface passivation. *Minerals*, 7, 42.

Rait, R., Trumm, D., Pope, J., Craw, D., Newman, N. & MacKenzie, H. 2010. Adsorption of arsenic by iron rich precipitates from two coal mine drainage sites on the West Coast of New Zealand. *New Zealand Journal of Geology and Geophysics*, 53(2-3)177-193.

Reddy, K.J., Wang, L. & Gloss, S.P. 1995. Solubility and mobility of copper, zinc and lead in acidic environments. *Plant and Soil*, 171, 53-58.

Reinmann, C. & Garrett, R.G. 2005. Geochemical background-concept and reality. *Science of the Total Environment*, 350, 12-27.

Reinmann, C., Filzmoser, P. & Garrett, R.G. 2005. Background and threshold: critical comparison of methods of determination. *Science of the Total Environment*, 346, 1-16.

Ritchie, A.I.M. 1994. The waste-rock environment. In: Jambor, J.L. & Blowes, D.W. (eds.), *The Environmental Geochemistry of Sulfide Mine-Wastes.* Short Course Handbook, Vol. 22. Pages 133-161.

Rose, A.W. & Cravotta, C.A. 1998. Geochemistry of coal mine drainage. In: Brady, K.B.C., Smith, M.W. & Schneck, J. (eds.), *Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania*. Pennsylvania Department of Environmental Protection, Harrisburg, Pennsylvania. Pages 1-22.

Rose, A.W., Hawkes, H.E. & Webb, J.S. 1979. *Geochemistry in Mineral Exploration*. Academic Press, New York. 657 pages.

RoyChowdhury, A., Sarkar, D. & Datta, R. 2015. Remediation of acid mine drainage-impacted water. *Current Pollution Reports*, 1, 131-141. DOI 10.1007/s40726-015-0011-3.

Salomons, W. 1995. Environmental impact of metals derived from mining activities: Processes, predictions, prevention. *Journal of Geochemical Exploration*, 52(1)5-23.

Sapsford, D.J., Bowell, R.J., Dye, M. & Williams, K.P. 2009. Humidity cell test for the prediction of acid rock drainage. *Minerals Engineering*, 22(1)25-36.

Scharer, J.M., Annable, W.K. & Nicholson, R.V. 1993. A tailings basin model to evaluate transient water quality of acid mine drainage. University of Waterloo, Waterloo, Ontario.

Scharer, J.M., Garga, V., Smith, R. & Halbert, B.E. 1991. Use of steady state models for assessing acid generation in pyritic mine tailings. In: Proceedings of the Second International Conference on the Abatement of Acidic Drainage, Vol. 2. September 16-18, Montreal, Canada.

Schmiermund, R.L. & Drozd, M.A. 1997. Acid mine drainage and other mining-influenced waters (MIW). In: Marcus, J.J. (ed.), *Mining Environmental Handbook*, *Effects of Mining on the Environment and American Environmental Controls on Mining*. Imperial College Press, London. Pages 599-617.

Schwertmann, U. & Murad, E. 1983. The effect of pH on the formation of goethite and hematite from ferrihydrite. *Clays and Clay Minerals*, 31, 277-284.

Scullion, J. & Edwards, R.W. 1980. The effects of coal industry pollutants on the macroinvertebrate fauna of a small river in the South Wales coalfield. *Freshwater Biology,* 10, 141-162.

Shaw, S. & Mills, C. 1998. Petrology and mineralogy in ARD prediction. Available at: http: //www. enviromine. com/ard/Mineralogy/Petrology%20and%20Mineralogy.htm.

Sherlock, E.J., Lawrence, R.W. & Poulin, R. 1995. On the neutralization of acid rock drainage by carbonate and silicate minerals. *Environmental Geology*, 25(1)43-54.

Singer, P.C. & Stumm, W. 1970. Acid mine drainage: Rate-determining step. *Science,* 167, 1121-1123.

Skousen, J.G. 1996. Acid mine drainage. In: Skousen, J.G. & Ziemkiewicz, P.F. (eds.), *Acid Mine Drainage Controls and Treatment*. West Virginia University, West Virginia. Pages 9-14.

Smith, K.S. & Huyck, H.L.O. 1999. An overview of the abundance, relative mobility, bioavailability, and human toxicity of metals. In: Plumlee, G.S. & Logsdon, M.J. (eds.), *The Environmental Geochemistry of Mineral Deposits - Part A: Processes, methods, and health issues*. Reviews in Economic Geology, Vol. 6A. Society of Economic Geologists. Pages 29-70.

Smith, K.S. 1999. Metal sorption on mineral surfaces: An overview with examples relating to mineral deposits. In: Plumlee, G.S. & Logsdon, M.J. (eds.), *The Environmental Geochemistry of Mineral Deposits - Part A. Processes, methods, and health issues- Part B: Case studies and research topics*. Reviews in Economic Geology, Vol. 6A and 6B. Society of Economic Geologists.

Smith, K.S. 2007. Strategies to predict metal mobility in surficial mining environments. In: DeGraff, J.V. (ed.), *Understanding and Responding to Hazardous Substances at Mine Sites in the Western United States*. Reviews in Engineering Geology, Vol. 17. Geological Society of America. Pages 25-45. DOI: 10.1130/2007.4017(03).

Smith, K.S., Ficklin, W.H., Plumlee, G.S. & Meier, A.L. 1992. Metal and arsenic partitioning between water and suspended sediment at mine-drainage sites in diverse geologic settings. In: Kharaka, Y.K. & Maest, A.S. (eds.), *Water-Rock Interaction*, Proceedings of the Seventh International Symposium on Water-Rock Interaction, Vol. 1. July 13-18, Park City, Utah. A.A. Balkema, Rotterdam. Pages 443-447.

Sobek, A.A., Schuller, W.A., Freeman, J.R. & Smith, R.M. 1978. Field and laboratory methods applicable to overburdens and mine soils. Report No. EPA-600/2-78-054. U.S. Environmental Protection Agency, Cincinnati, Ohio.

Soregaroli, B.A. & Lawrence, R.W. 1998. Update on waste characterization studies. In: Proceedings of Mine Design, Operations and Closure Conference. Polson, Montana. 10 pages.

South 32. 2017. Personal communication. South 32, Breyten, South Africa.

Stumm, W. & Morgan, J.J. 1970. *Aquatic Chemistry - An Introduction Emphasizing Chemical Equilibria in Natural Waters*. John Wiley & Sons, New York.

Stumm, W. & Morgan, J.J. 1981. *Aquatic Chemistry - An Introduction Emphasizing Chemical Equilibria in Natural Waters,* 2nd Ed. John Wiley & Sons, New York. 470 pages.

Stumm, W. & Morgan, J.J. 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. John Wiley & Sons, New York. 1022 pages.

Stumm, W. & Sulzberger, B. 1992. The cycling of iron in natural environments: Considerations based on laboratory studies of heterogeneous redox processes. *Geochimica et Cosmochimica Acta*, 56, 3233-3257.

Sverdrup, R.U. 1990. *The Kinetics of Base Cation Release Due to Chemical Weathering*. Lund University Press, Lund. 246 pages.

Swart, S.J., Pulles, W., Boer, R.H., Kirkaldy, J. & Pettit, C. 1998. Environmental risk assessment as the basis for mine closure at Iscor Mining. *The Journal of the South African Institute of Mining and Metallurgy*, 98(1)1-6.

Szlachta, M. & Chubar, N. 2013. The application of Fe-Mn hydrous oxides based adsorbent for removing selenium species from water. *Chemical Engineering Journal*, 217, 159-168.

Taylor, S.R. 1964. Abundance of chemical elements in the continental crust - a new table. *Geochimica et Cosmochimica Acta*, 28, 1273-1285.

The International Network for Acid Prevention (INAP). 2003. Treatment of sulphates in mine effluents. International Network for Acid Prevention Report.

The International Network for Acid Prevention (INAP). 2009. The Global Acid Rock Drainage Guide (GARD Guide). Available at: http://www. gardguide.com/.

Thompson, J.G. 1980. Acid mine-waters in South Africa and their amelioration. *Water SA*, 6(1)130-134.

United States Geological Survey. 2003. National field manual for the collection of water-quality data. U.S. Geological Survey Techniques of Water-Resources Investigations.

Udayabhanu, S.G. & Prasad, B. 2010. Studies on environmental impact of acid mine drainage generation and its treatment: An appraisal. *International Journal of Environment and Pollution*, 30(11)953-967.

Usher, B.H. 2003. The evaluation and development of hydrogeochemical prediction techniques for long-term water chemistry in South African coalmines. Institute for Groundwater Studies, University of the Free State, Bloemfontein, South Africa. (DPhil Thesis).

Usher, B.H., Cruywagen, L-M., De Necker, E. & Hodgson, F.D.I. 2003. Acid-base accounting, techniques and evaluation (ABATE): Recommended methods for conducting and interpreting analytical geochemical assessments at opencast collieries in South Africa. Report to the Water Research Commission, Report No. 1055/2/03. Water Research Commission, Pretoria, South Africa.

Van Coller, A.A. 2013. Open pit flooding as a post-closure option: A geochemical approach. Institute for Groundwater Studies, University of the Free State, Bloemfontein, South Africa. (M.Sc. Dissertation).

Van Heerden, E., Williams, P., Ojo, E., Kuloyo, K. & Posthumus, R. n.d. Bioremediation - Small solutions to big problems. University of the Free State, Bloemfontein, South Africa. (Unpublished Report).

Vermeulen, P.D. & Usher, B.H. 2006a. An investigation into recharge in South African underground collieries. *The Journal of The Southern African Institute of Mining and Metallurgy*, 106, 771-788.

Vermeulen, P.D. & Usher, B.H. 2006b. Sulphate generation in South African underground and opencast collieries. *Environmental Geology*, 49(1)552-569.

Vermeulen, P.D., Usher, B.H. & Van Tonder, G.J. 2007. Determination of the impact of coal mine water irrigation on groundwater resources. Report to the Water Research Commission, Coaltech. Water Research Commission, Pretoria, South Africa.

Vinceti, M., Wei, E.T., Malagoli, C., Bergomi, M. & Vivoli, G. 2001. Adverse health effects of selenium in humans. *Reviews on Environmental Health*, 16(4)233-251.

Waters, A.S. & Webster-Brown, J.G. 2013. Assessing aluminium toxicity in streams affected by acid mine drainage. *Water Science and Technology*, 67(8)1764-1772. DOI: 10.2166/wst.2013.051.

Weaver, J.M.C., Cave, L. & Talma, A.S. 2007. Groundwater sampling. A comprehensive guide for sampling methods. Prepared for the Water Research Commission, WRC Report No. TT 303/07. Water Research Commission, Pretoria, South Africa.

Webb, J.A. & Sasowsky, I.D. 1994. The interaction of acid mine drainage with a carbonate terrane: evidence from the Obey River, north-center Tennessee. *Journal of Hydrology*, 161, 327-346.

White, A.F. & Brantley, S.L. 1995. Chemical weathering rates of silicate minerals. Reviews in Mineralogy, Vol. 31. Mineralogical Society of America. Washington D.C. 583 pages.

White, W.W., Lapakko, K.A. & Cox, R.L. 1999. Static-test methods most commonly used to predict acid-mine drainage: Practical guidelines for use and interpretation. In: Plumlee, G.S. & Logsdon, M.J. (eds.), *The Environmental Geochemistry of Mineral Deposits - Part A: Processes, Techniques, and Health Issues*. Reviews in Economic Geology, Vol. 6A. Society of Economic Geologists, Littleton, Colorado. Pages 325-338.

White, W.W., Trujillo, E.M. & Lin, C-K. 1993. Chemical predictive modelling of acid mine drainage from waste rock: model development and comparison of modelled output to experimental data. In: Proceedings of America Society of Mining and Reclamation. Pages 157-166. DOI: 10.21000/JASMR94010157.

White, W.W., Trujillo, E.M. & Lin, C-K. 1994. Chemical predictive modelling of acid mine drainage from waste rock: model development and comparison of modelled output to experimental data. In: Proceedings of the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage. April 24-29, Pittsburgh, Pennsylvania. Available at: http://www.asmr.us/Portals/0/Documents/Conference- Proceedings/1994-Volume-1/0157-White.pdf.

Williams, D.J., Currey, N.A., Ritchie, P. & Wilson, G.W. 2003. Kidston waste rock dump design and 'store and release' cover performance seven years on. In: Farrell, T. & Taylor, G. (eds.), Proceedings of the Sixth International Conference on Acid Rock Drainage. Australasian Institute of Mining and Metallurgy, Melbourne. Pages 419-426.

Williams, T.M. & Smith, B. 2000. Hydrochemical characterization of acute acid mine drainage at Iron Duke mine, Mazowe, Zimbabwe. *Environmental Geology*, 39(3-4)272-278.

Williamson, M.A. & Rimstidt, J.D. 1994. The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. *Geochimica et Cosmochimica Acta,* 58, 5443-5454.

Wimberley, F., Jordaan, J. & Pulles, W. 2007. Best practice guideline A2: Water management for mine residue deposits. Department of Water Affairs and Forestry (DWAF), South Africa.

Witthueser, K.T. 2016. Hydrogeochemistry GEO6835. In: GEO6835 Class notes. Institute for Groundwater Studies, University of the Free State, Bloemfontein, South Africa.

Wood, S.C., Younger, P.L. & Robins, N.S. 1999. Long-term changes in the quality of polluted mine water discharges from abandoned coal workings in Scotland. *Quarterly Journal of Engineering Geology and Hydrogeology*, 32(1)69-79.

WWF-SA. 2011. Coal and water futures in South Africa. World Wildlife Fund Report. Available at: http://www.wwf.org.za/?7000/coal-and-water-report.

Younger, P.L. & Harbourne, K.J. 1995. To pump or not to pump: cost-benefit analysis of future environmental management options for the abandoned Durham Coalfield. *Journal of the Chartered Institution of Water and Environmental Management*, 9, 405-415.

Younger, P.L. & Robins, N.S. 2002. Challenges in the characterization and prediction of the hydrogeology and geochemistry of mined ground. In: Younger, P.L. & Robins, N.S. (eds.), *Mine Water Hydrogeology and Geochemistry*. Special Publications No. 198. Geological Society, London. Pages 1-16.

Younger, P.L. & Sapsford, D.J. 2004. Evaluating the potential impact of opencast coal mining on water quality (Groundwater Regulations 1998). An assessment framework for Scotland. Scottish Environmental Protection Agency, Scotland. Pages 1-75.

Younger, P.L. 1995. Minewater pollution in Britain: Past, present and future. *Mineral Plann*, 65, 38-41.

Younger, P.L. 1997. The longevity of mine water pollution: A basis for decision-making. *Science of the Total Environment*, 194/195, 457-466.

Younger, P.L. 2000. Predicting temporal changes in total iron concentrations in groundwaters flowing from abandoned deep mines: a first approximation. *Journal of Contaminant Hydrology*, 44, 47-69.

Younger, P.L. 2001 Mine water pollution in Scotland: nature, extent and preventative strategies. *Science of the Total Environment*, 265, 309-326.

Younger, P.L. 2007. *Groundwater in the Environment, An Introduction*. Blackwell Publishing, Malden.

Zhang, C.S. & Selinus, O. 1998. Statistics and GIS in environmental geochemistry - some problems and solutions. *Journal of Geochemical Exploration*, 64(1-3)339-354.

Zhao, B., Usher, B.H., Yibas, B. & Pulles, W. 2010. Evaluation and validation of geochemical prediction techniques for underground coal mines in the Witbank/Vryheid region. Report to the Water Research Commission. Pulles Howard and De Lange Incorporated, Institute for Groundwater Studies. Pretoria, Bloemfontein, South Africa.

LIST OF APPENDICES

All Appendices as listed below are provided on request:

1. Appendix A: ABA and NAG Methodology

2. Appendix B: Water Quality Data

3. Appendix C: ABA and NAG Results

4. Appendix D: Model Results

5. Appendix E: Sensitivity Analysis

ABSTRACT

The defunct Union Colliery located in the Vryheid Coalfields of South Africa is decanting excess mine water after decades of mining activities without any measures to prevent or control acid generation. Mine waters further indicate elevated concentrations of metal(loid)s. The mine has however made attempts to investigate a small pilot treatment system having a barium carbonate [$BaCO_3$] dispersed alkaline substrate for use in the at least partial remediation of mine drainage. This dissertation investigates potential geochemical risks from the geological mine waste resulting from underground coal mining with the aim to quantify these risks and evaluate long-term mine waste drainage stability. The evolution in the geochemistry of mine impacted waters as it evolves from the primary source minerals until final discharge is subject to site specific influences and necessitates site specific evaluation. A multidisciplinary, integrated assessment approach was implemented that included hydrogeochemical, mineralogical and geochemical assessment, and finally geochemical modelling techniques to predict the quality of water emanating from the mine waste over the long-term. Various data sets and sources were compiled and processed and served as input into geochemical models of the expected impacts on the conceptual mine waste environments. Forward reaction path models allowed the evaluation of the current system with thermodynamic and chemical reaction processes leading to the hydro-chemical composition of the groundwater and mine decant water as observed in the monitoring data sets. A review of the assessments that were undertaken to determine the long-term water quality risks after mine closure and comments of potential water management strategies thereon are presented with special focus on quantification of risks by means of forward reaction path models.

XRD analysis revealed that the mine waste comprises of varying proportions of primary, secondary and clay minerals with calcite as the dominant carbonate phase and pyrite the dominant sulphide bearing mineral. ABA assessments indicated that the coal discard material have high likelihood to produce acid, whereas the hanging wall coal sample collected from the Susanna compartment suggested neutral conditions. It is however important to contextualise the ABA results with the hydrogeochemical conditions of the study area and existing water monitoring data. For hydro-chemical assessment and modelling purposes the area was divided into different hydrogeochemical components, each representing different systems exposed to dynamic processes. From the water quality monitoring data sets, baseline hydrogeochemical conditions for the study area, including the different hydrogeochemical components, could be inferred. Based on the hydro-chemical plot assessment, sodium was identified as the dominant cation in the groundwater, whereas calcium dominates in the mining-influenced waters (MIW). Bicarbonate is a significant anion along with sulphate in the groundwater, surface water and eastern operation components; whereas sulphate is the dominant anion in the western operations. The ion distributions in the different hydrogeochemical components are expected considering the mineralogy of the mine waste material. Processes such as sulphide mineral oxidation and carbonate dissolution as an attempt to neutralise any acidic environments formed, are responsible for the elevated sulphate, bicarbonate and calcium concentrations. As expected in a mining affected area where sulphidic waste was produced, there is a distinct trend in all areas, except for groundwater in the unmined land,

to be or to become sulphate dominated. A bimodal pH distribution was observed between the hydrogeochemical components which is a phenomenon observed in many mining influenced areas. The western operations decant water are distinctly acidic, whereas the other hydrogeochemical areas indicate circum-neutral to alkaline conditions.

Based on the site characterisation and hydrogeochemical and geochemical assessments, representative conceptual models were developed as a foundation for the kinetic geochemical models. The main purpose of the geochemical models was to reduce uncertainty through constant sensitivity analyses, and to facilitate understanding of the interaction of geochemical processes with a focus on metal(loid) mobility to a level at which potential liability can be quantified. The weathering models simulated for the coal discard dumps and eastern operation components suggested that circum-neutral to alkaline pH will prevail in the long-term which may be attributed to weathering reactions of the carbonate and mafic minerals within the local geology that does not allow acidic environments to develop. Manganese and selenium remain in solution after the simulation period and therefore create several risks. Selenium specifically may reach concentrations in the groundwater that may pose high level risk to humans. Therefore, although alkaline conditions prevail in the groundwater and MIW, selenium may remain mobile in the long-term. The western operation weathering models indicated acidic conditions throughout the simulation period which may be attributed to the depletion of carbonate minerals along flow paths. Associated with the acidic nature of the decant water are elevated concentrations of manganese, aluminium, lead, nickel and selenium that may reach concentrations that pose high level risk to several aquatic tropic levels as well as humans. Main risks associated with the mine waste included contamination of shallow groundwater resources as well as ecological impacts and regional impacts of major river systems associated with decant of MIW at the surface. The model findings suggest that risks will remain in the long-term and it therefore invokes certain mitigation implications.

The study highlighted the importance of representative and complete data sets of especially the mineralogy of the mine waste which is used as vital inputs to the geochemical models. As the study lacked mineralogical input of especially the underground floor and roof lithologies, it is recommended for the mine that the study be furthered by extensive solid waste sampling of the underground waste material. This will lead to better calibration, and hence higher confidence outcomes of the current geochemical models. Conventional active and passive treatment methods may be successful to reduce current risks, especially of that posed by the acidity in the western operations, however, as these methods may not be feasible in the long-term (>100 years) due to waste generated by lime dosing or desalination plants, the evaluation of in situ methods such as bioremediation is recommended.