School of Mining Engineering

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MINERALOGICAL AND GEOCHEMICAL CHARACTERISATION OF IRON ORE TAILINGS AND THEIR POTENTIAL TO GENERATE TOXIC ELEMENTS AT KHUMANI MINE.

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DECLARATION

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“You never know what's around the corner. It could be everything. Or it could be nothing. You keep putting one foot in front of the other, and then one day you look back and you've climbed a mountain”.

Tom Hiddleston

ABSTRACT

Iron ore mining in South Africa has resulted in clearance of vast areas of land, large pits and volumes of waste material disposed as tailings dumps. Recently, poor management and compromised engineering of tailings dump in iron ore mines have led to incidences of wall failures, spilling tailings material over large areas of land. Inhabitants living near these mines often suffer injustices through contamination of water resources, dam siltation and soil contamination. Although many iron ore tailings dumps have been associated with generation of alkaline drainage, their contaminated footprints have been reported to contaminate groundwater aquifers. This research characterises the tailings material from the Khumani Iron Ore Mine through chemical and mineralogical analyses of leachable potential toxic elements using inductive coupled plasma spectrometry, mineralogical characteristics using x-ray diffraction, physicochemical properties, and acid base accounting. The study also investigates the interaction between tailings geochemistry and groundwater quality.

Groundwater in the study is characterised by near neutral to alkaline pH with high concentrations of $CaCO_3$ owing to the geological formation of the area. The groundwater waters are classified as Ca–type in summer and as-non dominant in winter. Concentration of As (21.48±8.98 µg/l), Fe (22730.5±1827.57 µg/l), Mn (478.3±76.28 µg/l), Cu (60.8±4.34 µg/l), Zn (204.7±21.98 µg/l), Al (300.4±11.47 µg/l ,) Pb (65.7±6.9 µg/l), Co (20.1±4.1 µg/l) and Ni (41.4±6.85 µg/l) exceed the permissible limits of the Department of Water Affairs and Forestry (1996) in winter but are compliant in summer owing to the increase in the water table and a dilution effect due to heavy rains.

Tailings material contains high concentrations of Mn, Zn, B, Ni, Ba, Mo, Co, and Pb and relatively low concentrations of Cu, Cd, As, and Hg minerals in the tailings deposits which include quartz, haematite, magnetite, siderite, calcite, dolomite, K feldspar, plagioclase, talc, clinochlore, and anatase. Kaolinite minerals were shown to increase the adsorption sites for trace elements. Acid base accounting test classified the tailings material as non-acid producing with NP to AP ratio > 2. However, the high concentrations of PTEs, including Fe, Pb, and As, in the groundwater samples suggest that there is vertical movement of these elements from the tailings into the groundwater reserves. Therefore, the TSF material cannot be discarded in an unused pit without further treatment or lining to prevent contamination of groundwater resources.

Keywords: potential toxic elements, iron ore, tailings dumps, groundwater

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a) Acid Potential (AP)

$$AP = (total\ S\%) X\ 30.6$$ *Equation 1*

b) Acid Neutralisation Potential (ANP)

$$ANP = 50a \left\{ X - \left(\frac{b}{a}\right) y \right\} / c$$ *Equation 2*

LIST OF ACRONYMS USED IN THE REPORT

Acronym	Definition
ABA	Acid-Base Accounting
AMD	Acid Mine Drainage
AMSL	Above Mean Sea Level
ANP	Acid Neutralisation Potential
AP	Acid Potential
ASLP	Australian Standard Leaching Procedure
BIF	Banded Ironstone Formation
CEC	Cation Exchange Capacity
CPTu	Cone Penetration Testing Rig
DMRE	Department of Mineral Resources and Energy
DWAF	Department of Water Affairs and Forestry
EC	Exchange Capacity
GISTM	Global Industry Standard on Tailings Management
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
LC	Leachable Concentrations
LCT	Leachable Concentration Threshold
NEM:WA	National Environmental Management: Waste Act
NNP	Net Neutralisation Potential
MPRDA	Mineral and Petroleum Resources Development Act
PTE	Potential Toxic Elements
PHE	Potential Harmful Elements
REE	Rare Earth Elements
SANAS	South African National Accreditation System
SI	Saturation Index
TCT	Total Concentration Threshold
TSF	Tailings Storage Facility
WHO	World Health Organisation
XRD	X-Ray Diffraction

LIST OF CHEMICAL SYMBOLS USED IN THE REPORT

Chemical Name	**Chemical Symbol**
Aluminium Hydroxide	$Al(OH)_3$
Arsenic	As
Cadmium	Cd
Calcium Sulphate Dihydrate	$CaSO_4.2H_2O$
Calcium Carbonate	$CaCO_3$
Carbon Monoxide	CO
Chromate Ion	CrO_4^{2-}
Chromium	Cr
Copper	Cu
Dichromate	$Cr_2O_7^{2-}$
Dimethyl Mercury	$(CH_3)2Hg^0)$
Ferrous Ion	Fe2+
Hydrochloric Acid	HCl
Hydrogencarbonate	HCO_3
Hydrogen Chromate	$HCrO_4^-$
Hydrogen Peroxide	H_2O_2
Iron	Fe
Manganese	Mn
Mercury	Hg
Methyl Mercury	CH_3Hg^+
Nitric Acid	HNO_3
Selenium	Se
Sodium Hydroxide	NaOH
Uranium	U
Vanadium	V
Zinc	Zn

1 INTRODUCTION

1.1 Purpose of the Study

The current study seeks to characterise tailings storage facility (TSF) material from Khumani Iron Ore Mine through chemical and mineralogical analyses to ascertain the viability of using this material for backfilling unused pits. The purpose of the research study is in line with the environmental obligation of Khumani Iron Ore Mine, to mitigate pollution due to mining, and ensure the safety of the TSF through size reduction. The primary aim of the study is to determine the geochemical behaviour of tailings and the influence of that behaviour on use of the tailings for backfilling disused open pits.

The specific objectives of the study are:

- The characterisation of the TSF material through chemical analyses to identify potential toxic elements (PTEs) which include arsenic (As), lead (Pb), chromium (Cr), nickel (Ni), vanadium (V), uranium (U), selenium (Se), zinc (Zn), copper (Cu) and rare earth elements (REEs);
- The mineralogical characterisation of the TSF material to identify essential minerals in the formation of acid mine drainage;
- To analyse the particle size distribution of the TSF material to ascertain its rheologic performance;
- To determine the physicochemical properties (pH and electrical conductivity (EC)) which influences mobility of PTEs;
- To conduct acid-base accounting (ABA) to determine the nature of drainage likely to be formed when the TSF material subjected to water and oxygen; and
- To conduct geochemical modelling using PHREEQC software to determine the saturation indices of minerals in groundwater which are indicator of the oxidation states of PTEs.

This research is motivated by the need to determine the geochemical evolution that the TSF material will undergo when used for backfilling of the old pits. The laboratory analyses and geochemical modelling will determine the field conditions to ascertain the behaviours of PTEs in the TSF material. Groundwater samples around the existing TSF will be collected to determine the concentration of PTEs and calculate the enrichment factors of identified PTEs.

1.2 Research Background

The increase in environmental awareness and stringent environmental regulations governing extractive industries has triggered the need for initiatives to avert environmental impacts and promote the ecological comfort and health of local inhabitants. Khumani Iron Ore Mine has initiated the need to re-use the tailings material to fill old mining pits for safety, engineering, and environmental reasons. Tailings have been documented as a major source of PTEs to surrounding environments during mining and at closure (Adler & Rascher, 2007).

Several cases of poor management and compromised engineering which led to TSF walls collapsing and compromising the health and safety of local inhabitants and the surrounding environment have been documented in Bolivia (Vlillarroel, et al., 2006), Brazil (Gama, et al., 2020), China (Zhao, et al., 2007), Italy (Pirulli, et al., 2017), Japan (Ishihara, et al., 2015), Romania (Levei & Frentiu, 2009), Russia (Glotov, et al., 2018), South Africa (Fourie, et al., 2000), and Spain (Benito, et al., 2001),

The use of tailings material for backfilling purposes has gained popularity in achieving land restoration (Ivannikov, et al., 2019). Several factors must be considered in the use of tailings material for backfilling, which includes operational costs, geotechnical properties of the material and environmental acceptability.

Thus, the current study seeks to characterise the tailings material of the iron ore mine for the backfilling of the old pits to avert spillages after slope failure and to avoid deforestation by expanding the TSF. This requires an assessment of the tailings material which includes its potential to generate acid mine drainage (AMD) and the determination of PTEs such as As, Pb, Cr, Zn, Cu, Ni, Se and REEs that are likely to be leached. This will include the assessment of the environmental conditions to simulate laboratory procedures such as ABA.

1.3 Research Motivation

The recent catastrophic collapse of Brumadinho TSF in Minas Gerais, Brazil has awakened the mining industry on issues of tailings dam safety, environmental contingency planning and overall proper management of these facilities (Gama, et al., 2020). The failure of TSF walls resulted in tailings slurry spilling over a large area affecting the surrounding environments, and polluting surface waters and soils. These failures also resulted in multiple fatalities over the years (Williams, 2021). Mining companies are taking cognisance that designs of TSFs must consider the site's climatic conditions, topographic and seismic settings Global Industry Standard on Tailings Management 2020 (GISTM), (Williams, 2021).

The current study is an initiative to curb the expansion of the TSF at Khumani Iron Ore Mine by using the current tailings slurry to backfill unused pits. This initiative aims at addressing environmental concerns which include deforestation of land, erosion of tailings fines to rivers and further addresses safety concerns which comes with subaerial tailings impoundments. Lu & Cai (2012) report that backfilling surface mines improves stress distribution and prevents the accumulation of water in pits which can have undesirable health consequences (such as providing breeding sites for malaria-carrying mosquitos). The ever-growing population and need for land for agriculture and settlement had further emphasised the need to remove TSFs by backfilling old mine workings and re-purposing the tailings material (Henderson, et al., 1998). Additionally, some countries or regions have established legal mandates or at least require a thorough assessment to determine the technical and economic feasibility of backfilling mine pits (Earthworks, 2022).

The comprehensive utilisation of TSF materials to backfill disused mine workings may compensate for land shortages and present further environmental and safety benefits (Williams, 2021). The recent spike in incidences of tailings impoundment failures has prompted the need to classify the Khumani Iron Ore tailings material and to further explore its use for backfilling the exhausted pits.

1.4 Problem Statement

The rapid growth of the Khumani Iron Ore mining activities has led to an increase in production to meet market demands and thus, more slurry is produced daily.

This has led to a need to expand the tailings impoundment which in turn might compromise its safety and requires vast land areas for expansion. The increased expansion of the tailings impoundments not only threatens the land availability but also exposes more surface land and waters to contamination. The mine produces 13.5kt of ore annually and 46kt of waste. The current study seeks to determine the mineralogical and chemical nature of the tailings material to understand the ecological risk it may pose when utilised to backfill the unused pits at Khumani Mine.

1.5 Assumptions

The following points highlight the factors that make iron-rich tailings material suitable for backfilling in the Khumani Mine area:

- The iron-rich tailings material is rich in clay minerals, carbonates and silicate minerals which are buffers for AMD. The clay minerals present a high cation exchange capacity of the material, which retain PTEs rendering the material suitable for backfilling without threatening the groundwater.
- Khumani Mine area receives an annual rainfall of 100-200mm yearly with temperatures reaching a low -4°C in winter and a high of 41°C in summer (WeatherSA, 2022)., The region is characterised by low rainfall which will present favourable conditions for the use of tailings material for backfilling the mined pits.
- These conditions include less interaction of water with the tailings slurry that may leach some PTEs due to low rainfall and deeper aquifers due to low infiltrations and high temperatures.

1.6 Previous Work

The environmental impact consequences associated with the collapse of tailings storage facilities have always been a major environmental concern associated with mining. Research conducted by Van Niekerk & Viljoen (2005) showed that the collapse of the TSFs of the Harmony Gold mine in 1994 affected more than 200 households from the Merriespruit suburb. The same study showed that the water systems downstream were enriched with potential harmful elements (PHEs) which impacted the survival of fish species and aquatic plants. In a recent study carried out by Motsau & Van Wyk (2022) in Jagersfontein diamond mine in Free State Province an estimate 300 households from Itumeleng Township and Charlesville were severely affected by the collapse of TSFs and are most likely to suffer ill-health through the inhalation, dermal contact and drinking contaminated water.

A study by Paulelli, et al. (2022) discovered that the population of the Minas Gerais State have been exposed to Al, As, Cd, Co, Cu, Hg, Mn, Ni, Pb, Se, and Zn due to the collapse of the iron-ore Fundao TSFs. The collapse of the Fundao TSFs released more than 43 million m^3 of mine waste dispersed over 600 km through the Doce River which later poured to the Atlantic Ocean (Fourie, et al., 2022). In a related study undertaken in Brumadinho, on the river health of Paraopeba River draining the collapsed TSFs, results showed high concentration of As, Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn was in stream sediments, fish and macrophytes (Parente, et al., 2021). Laureano et al. (2022) detailed that livelihoods inhabitant in the Minas Gerais area were severely affected since the river is their primary source of food and water for domestic use.

The collapse of these TSFs have been associated with poor engineering designs and TSF monitoring and management and has severe environmental consequences on receiving environments. The collapse of the Mount Polley TSFs in Canada in 2014 released large amounts of TSF material into Polley Lake and severely affected the aquatic species and the lake capacity (Bird, et al., 2021) Rehabilitation of contaminated environments due to release of TSF material as results of failures often present a mammoth task almost impossible to achieve (Laureano, et al., 2022).

A recent study by Gupta & Paul (2015b) reviewed the use of tailings material from a coal mine for backfilling old mine workings as a sustainable approach to resolve environmental problems associated with disposal of waste refuse on the surface. According to Gupta & Paul (2015b) the use of tailings material for backfilling old mine workings minimises the piling of waste material in the surface as refuse stockpile and eliminates the risk of erosion of the exposed material thus, reducing land pollution and contamination of stream water. Backfilling disused workings also enhances ground stability, prevents highwall collapses in open pits, and mitigates land subsidence in underground voids (Kesimal, et al., p. 2005). The geotechnical and physicochemical characterisation of the backfilling material influences the viability and suitability for usage in backfilling (Behera, et al., 2021).

River sand has been widely used worldwide in backfilling old mine workings especially underground voids due to its inert grains (Gupta & Paul, 2015a). River sand is easy to mine, the material is characterised by stable geochemical sediments and minimal organic matter presenting suitable geotechnical properties for construction. The use of river sand however has been met with criticism due to overexploitation and destruction of riverine ecosystems (Gupta & Paul, 2015a). The use of tailings material for backfilling has gained traction in recent years due to the high operational cost involved in sand mining (Behera, et al., 2021; Henderson, et al., 1998; Helinski, 2007; Puhalovich & Coghill, 2011). Lu & Cai (2012) echoed the benefit of backfill underground mine voids using tailings material as low operation costs and reduction of exposed mine wastes and elimination of environmental hazards such as air pollution and soil contamination.

Recent research has assessed the viability of the use of TSFs material for backfilling exhausted mine workings (Kesimal, et al., 2002). The use of these mine tailings material however has presented a major environmental concern especially the contamination of groundwater (Gupta & Paul, 2015a). Recently, TSFs from gold mines in the Witwatersrand Basin were investigated for chemical and mineralogical characteristics for environmental and rehabilitation management purposes (Tutu & McCarthy, 2008; Makgae, 2011). It was discovered that the TSFs material contains sulphide minerals that are likely to generate acid mine drainage (AMD) which can contaminate both ground and surface waters Similarly, tailings material from Margherita coal mine in India was characterised by high sulphur content (2-12%) and acidic drainage (pH=2.0-3.0) by Baruah & Khare (2010).

The use of acidic generating tailings material for backfilling presents ecological concerns and prolongs land restoration as it can only accommodate tolerant taxa (Gupta & Paul, 2015b). Nonetheless, Gupta & Paul (2015) urged the usage of tailings material especially the sulphide rich as backfill to reduce surface exposure to oxygen and water which can subsequently lead to acid generation.

Williams (2021) revealed that the use of metalliferous tailings material in backfilling must be coupled with binders to eliminate chemical reactions and further obtain maximal engineering stability. The mixing of tailings material with cement produces higher viscosity which is likely to clog pipelines (Wu, et al., 2013). The method is often accompanied by high operational costs due to extensive maintenance of pipeline required (Fall & Benzaazoua, 2005). It is against this background that a study on the potential usage of the tailings material of the iron ore mine will be carried-out to assess the viability of its use in backfilling disused pits.

1.7 Research Methods

To achieve the objectives of the study, a structured approach ensuring that each aspect of the research is thoroughly addressed will be followed. By integrating a desktop study, field investigation, and laboratory analysis, the methodology aims to cover all necessary facets to understand and evaluate the use of tailings materials for backfilling disused mine workings.

1.7.1 Desktop study

This part of the study involves review of international and local scientific literature on the usage of tailings materials for backfilling disused mine workings. This will also include a detailed literature review of the geology, the climatic conditions, the hydrological characteristics, and the land use of the study area. The review will also explore the methodologies used to assess the physicochemical properties of tailings material for usage as backfill like the objectives to the current study. The desktop study also includes map production of the study area using ArcGIS and Google Earth to determine the sampling sites.

1.7.2 Field investigation

The field investigation involves sampling (water and tailings) including documenting the physical conditions of the collected samples and the surrounding environmental characteristics. Two types of samples (tailings and groundwater) were collected for the purpose of this study. Groundwater sampling methods and sampling handling described by Sundaram et al. (2009) were adopted. Groundwater sampling was conducted to assess the current water quality conditions and monitor the water table over change of season. Tailings samples were collected and handled for laboratory analyses as prescribed by Ixtiyorovich & Abdurashidovich (2022). Tailings material was characterised in the laboratory in terms of potential to generate acid, the chemical and mineralogical and physicochemical characteristics.

1.7.3 Laboratory analysis

Samples were analysed at the Council for Geoscience (Pretoria) for Inductively coupled plasma-mass spectrometry (ICP-MS), cation exchange capacity (CEC), ion chromatography (IC), and batch leach and for X-ray diffraction (XRD) and ABA. These analyses provided detailed insights into the elemental composition, mineralogy, and chemical characteristics crucial for assessing the suitability of tailings material for backfilling.

a) ICP-MS was used to determine the total elemental concentrations of major, minor and trace elements in water and tailings material.

b) Procedures defined by Ross and Ketterings (1995) were adopted for the CEC analyses. IC was be used to analyse major anions (Cl^-, F^-, Br^-,NO_3^{-2} and SO_4^{-2}) as well as the CEC of tailings material.

c) WTW Multi 3430 Digital Multi Parameter Meter were used to determine the pH and EC of water and solution samples. The pH and EC probes was calibrated using buffer solutions with pH values 4.01, 7.00 and 10.01 and standard solution (0.01 mol/ℓ KCl) respectively.

d) Procedures outlined by Skousen et al. (2002) were adopted for ABA. ABA was conducted to measure the potential of the tailings material to produce acid drainage.

e) XRD was used to analyse the mineralogical identities and the mineral phase compositions of TSF samples all of which could influence the pH dynamics of the tailings material. These were included the identification of mineral phases which contribute to the formation of AMD such as iron compounds including pyrite and iron oxides (hematite, goethite, and jarosite). XRD was also used to reveal the presence of carbonate minerals (calcite, dolomite and ankerite), silicates minerals (albite, clinochlore, illite, kaolinite, montmorillonite, muscovite, orthoclase, quartz) and common sulphates (gypsum and melanterite).

1.8 Structure of the Research Report

The research report is structured into five interlinked chapters addressing approaches used to achieve the main aim of the study. Each chapter provides a detailed examination of various aspects of the research, ensuring a comprehensive understanding of the subject:

Chapter 1: This chapter provides background of the study area and the nature of the problem to be investigated including the justification for investigation. The justification for investigation is based on the increase in environmental awareness, a spike in tailings dam failures and the need for more sustainable mining. The chapter also outlines the main aim of the study and specific objectives.

Chapter 2: This chapter details existing literature on the factors considered in the usage of tailings material for backfilling old mining pits. The review also highlights existing scientific knowledge of the environmental concerns which may emanate from the usage of the tailings material in back filling old mine working.

Chapter 3: This chapter details the analytical methods used to achieve each specific objective of the study. This includes the desktop review, field work which included sampling and the handling of samples for laboratory analyses.

Chapter 4: This chapter contains a detailed presentation and the discussion of the results reported in chapter 3. It outlines all procedures and techniques employed during the fieldwork, covering the sampling of groundwater and tailings, laboratory testing and the analysis of the collected data.

Chapter 5: This chapter contains a conclusion based on all the results obtained from the study and provides recommendations based on all the findings. The discussion will be derived from the results of the groundwater characteristics, the pH levels of the tailings and the leaching concentrations.

2 LITERATURE REVIEW

2.1 Introduction

South Africa is amongst the leading world suppliers of metals such as iron, platinum, manganese, chrome and gold, accounting for 7.53% of the GDP (Minerals Council, 2022). Minerals are exploited through various methods including, opencast, underground, alluvial and offshore. Often, high volumes of tailings (comprising sub-economic ore and gangue minerals) are produced in the process of recovering these metals. These low-grade ores are stored in TSFs, have the potential to leach PTEs that can affect surface and groundwater quality and surrounding environments when liberated (Bell and Bullock 1996). Communities around these mining areas often suffer injustices due to contamination because of erosion of TSFs material which often compromise their health (Sibiya, 2019). In recent years, governments worldwide have suffered huge financial losses due to litigation from civil societies and communities over environmental contamination due to mining (Armah et al., 2011; Ishkanian et al., 2013; Tysiachniouk et al., 2018).

Globally, governments are facing a mammoth task to rehabilitate mines that have closed prematurely and whose owners have disappeared without a trace (Sibiya, 2019). These mines continuously release wastes enriched with chemical elements to surrounding environments as they are not maintained (McCarthy, 2011). Poor maintenance of mine workings often results into flooding and formation of drainages which threatens water resources . Poorly rehabilitated TSFs often suffer wind and hydraulic erosion dispersing PTEs to surrounding environments (Kříbek, et al., 2023). Residents from the Witwatersrand area are exposed to PTEs such as U, As, Pb, Cd emanating from the old abandoned TSFs (Mkhize, 2020). Dispersion of PTEs to surrounding environments are dependent on various factors including, rainfall patterns, particle size distribution (Gitari, et al., 2018).

The nature of a TSF is dependent on the nature of the mineral mined and the metallurgical methods used in mineral processing (Kossoff, et al., 2014). The major environmental threat posed by TSFs emanates from dam failures, dust dispersion, leaching of PTEs and erosion (Macklin, et al., 2003). Most recently, more considerations and emphasis have been placed on resultant mine waters from the interactions of rainwater with mine waste (Blowes, et al., 2014; Wilson, et al., 2019). As mentioned in Section 1.4, the size of the TSF at Khumani Mine is increasing significantly due to the high mill production rate of 13.5kt per annum. This trend is common in large operating mines worldwide with a boom in demand for mineral commodities and often presents a challenge in ensuring the stability of TSFs due to the high waste deposition rate (Morgenstern & Kupper, 1988). Increased production rates, especially of open-pit mines, have also presented challenges to land availability over the years due to the increased volumes and sizes of both pits and TSFs (Ferreira & Leite, 2015).

Several scholars have explored the usage of TSF material to backfill old mine workings for environmental and economic considerations (Henderson, et al., 1998; Puhalovich and Coghill, 2011; Ivannikov, et al., 2019). The safe use of these TSF materials is dependent on the consolidation and the geochemical behaviour of the material which includes capacity to generate AMD, cation exchange capacity and leachability of PTEs (Kossoff, et al., 2014; Ivannikov et al., 2019).

Several scholars have emphasised the use of binder cement to ensure and maintain stability and eliminate the undesired chemical reactions including the oxidation of sulphide minerals (Thomas & Holtham, 2021; Kesimal et al., 2005; Helinski, 2007). The successes and failures of the usage of TSF material to backfilling old mine workings have been documented in Coroner's Report (2001), Baldwin (2004), Landriault (2006) and Revell and Sainsbury (2007). Belem (2004) stated that the success of backfilling a mine stope is based on the rheological and strength performance of TSF material, which is influenced by particle size distribution, suitable binder to ensure effective consolidation of the paste with the mine stope, and the used mechanism which involves gravity and water.

2.2 Iron Ore Extraction and Beneficiation

The extraction of iron ore is performed through surface mining which employs blasting of ore blocks and heavy diesel-driven machinery for haulage (Ferreira & Leite, 2015). The same author also mentioned that surface mines are characterised by high production and low safety risk compared to underground mines but often present major environmental hazards such as dust and TSF failures. Recovered ore from the blast undergoes processing, further particle size reduction through electrically driven primary and secondary crushers, and latter metallurgical segregation through gravity and magnetic separation (Seifelnassr et al., 2012; Wills and Finch, 2016; Özcan, et al., 2021).

The gravity separation is done through jigging technology for low grade ores (Panda & Buwa, 2017). Ore particles are separated based on physical laws of gravity and density (Rath & Singh, 2007). The jigging technology recovers ore particles of density greater than 4.6 t/m3 as product and rejects ore particles with densities below 4.6 t/m3 (Özcan, et al., 2021). Silica rich waste generated at the processing plants are transported into thickeners as slurry for water recovery before disposed into TSF dams (Behera, et al., 2021).

2.3 Chemical Composition of Iron Ore Mine TSF

The nature of these TSF varies from place to place depending on the depending on the geology and mineralogy of the iron ore deposit but often contain PTEs which include Pb, As, Hg (Lottermoser, 2010). Comparison of the chemical composition of the iron ore TSF from Australia, south India and north India showed similar chemical composition (Ferreira & Leite, 2015). The nature of the technology employed in the crushers, screens and mills influences the recovery of the product and the nature of the waste material. According to an inventory study by Ferreira and Leite (2015) mine wastes from Samarco Mineraçao in Brazil showed presence of Cd and As and appear as a soil contaminant in surrounding areas. Sidkina et al. (2022) reported high contents Fe, Zn, Cu, Pb, Cd, and Ni at the Lupikko iron mine area in Russia.

Most of the iron ore TSF dumps are dominated by silica mineral phases at an average of 75 percent (Ferreira & Leite, 2015). The same author also mentioned that the concentration of silica minerals in iron ore TSF dumps corresponds to the mineralogical characteristics of the processed ore. The geochemical enrichment of silica minerals is also influenced by its resistance to weathering compared to other minerals, especially sulphide minerals (Akcil & Koldas, 2006). Sulphide minerals are often depleted in the TSF materials as they undergo oxidation in the presence of oxygen and water leaving behind secondary minerals including gypsum ($CaSO4.2H2O$) and jarosite ($KFe3(S04)(OH)6$) (McCarthy, 2011). Sulphide minerals are often depleted on the TSF surfaces due to continuous chemical weathering (Akcil & Koldas, 2006).

Donskoi, et al. (2021) reported a high percentage of hematite, magnetite, larnite, and aluminosilicates in TSF material which are likely to affect the water chemistry and leaching of PTEs. According to Gutzmer et al. (2008) the iron ore mined at Khumani Iron Ore Mine is comprised of hematite, martite and magnetite and is likely to have high SiO2 values which corresponds to the high silica (up to 60.1 wt%) hosted in the banded iron formations (BIF). Low grade ores are mined with carbonate successions which are blended with iron rich grade to obtain the required 64% and above iron grade as per customer specifications (Van Schalkwyk & Beukes, 1986). These carbonates are removed through beneficiation at jigs and deposited as slurry at the TSF and are most likely to control the acid-neutralisation capacity of the TSF material (Du Toit & Crozier, 2012).

2.4 Common Factors Controlling Leaching of PTEs

The behaviour of PTEs in tailings material is dependent on various factors including grain size distribution, water table change, infiltration rates of oxygen and water, and temperatures of TSFs (Yibas, et al., 2012). The various components of TSFs material are strongly influenced by the nature of the orebody exploited and its mineral associates and the technique employed for mineral extraction (Chen, et al., 2017). Other environmental variables controlling the leachability of PTEs in TSFs besides the geological conditions includes amongst the climatic conditions, biological activities and pH (Schowe et al., 2013; Lindsay et al., 2015; and Najafi & Jalali, 2016). PTEs in TSFs undergo chemical interactions to form complex chemical compounds (Akcil & Koldas, 2006).

2.4.1 Influence of geological material

Iron is recovered as hematite and limonite which is associated with iron sulphide minerals such as pyrite, arsenopyrite, pyrrhotite and chalcopyrite which present are associated with acid generation (Soltani, et al., 2017). AMD is formed through the oxidation of the sulphide minerals on exposure to oxygen and water (Canovas et al., 2007; Zhao et al., 2007). The reaction rate of the oxidation of sulphide minerals is catalysed by temperature, pH, humidity and micro-organisms (Komnitsas & Modis, 2006). Dlamini et al. (2013) reported evidence of acid mine drainage at the abandoned Ngwenya Iron Ore Mine in Swaziland derived from the two oxidations of Fe compounds in haematite and pyrite. Hakkou et al. (2008) reported 1.6 - 14.5 wt% of sulphur and carbonates of less than 1 wt% in tailings from the abandoned Kettara iron sulphide mine in Morocco which has been generating acid mine drainage for more than two decades.

The formation of AMD enhances the leaching PTEs such as Al, Fe, Cu Sb, As, Cd, Mo, Se, and Zn (Bell & Bullock, 1996; Ogola, 2010). Soltani et al. (2017) revealed the presence of these PTEs in tailings samples collected at the Gol-E-Gohar iron ore mine in Iran which were later revealed in soils and stream waters in the surrounding area. High levels of Fe and As in Nan-tank-pauk stream in Myammar have forced the suspension of mining operations in the Pinpet Fe deposit (Zay Ya, et al., 2020). According to Zay Ya et al. (2020) haematite ore deposits with as little as 2 wt% of sulphur have been reported to trigger acid generation.

Rösner (1998), reported that the liberation of PTEs in acid generating TSF continues until the sulphur-bearing minerals are exhausted. These oxidation zones, typically found in arid and semi-arid regions, are characterized by hardpans and salt layers formed from the precipitation of iron hydroxides (DeSisto, et al., 2011). DeSisto et al. (2011) further stated that some precipitate layers are a barrier which inhibits leachability of PTEs. These precipitate layers form when iron hydroxides and other minerals precipitate out of solution during the oxidation of sulfide minerals. This process typically occurs in the oxidation zones of sulfide ore deposits, where the exposure of sulfide minerals to oxygen and water leads to the formation of acidic conditions. The acidic environment promotes the dissolution of iron and other metals, which then precipitate as hydroxides or other mineral phases, creating a hardpan or crust. These precipitate layers can effectively trap PTEs, preventing them from leaching into surrounding soils and groundwater. Dauvalter (2019) revealed that the iron ore Olkon operations in Murmansk (Russia) have liberated PTEs into surrounding water bodies, altering the total dissolved solids. This was attributed to the continuous oxidation of the iron sulphide minerals in the mine wastes which amongst other altered the water type from hydrocarbonate to sulfate (Dauvalter, 2019).

On the contrary, the presence of buffering minerals such as $CaCO_3$, $Al(OH)_3$ and NaOH in TSFs promotes the generation of neutral mine drainage with pH values ranging between 6.5 to 7.5 (McCarthy, 2011). Lindsay et al. (2015) alluded to the fact that all TSFs contain buffer minerals, however the continuous oxidation of the sulphide minerals depletes the TSF buffering capacity hence the formation of AMD. The generation of aqueous carbonates species in a TSF is controlled by the grain size of the waste material which is a significant factor in surface area reactions (Gray, 1997). Klebercz et al. (2012) further stated that the precipitation of Fe^{3+} in sulphide bearing tailings wastes accounts for limited surface areas for carbonate dissolution. A geochemical risk assessment of TSF material from Rio Tinto's Pilbara Iron Ore Mines conducted by Green & Borden (2011) revealed that the material has Acid Neutralising Capacity (ANC) of up to 885 kg H_2SO_4/t. Similarly, TSF material from the iron ore mine of Boukhadra in Algeria was characterised by a high concentration of calcite 34.56 wt % which is likely to generate neutral drainage (Rouaiguia, et al., 2021).

Neutral mine drainage generated from carbonate ($CaCO_3$) rich TSFs contains high concentrations of divalent cations (for example, Ca and Mg) and most likely to mobilise PTEs such Fe^{2+}, Zn and Cd (Brunori, et al., 2005). Neutral mine drainage occurs when concentrations of acid-generating and acid-consuming materials are equal and the sulphide oxidation is weak (Heikkinen, et al., 2009). The increasing salt concentrations due to precipitation of iron hydroxide and alumina silicates increase competition for sorption sites on solid surfaces resulting into less effective cation exchange capacity. Clay colloids and hydroxides influence the cation exchange capacity of the tailings material (Choe, et al., 2008).Tailings which are rich in clay minerals act as retention of PTEs thus reducing their mobility (Choe et al., 2008).

The rate of generation of aqueous carbonates species in a TSF is controlled by the grain size of the waste material which is a significant factor for the surface area reactions (Strömberg & Banwart, 1999). Furthermore, oxyanion-forming elements such as Al, As, Cr, Mo and V are soluble under neutral conditions (Heikkinen, et al., 2009). Neutral drainage containing significant metal concentrations can pose a threat to aquatic ecosystems, affecting aquatic life, water quality, and overall ecosystem health (Nriagu, 1996; Tipping, et al., 2011). An early study by Benzaazoua, et al., 1999, revealed that the backfilling of the old mine stopes in the Abitibian mines in Quebec, Canada suffered a major setback as the material oxidised. According to Benzaazoua, et al. (1999) the sulphide rich tailings material underwent chemical changes which resulted in the degradation of the backfill tailings. Benzaazoua et al. (1999) recommended the use of a calcium-rich binder when backfilling sulphur-rich tailings to alleviate sulphur attack which will compromise the strength of the backfill material. The understanding of geochemical processes is crucial for assessing potential risks and optimising backfilling strategies in both underground and open-pit mining.

2.4.2 Influence of pH

Sulphur-oxidation influences the generation of acid mine drainage in tailings material thus influencing the mobility of PTE (Bosecker, 1997). According to Salomons (1995), low pH values are derived from the liberation of H^+ in sulphide-rich tailings material. The lowering of the pH values due to acid formation which contributes to the leaching and mobility of the PTEs except for Mo which is more mobile in neutral alkaline conditions. Munyai et al. (2016) echoed that PTEs, such as Fe, are leached out and mobilised into the environment under low pH conditions. The formation of AMD on TSFs intensifies the concentration of PTEs which strongly adhere to Fe oxyhydroxides (McCarthy, 2011). High concentrations of Fe, Al, and Mn species under acidic conditions present a suitable substrate for the adsorption of As and P species (Alloway, 1994). As and P species are less mobile in acidic conditions compared to the alkaline conditions (Lee, et al., 2005).

The capacity of TSF material to resist acid generation controls the fate of heavy metal solubility and mobility (Curtin & Trolove, 2013). There is very little literature on neutral mine drainage relative to acid mine drainage (Kirby & Cravotta III, 2005). Geochemical analyses of a TSF at Luikonlahti, Finland, which was conducted by Heikkinen et al. (2009) revealed that low sulphide-containing tailings material produces neutral mine drainage due to a high concentration of buffer minerals. Acid mine drainage in the Gol Gohar iron ore mine in southern Iran investigated by Jahanshahi and Zare (2015) are characterised by high concentration of Al, As and

Mn. Most PTE which include Pb, Cd, Ni and Cu precipitate and are rendered immobile under high pH conditions (De Giudici, et al., 2017).

2.4.3 Influence of climatic conditions

Climatic conditions control the rate at which PTEs undergo chemical change (Ogunkunle, et al., 2013). The redox reactions in tailings are somewhat controlled by climatic conditions which influences water availability, temperatures and biological activities (Sracek, et al., 2018). More PTEs are leached in TSFs in tropical areas with high temperatures and rainfall (Lindsay, et al., 2015). Earlier Alloway (1994), documented that chemical weathering is more rapid in wet areas with humid conditions than in arid areas. Wet climates result in sufficient water in tailings which releases H^+ ions that form weak acids which increase the solubility of PTEs and act as a conduit for chemical species formed through surface runoff or ground infiltration (Bourg & Loch, 1995). In India, Krishnaswamy et al. (2006) documented a severe leaching of PTEs from the Kudremukh iron ore mining tailings to the surrounding Bhadra river because of intensive rains of the monsoon seasons of 2002 and 2003.

2.5 Toxicity of Chemical Elements

Chemical elements are rendered toxic at defined concentrations when they give rise to negative health effects in both flora and fauna (Soltani, et al., 2017). Chemical elements enter trophic levels through various pathways which include water, food crops, inhalation and dermal contact (Hosseini, et al., 2018). A study in the province of Ardabil in northern parts of Iran has shown that inhabitants growing crops in soils around an abandoned iron ore mine are at risk of exposure to As, Pb, Ni, Cu, Co and Cr through crop consumption (Hosseini, et al., 2018). Diami et al. 2016 reported high concentrations of Fe, Mn, Cu, Zn, Pb, Cr, Ni and Cd in soils near an abandoned Bukit Ibam iron ore mine in Pahang, Malaysia, consequent to the erosion of the TSF. Similarly, Badhdady et al. (2018) revealed high concentration of Ba, Cr, Cu, Fe, V in soils used for agricultural purposes near Bahariya Oasis iron ore in Egypt. Soltani et al. 2021 reported high concentration of Cu, Fe, v, Co, Ni and Zn in dust samples near Gol-E-Gohar iron ore mine in Iran.

Maseki, et al. (2017) revealed that the communities Krugersdorp living at the vicinity of the TSF dumps in the Witwatersrand are at risk of contracting respiratory related complications through dust inhalation from the poorly rehabilitated TSF dumps. Omoniyi (2017) assessed the degree of contamination of soil and water near the abandoned Itakpe iron-ore mines in Nigeria and revealed enrichment of these resources with Fe, Mn, Zn, Cu, Ni, Cd, Cr, Co Pb and As. Omoniyi (2017) revealed that usage of surface water from areas draining the abandoned Itakpe iron-ore mines may induce health implications. The collapse of Fundao Dam, elevated concentration of As, Cr, Cu, Ni, V and Zn in Doce River Basin over an area of 15 km^2 (Dávila, et al., 2018). Several studies have revealed high Fe concentration in sediments in streams draining iron ore mines due to poorly managed TSF (Soltani, et al., 2021).

2.6 Geochemical Behaviour of Specified Trace Elements

This section discusses the common PTEs in iron ore tailings and their geochemical behaviour as per literature review. This will include PTEs such as As, Pb, Cr, Zn, Cu, Ni, Se, and REEs which are prone to leaching.

2.6.1 Arsenic

Arsenic is most abundant as arsenopyrite and it occurs as orpiment (Garelick, et al., 2008). Typical examples are: the siderite mineralization in the Sava Caves in the Western Karavanke Mountains of Slovenia (Kos, et al., 2022), Kudremukh mine in India (Krishnaswamy, et al., 2006), Samarco mine in Brazil (Pereira, et al., 2008) and iron oxide–apatite deposits in Bafq District of Iran (Majidi, et al., 2021). In nature, As takes the form as As^0, As^{+3}, As^{-3} and As^{+5} of which mobility or stability is strongly influenced by Eh and pH in aqueous solutions (Smedley & Kinniburgh, 2002). Sulphide minerals mainly arsenopyrite, undergo oxidation to Fe oxides under aerobic systems releasing As and sulphate ions. Arsenates in solution are stable at high Eh compared to arsenite species with As^0 species are stable at very low Eh. The arsenate in acidic TSFs shows low mobility as they are adsorbed onto hydrous Fe, Mn and Al oxides and clay and calcite substrates (Brannon and Patrick, 1987). Adsorption of arsenite is very effective in circum-neutral pH of TSF between 7 to 9. In anaerobic conditions, As species co-precipitate and can be released into the aqueous solution by the dissolution of Fe and Mn oxides (Brannon & Patrick, 1987).

2.6.2 Mercury

In nature mercury occurs as inorganic Hg^{2+} and elemental mercury (Hg) (Duffus, 2002). Reports of occurrence of Hg in iron ore mines have been documented in the Upper Peninsula of Michigan, USA (Al Rahbi, 2021) in taconite in the Mesabi Iron Range of the USA (Berndt & Engesser, 2005) in banded iron formation (BIF) at Rio Tinto's Pilbara Iron Ore Mines Western Australia (Green, 2009). Most Hg in iron ore waste is released during the pyrite oxidation minerals in the presence of oxygen. Hg in the TSF dumps undergoes biological reactions subsequent to percolation of organic matter from the surface of the TSFs to form the more toxic methylmercury (CH_3Hg^+) and dimethyl mercury (CH3)2Hg0) (King, et al., 2000; Kritee, et al., 2009). Under alkaline pH conditions, Hg forms high stable complexes in organic rich substrates which are characterised by low solubilities. Hg has a high affinity to the highly soluble OH− and Cl− ligands leading to high Hg mobility, and this is prevalent under acidic conditions.

2.6.3 Cobalt

Cobalt in tailings material occurs in the oxidation state of +2 and +3. Mobility of Co species is minimal in oxidised environments as they strongly absorb to on Mn-oxides. Co also occurs with Fe species and normally replaces the Fe in oxides structures. Co is highly mobile under low pH conditions due to decreased sorption. Under alkaline conditions, Co sulphides precipitates thus inhibiting mobility.

2.6.4 Chromium

In tailings material chromium occurs in the state Cr (III) and Cr(VI). The hexavalent chromium at pH less than 6.5 are as chromate ion $HCrO_4^-$ and dichromate $Cr_2O_7^{2-}$ at high pH. Cr is immobile in low pH conditions due to increased sorption on Fe-oxides substrates and silicate clays. Cr^+ occurs with Fe species and often replaces them in the crystal lattice. Cr hydroxides and oxides precipitates in high pH conditions rendering them insoluble, stable and immobile. $HCrO_4^-$ is less adsorbed by tailings constituents with lower organic content and its mobility is higher under acidic conditions compared to alkaline conditions.

2.6.5 Copper

Copper mainly occurs in tailings in the oxidation state of Cu^{2+} (cupric) and reductive states Cu^{+} (cuprous). Cu^{+} form insoluble minerals such as CuS under reducing conditions thus reduced mobility. Under oxidation conditions, cupric absorbs into Fe-, Mn- and Al oxides in most colloidal tailings materials rendering it immobile especially under increased pH of the tailing material. Adsorption increases with increasing soil pH. Copper complexes that form at very high pH show lower adsorption and therefore more mobile.

2.6.6 Nickel

Ni occurs in the oxidation state Ni^{2+} and reductive state Ni^{+}. Like Cu, Ni is stable as Ni^{+} in the tailings. Under oxidation conditions Ni adsorbs onto Fe-, Mn-oxides, silicate clays and organic matter. Ni is highly mobile under acidic environments as compared to neutral to alkaline conditions.

2.6.7 Zinc

Zinc occurs in tailings in the oxidation state of 2+. Zn^{2+} adsorbs onto various organic and clay colloidal surfaces and is highly soluble and mobile in acid condition. In neutral media, the mobility of Zn^{2+} is reduced as it adsorbs Al-oxides to form stable chemical complexes. Under alkaline conditions high concentration of Zn^{2+} forms soluble compounds of Zn-organo and Zn-hydroxyl anions which increase mobility. However low concentrations of Zn^{2+} under alkaline conditions forms insoluble precipitates of Zn-oxide, hydroxide and hydroxycarbonate.

2.7 Environmental Considerations

The awareness of environmental contamination arising from release of PTEs from mine wastes have gained worldwide traction and scholars and lawmakers are grappling to find sustainable solutions to alleviate damages to limited water and land (Parente, et al., 2023). The recent spikes in collapse in tailings dams have seen vast areas contaminated with mine wastes which includes rivers and agricultural lands (Parente, et al., 2023). Contaminants released from the mine wastes are often persistent and require substantial financial capital for clean-up and land restorations (Zay Ya, et al., 2020). Governments in many countries are struggling with environmental contamination as a result of mines which prematurely closed and owners who cannot be traced (Sibiya, 2019). More stringent policies have been developed by governments to govern mines during and post closure (Zay Ya, et al., 2020)

There are few studies in South Africa which looked at the usage of mine waste for backfilling open mine workings (Dill, et al., 2007; Falayi, 2018). Other studies in South Africa explored the usage of mine wastes for other purposes other than backfilling such as brick manufacturing (Ogola et al., 2017; Sibanda & Broadhurst, 2018). Studies by Benzaazoua et al., (2008) and Belem et al., 2000 are insightful on the viability of using tailings material for backfilling old mine workings.

The National Environmental Management: Waste Act No.59 of (2008) (NEM:WA) requires classification of waste material prior to disposal to determine the ecological risk for contamination level values of PTEs in soils, water, groundwater and atmosphere. Various maximum permissible content of PTEs have been set for various spheres of the environment aiming at triggering interventions to avoid harm to ecological functions and latter human health calamities. Any rehabilitation efforts to rehabilitate mine wastes must be compliant with standards set by the Department of Mineral Resources and Energy (DMRE) prescribed under various sections of the Mineral and Petroleum Resources Development Act (MPRDA) of 2002 to ensure healthy well-being of humans long after mining ceased. These include ensuring that the tailings facilities are stable with minimal risk of collapsing, and well vegetated to avoid erosion of fine material to surrounding water bodies and air and ensuring that soils and water resources (including groundwater) are protected from pollution (NEM: WA Act No 29 of, 2008).

According to the NEM: WA Act No 59 of 2008, wastes generated from mining activities are classified under as hazardous waste (Category A). Environmental Protection Agency of the USA (2023) defined hazardous wastes as *“wastes with properties that make it dangerous or capable of having a harmful effect on human health or the environment”.* According to the NEM: WA Act No 59 of 2008, hazardous wastes as “*waste that contains organic or inorganic elements or compounds that may, owing to the inherent physical, chemical or toxicological characteristics of that waste, have a detrimental impact on health and the* *environment”*. Hazardous wastes are then classified according to the potential to contaminate the environment (example, air, water, and land).

This classification involves standardised scientific assessment methods which include identification of the waste and chemical sampling; chemical analyses in a lab accredited by the South African National Accreditation System (SANAS) for total elemental concentration using inductively couple-plasma spectrometry; leachable concentration analysis based on the Australian Standard Leaching Procedure (ASLP) (AS 4439.1, 4439.2 and 4439.3) to determine the leachable concentrations (LCs) and comparing them to total concentration threshold (TCT) leachable concentration threshold (LCT) from NEM: WA Act No.59 of 2008; Classification is done based on the analytical results in order to ensure safe handling of the waste and proper disposal as per criteria prescribed by NEM: WA Act No.59 of 2008.

In conclusion, the literature review conducted sheds light on the complexity surrounding the management of mine tailings. The extraction and processing of iron ore generate significant volumes of tailings, which can pose environmental and health risks due to their potential to release PTEs into surrounding ecosystems. Multiple factors, including the geology, the climate, the geochemical composition of tailings and the presence of specific minerals influence the leaching behaviour of PTEs. Efforts to mitigate the environmental and health risks associated with mine tailings include exploration for other uses such as backfilling old mine workings and implementing regulatory frameworks in order to manage mine waste effectively. However, challenges remain, particularly in addressing the legacy of abandoned mines and the financial liabilities associated with their rehabilitation.

3 STUDY AREA

3.1 Description of the Study Area

This section presents an overview of the study area. It focuses mainly on the physical and geological characteristics of the area which include the geographical location, climate, topography, vegetation and the geology.

3.1.1 Locality and site history

The Khumani Iron Ore Mine is an opencast mine situated in the Northern Cape Province of South Africa, approximately 30 km west of Kathu in the farms Parsons 564, Bruce 544, King 561 and Mokaning 560 as shown on Figure 1. The Khumani open pits are adjacent to Kumba Iron Ore's Sishen mine (Kadzviti, 2022). Khumani mine is a property of Assmang Limited which is owned jointly by African Rainbow Minerals Limited (ARM) and Assore Limited.

Khumani mine commenced in 2007 producing over 10 million tonnes of ore at 64.2% iron and over 40 million tonnes of wastes per annum (Kadzviti, 2022) . To date, a tailings dam of a capacity of approximately 1 152 094 m^3 has been established. The increased demand of iron ore has resulted in the need to expand the current tailings dam facility, requiring a land of over two hectares.

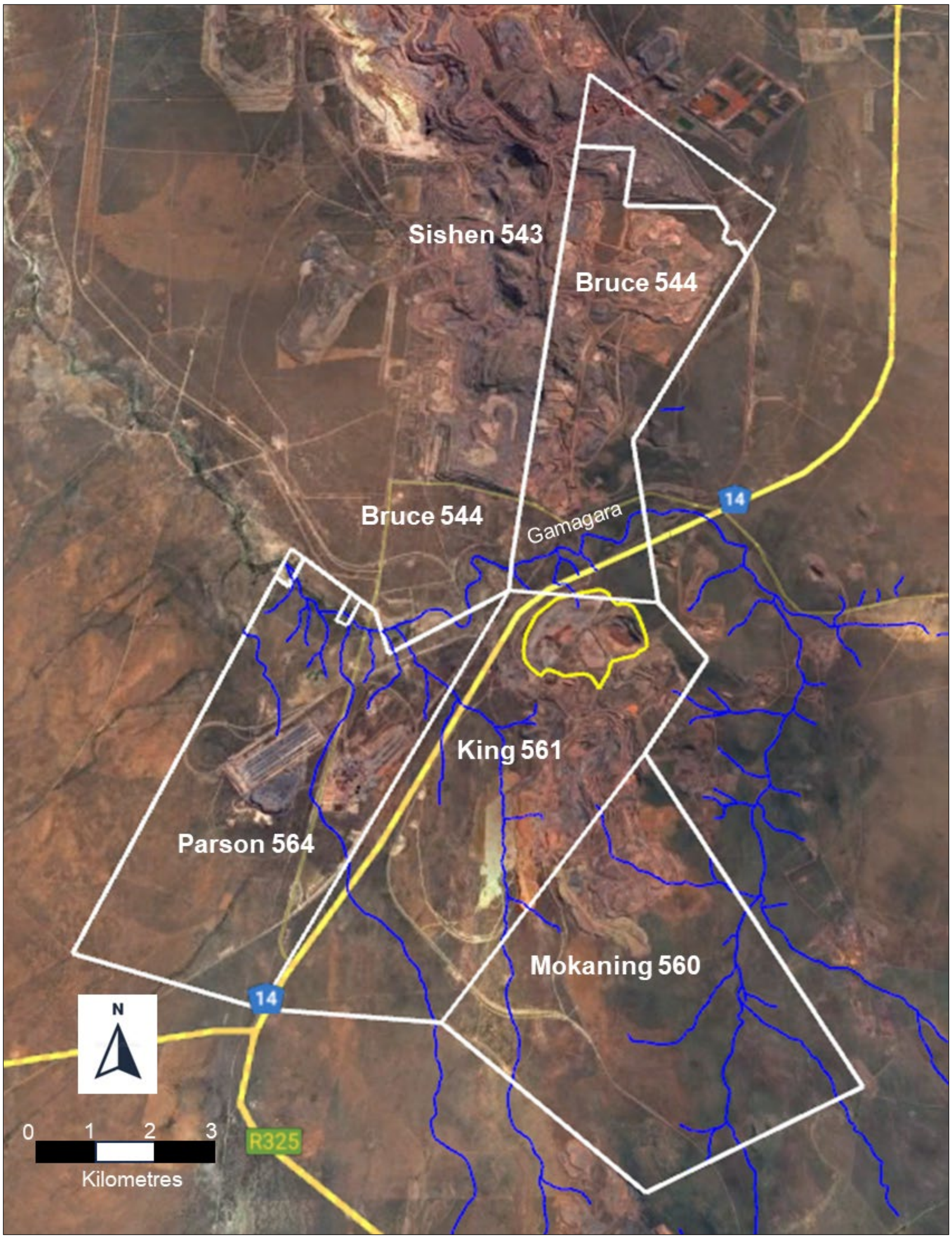


Figure 1. Locality Map of Khumani Mine showing the Khumani TSF August 2023 (Google Earth Image)

3.1.2 Climate

The mining area is typical semi-desert to desert conditions, with temperatures averaging between 20.3°C to 40ºC in summer and 2°C to 18ºC in winter. The area receives annual summer rainfall of approximately 161mm, occurring mainly between December and March. The high temperatures and minimal rainfall in the region have seen high evaporative rates, deeper water tables and low water levels both in dams and rivers. The area is characterised by high velocity dry winds (up to 18.6 km/h) of north, southeast and northeast direction mostly in the month of November (Atlas Weather, 2023).

3.1.3 Topography and drainage

The topography around Khumani Mine is characterised by an undulating slope, with the highest elevation of 1270 m above mean sea level (amsl) on the southern portion of farm Bruce and the lowest elevation of 1200 m (amsl) in the floodplain of the Gamagara River (Bekker, 2019). The mining area falls within the Lower Vaal Water Management Area which supplies water through the Sedibeng Water Supply Scheme into mining and industrial sectors from the Vaal Gamagara Water Treatment Plant near Delportshoop. The Khumani Mine is drained by the Gamagara River, which runs between the eastern valley of King Farm to west north of the Parson Farm and joins Kuruman River in the north of the mine as shown in Figure 1. There are few tributaries running from the tailings dam and mining pit areas feeding into the Gamagara River (Bekker, 2019). Dominant primary activities along the Gamagara River includes other iron ore mines (Sishen, Afrimat and Mikhovhe mines), diamond (Baken mine) and manganese mines (Mokala mine), livestock farming, and rain fed cultivations. The Gamagara River is mainly periodic (or intermittent) characterised by unreliable water flows, as a result, endpoint users along the river heavily rely on groundwater for waters (Piesold, 2005).

3.1.4 Vegetation

The study area is located in the Savanna Biome of South Africa and Swaziland, characterised by the Kalahari Thornveld, Shrub Bushveld type and Kathu Bushveld type (Mucina & Rutherford, 2006). This biome borders with the Nama-Karoo Biome on the central plateau, the Grassland Biome at the eastern seaboard and in the Eastern Cape. The vegetation cover is dominated by open tree layers of *Vachellia erioloba*, *V. karroo, Searsia lancea* and *Ziziphus mucronate* and shrub layers of *Grewia flava* and *Tarchonanthus camphoratus* (Mucina & Rutherford, 2006).

3.1.5 Geology

The study area underlain by sedimentary rocks of the Transvaal Supergroup overlaid by the Koegas and Asbesheuwels Subgroup of the Griqualand West Basin in the Maremane Anticline as shown in Figure 2 (Carney & Mienie, 2003). Transvaal Supergroup is represented by the Kanye, Griqualand West and Transvaal Basins which are separated by the Vryburg Rise (Beukes, 1983). The Griqualand West Basin borders with the Keis Terrane Province in the northern part and Namaqua-Natal metaphoric provinces in the southern part. The base of the Griqualand West Basin consists of mixed volcano-clastic of the Schmidtsdrift Subgroup which is overlaid by the Ghaap and Chuniespoort Group (Beukes, 1983).

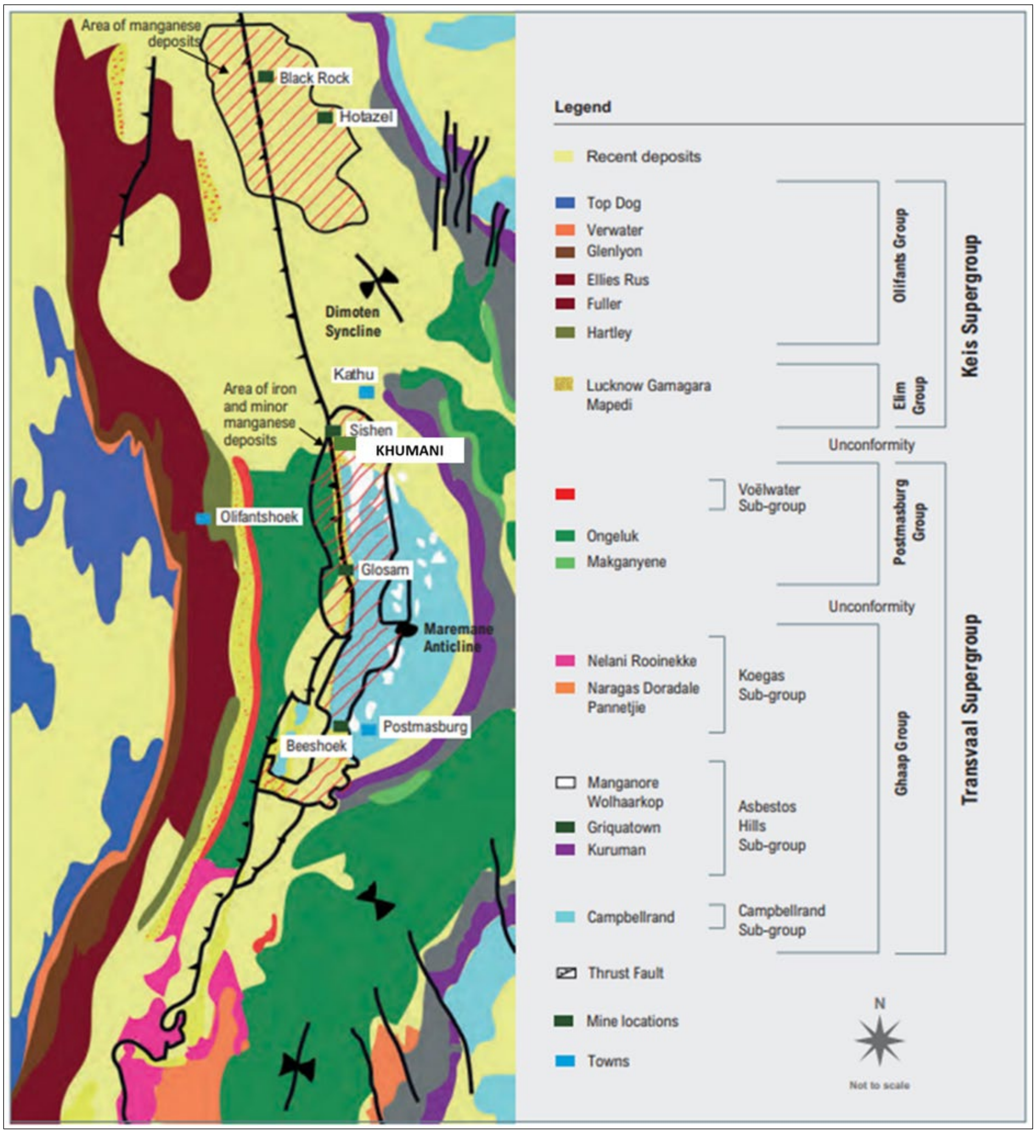
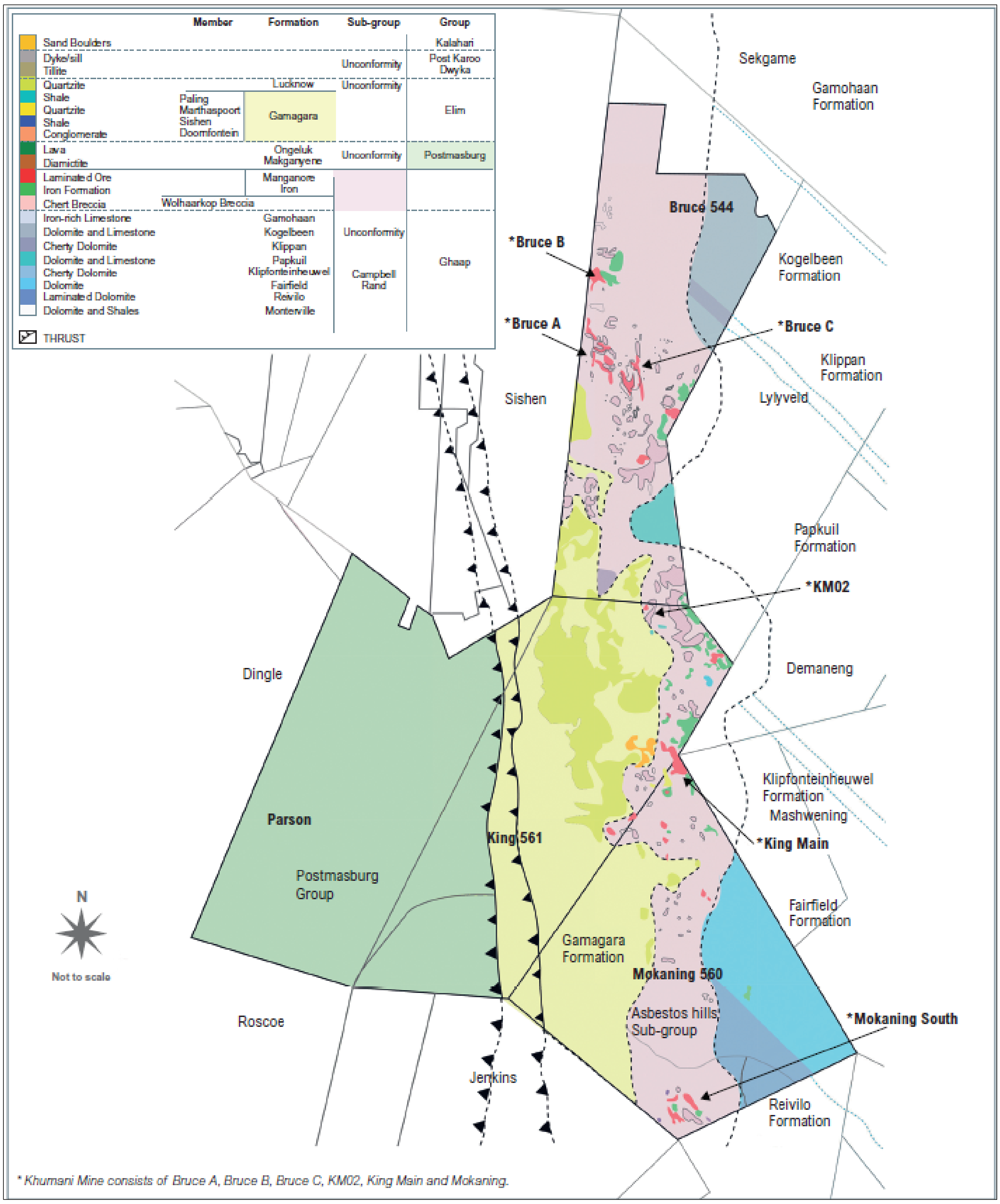


Figure 2. Regional Geological Map of the Griqualand West Basin in the Maremane Anticline (Carney & Mienie, 2003)

The Ghaap Group and the Chuniespoort Group are overlaid by the younger Postmanburg Group and the which is covered by the younger Pretoria Group

(Sumner & Beukes, 2006). The Schmidtsdrift Subgroup consists of the Vryburg, Boomplaas and Lokammona Formations (Beukes, 1983). The Vryburg Formation consists of basal conglomerates and basaltic lavas and varies in thickness between 100 m in the south-westerly and 340 m north-east (Altermann & Siegfried, 1997). The Boomplass Formation mainly consists of oolites and stromatolites overlaid by the siderite lutites and micrite of the Lokmmona Formation.



* Khumani Mine consists of Bruce A, Bruce B, Bruce C, KM02, King Main and Mokaning.

Figure 3. Khumani Surface Geology Map (Kadzviti, 2022).

The Schmidtsdrift Subgroup is overlaid by stromatolites of the Campbellrand Subgroup (Altermann & Siegfried, 1997). The stromatolites limestone of Campbellrand Subgroup consist of the Monteville, Reivilo, Fairfield, Klipfontein Heuwel, Papkuil, Klippan, Koggelbeen, and the Gamohaan and are overlaid by the superior-type iron formations of Asbesheuwels Subgroup (Sumner & Beukes, 2006). The Asbestos hills Subgroup consists of Kuruman Iron Formation (Kliphuis, Groenwater, Riries, and Ouplaas Members) and granular iron formation of Griquatown which host the iron ores mined at Khumani Mine (Gutzmer, et al., 2008) as shown in Figure 3. This iron ore rich Formation is overlaid by mudstones, quartzite and siltstones of the Koegas Subgroup (Beukes & Gutzmer, 2008).

3.1.6 Pedology

The undulating slopes of the mine property are highly characterised by outcrops of quartzite and iron ore bearing rocks Wiehahn, L. (2022). As a result, weathering is minimal and soil horizons are shallow to non-existent. Soils in these undulating steep slopes occur as orange sand pockets as deep as 1 m and are classified as Mispah Form. The gentle slopes of the mine property are characterised by calcrete and dolomite and isolated boulders outcrops and soil formed in these parts of the mining areas are classified as Plooysburg Form with horizons between 0,3 m to 2 m Wiehahn, L. (2022). The same author also mentioned that on the lower slopes, the soil pockets in boulders moved through mass movement by gravity from the upper slopes is classified as Hutton Form.

3.1.7 Hydrogeology

The groundwater resources occur in Quaternary catchment and the occurrences vary greatly due to complex geological formations and elevation effects (Relou, 2017). Three identified aquifers in the mining area comprise of:

1. Kalahari Group Sediments – These occur in the north central part of the Quaternary catchment and are shallow with have a high-water retention potential. The sediments are characterised by small to fine grains of sands gravel and calcrete, with low permeability and inhibits the flow of water.
2. Banded Ironstone Formation (BIF) - These aquifers are confined to the eastern region of the Kuruman Hills and underlie the dolomite karst aquifers in specific areas of the Khumani mine. The BIF exhibit characteristics of

being highly weathered and fractured, facilitating borehole yields exceeding 45 l/s for 24 hours per day.

3. Dolomite karst aquifers – These aquifers are classified as unconfined- to confined- aquifer system in between aquitards dolerite dykes which normally occur perpendicular to the groundwater flow. Fully recharged karst aquifers can support borehole blow yields of over 40 l/s for 24 hours per day.

In summary, the tailings dam highlights the scale of waste management challenges faced by Khumani mine. The region experiences semi-desert to desert conditions, with extreme temperatures and minimal rainfall, necessitating careful water resource management. The topography is characterized by undulating slopes, while the vegetation comprises predominantly savanna biome flora. Geologically, the area is underlain by sedimentary rocks of the Transvaal Supergroup, hosting significant iron ore deposits within the Griqualand West Basin. Soil formation is limited due to the prevalence of quartzite and iron ore-bearing rocks, with shallow to non-existent horizons. Groundwater resources, vital for both mining and local communities, are found in various aquifers, including Kalahari Group Sediments, Banded Ironstone Formation, and Dolomite karst aquifers. Understanding the intricate hydrogeological dynamics is crucial for sustainable water management practices within the region.

4 MATERIALS AND METHODS

4.1 Field Work

The fieldwork was conducted between December 2021 and June 2022. The field exercise included groundwater sampling and monitoring as well as the tailings dump sampling. Groundwater was sampled from four boreholes around the tailings dump, and water levels were monitored for the period of six months. Tailings samples were collected from eight points along the tailings dump facility. Tailings samples were collected to a maximum depth of 2 m to monitor the water table in the tailings dump facility. These would be used for mineralogical and geochemical analyses (see Figure 4 below)

Figure 4. Tailings samples collected at Khumani TSF in June 2022

4.1.1 Groundwater sampling

Groundwater sampling was conducted in wet summer (January 2022) and dry winter (June 2022) seasons. The locations of the sampling points are shown in Figure 5. Groundwater moves in a southeast to northwest direction with KMNO2 being highest and RCFK1 315 being the lowest. Four water samples were collected at strategic sites for laboratory and onsite analysis from boreholes which are fitted with electrical low flow pumps. Collected water samples were stored in high density polyethylene bottles which were decontaminated with representative groundwater samples at each sampling point. In the laboratory, these samples were further stored in refrigerated conditions to maintain their integrity and prevent any potential degradation or contamination until analysis. Four sets of groundwater samples were collected from each borehole (Figure 6) for separate laboratory analyses of major cations and anions.

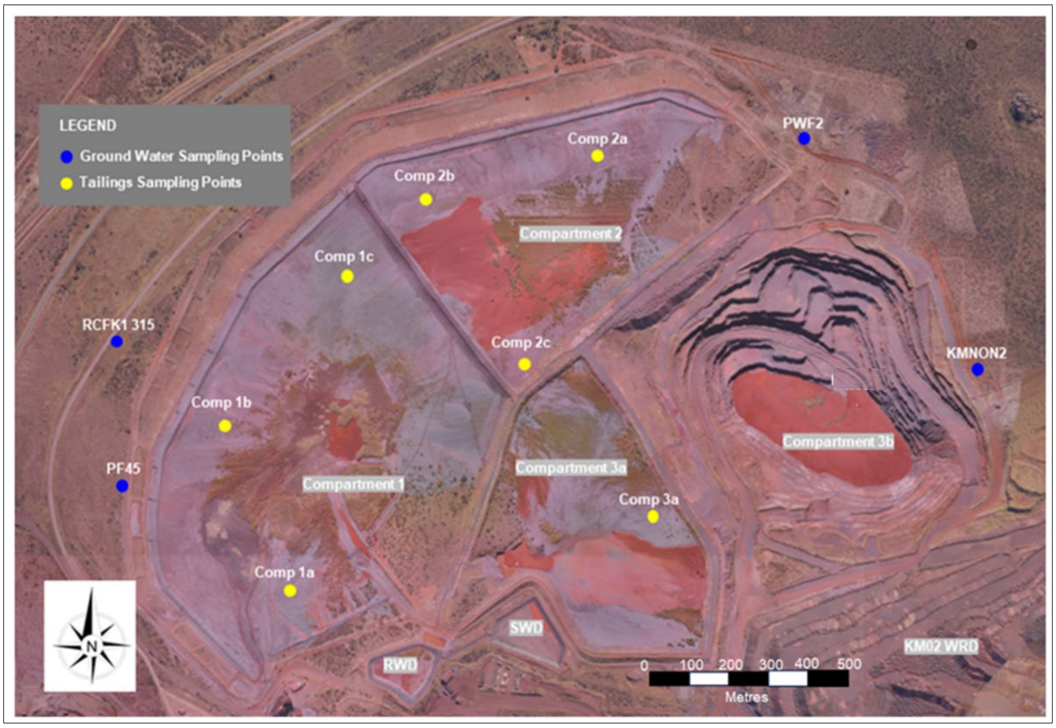


Figure 5. Location of groundwater and tailings sampling sites (June 2022)

The sample aliquots collected for analysis of major cations and trace elements were filtered using a 0.45 µm cellulose acetate membrane and acidified with approximately 1 ml of concentrated nitric acid (HNO_3) to pH lower than 2. The sample aliquots for analysis of anions were filtered but not acidified. Collected water samples were stored in a cooler box at temperatures below 5°C in the field and during transportation to the laboratory. Onsite analyses (temperature, electrical conductivity (EC), pH, alkalinity and dissolved oxygen were measured using the WTW Multi 3430 digital multiparameter probe. For quality assurance, the pH and EC probes were calibrated using buffer solutions with pH values 4.01, 7.00 and 10.01 and standard solution (0.01 mol/l KCl) respectively.

Figure 6. Ground water samples collected at KMN0N2 June 2022

4.1.2 Tailings dump sampling

Tailings samples were collected in June for safety reasons. This was done to facilitate the deployment of the drill rig in dry and accessible areas and to prevent it from being bogged down. The Cone Penetration Testing Rig (CPTu) as shown in Figure 7, was used to collect samples between 0 m to 2 m depth. At each sampling point, a set of two vertical samples (Figure 4) were withdrawn at an interval of 1 m through drilling and were sent to the laboratory for mineralogical, geochemical analyses and acid base accounting.

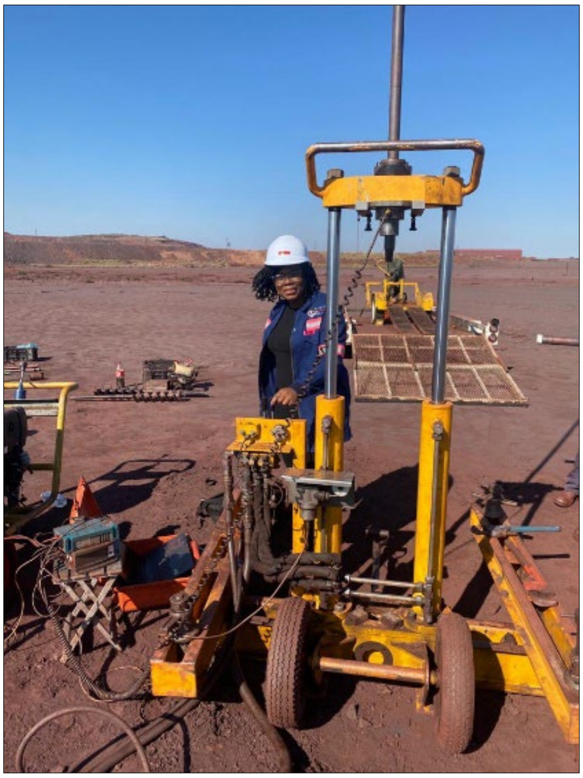


Figure 7. CPTu Rig AT Khumani mine TSF June 2022.

4.2 Laboratory Analyses

All laboratory analyses were carried out at the Council for Geoscience laboratories in Pretoria. These included X-ray diffraction (Siemens D diffractometer), inductive coupled plasma spectrometry (Perkin Elmer ELAN® DRC II), alkalinity (Metrohm 848 titrino plus) and ion chromatography (Thermo Gallery Plus).

4.2.1 Water analyses

a) Inductively coupled plasma mass spectrometry (ICP-MS)

The total multi-elemental analyses of water samples were determined using ICP-MS (Perkin Elmer ELAN® DRC II) with a margin error of less than 5% as shown in Figure 8. Water samples went through filtration using a 0.4 μm membrane and acidified with ultra-pure nitric acid until the pH levels were reduced to less than 2. A procedure described by *(Garbarino & Taylor, 1996)* was adopted for total multi-elemental analyses of water samples.

Figure 8. Perkin Elmer ELAN® DRC-e with auto sampler (Loyola Marymount University, n.d.)

b) Ion chromatography

Concentrations of anions and cations were determined using ion chromatography (Thermo Gallery Plus) as shown in the Figure 9. The anions and cations were segregated according to their interactions with a resin. The separation of ionic species was influenced by their type and size. Procedures described by (Zhao, 2010) were adopted for anions and cations analyses.

Figure 9. Thermo Gallery Plus (Thermo Fisher Scientific, 2023)

c) Alkalinity

The alkalinity of the water samples was measured by titration hydrochloric acid (HCl) using a Metrohm 848 titrino plus as shown in Figure 9. A water sample of 250 cm^3 was titrated using 1.0004 M HCl to pH of 4.3 for a period of less than 3 minutes to avoid loss of Carbon Oxides (Cos).

Figure 10. Metrohm 848 titrino plus

d) Groundwater modelling

Groundwater chemistry was interpreted with the use of aqueous geochemical software PHREEQC. PHREEQC calculates the saturation indices of certain minerals under oxidation-reduction environments deducing the probable chemical behaviours.

4.2.2 Tailings dam samples

a) Tailings pH

The tailings pH was also carried out to measure the potential of material to form acid mine drainage (Sobek, 1978). Procedures described by Briggs and Meier (2002) were adopted for this analysis. An accurately measured 1 g powder sample was thoroughly mixed with 10 ml of deionised water. The tailings pH was then measured after 24 hours using WTW Multi 3430 digital multiparameter pH probe.

b) *Inductive coupled mass spectrometry (ICP-MS)*

EPA 3052 (Environmental Protection Agency, 1996) method was adopted to carry out total multi-elemental concentration analyses of tailings samples. TSF samples were ground and sieved to a 2 mm particle size. An accurately weighed 1.0 g TSF samples were placed in a prewashed Teflon beaker. The sample was digested using a 5 ml of (65%) nitric acid (HNO3) and 1 ml of (30%) hydrogen peroxide (H2O2) at 95°C for 1 hour and evaporated to dryness at 190 °C (5 min). After cooling, the sample was diluted with 10 ml of ultrapure deionised water. The same procedure was applied when preparing for reagent blank.

c) *X-ray diffraction*

X-ray diffraction was employed to determine the mineralogical characteristics of the tailings samples as proposed by Jambor (1994). Tailings samples were dried at room temperature (25°C and 35°C) and milled to 150 µm. Polished thin sections were prepared from milled samples with minimal use of water to avoid dissolution of soluble minerals. Polished thin sections were analysed using the Siemens D diffractometer with copper X-ray tube (λ = 1.54 Ǻ),mA) and equipped with monochromator.

d) *Acid base accounting*

Modified procedures described by Sobek et al., (1978) were adopted for acid base accounting. Total sulphur and carbon analyses were measured using LECO furnaces.

e) *Acid Potential (AP)*

$$AP = (total\ S\%) X\ 30.6$$

Equation 3

Where: S is the total sulphur, and 30.6 is the number of tons of $CaCO_3$ required to neutralise 1000 tons of pyritic material containing 1% S (Parker & Robertson, 1999).

f) *Acid Neutralisation Potential (ANP)*

A 2.00 g sample was digested with 0.5 M hydrochloric acid (HCl) for 24 hours at room temperature to dissolve sulphates and carbonates. The pH of the solution was monitored at six-hour intervals. The pH of the solution was required to be range between 1.0 to 2.0 for the test to be valid. The solution was titrated with sodium hydroxide (NaOH) to pH 7.

The acid neutralisation potential (ANP) was then calculated as:

$$ANP = 50a\left\{X - \left(\frac{b}{a}\right)y\right\}/c$$

Equation 4

Where: a is Normality of HCl; b is Normality of NaOH; c is the sample weight in grams; x is the volume of HCl added in ml; y is the volume of NaOH added to pH 7.0 in ml.

4.3 Quality Assurance

Quality control for all sampling, sampling handling and laboratory analyses was carried out to ensure the results obtained are precise and accurate. All the sampling equipment used for collecting the samples were decontaminated prior to usage at each sampling point. Water sampling bottles were decontaminated using deionised water before use. New cellulose acetate membrane filters were used to filter water samples collected for anions and metals analyses. All collected samples were immediately kept in a cooler box below (5ºC) until transportation to the laboratory for analyses. All onsite field analyses were carried out using equipment which was calibrated for each procedure. Similar procedures for sampling preparation were used to prepare reagent blanks for each leach test method for the analytical batch. During laboratory analyses one duplicate was run with each analytical batch and a margin error of <5% was obtained.

4.4 Data Analyses

4.4.1 Correlation coefficients

Correlation coefficients were calculated using a Mann-Whitney Test for elements identified in groundwater and tailings samples using SPSS® 22.0. This was aimed at identifying any trend in elemental concentrations between the two variables, to ascertain whether tailings material currently impacts the groundwater quality.

In conclusion, the detailed procedures and techniques utilised during the fieldwork are outlined, covering the sampling of groundwater and tailings, laboratory testing and the analysis of the collected data. This thorough approach ensures the validity and precision of the results, enabling the identification of correlations between groundwater quality and the influence of tailings material on the environment.

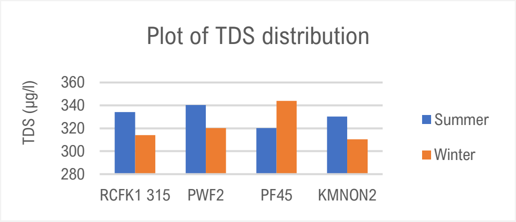
5 RESULTS AND DISCUSSION

5.1 Introduction

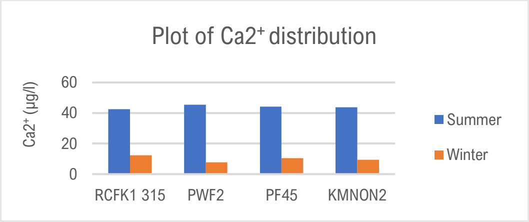
This chapter present and discuss the both the onsite and laboratory analyses results on the assessed water and tailings dump samples. The discussion includes the analysis of water pH, total dissolved solids and electrical conductivity and comparison to maximum permissible limits for domestic usage stipulated in the Department of Water Affairs and Forestry (DWAF) (1996) and World Health Organisation (WHO) (2011). Discussed results include tailings pH, total elemental and leaching concentration of leach tests. The groundwater characteristics are presented in a piper trilinear diagram to analyse the possible water types and identify dominating metal ions. Discussion of the potential generation of acid drainage by tailings dump material is presented including the XRD data which reveals the minerals likely to buffer or generate acid.

5.2 Spatial Distribution of Pollution in Groundwater

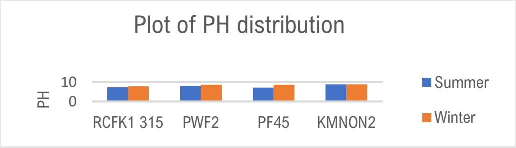
The study involved the analysis of groundwater collected from boreholes around the tailings dump, as discussed in Section 4.1.1. Graphs showing seasonal variations in anions and cations concentrations were generated from laboratory results (Figure 11).



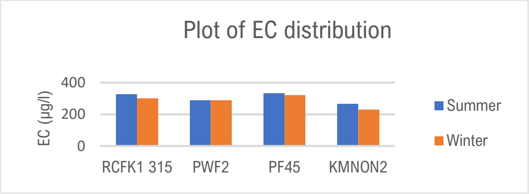
a) TDS seasonal variation



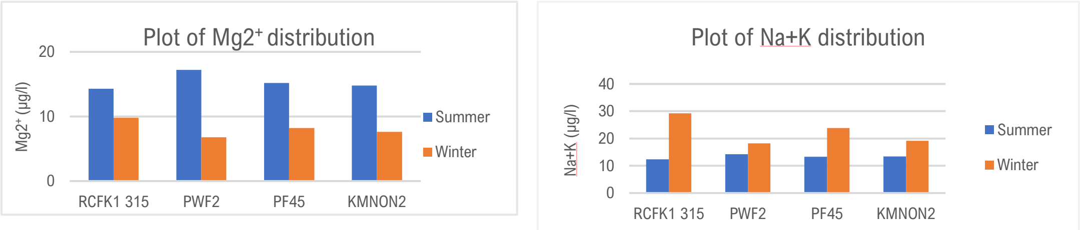
b) Ca2^{+} seasonal variation



c) Ph seasonal variation

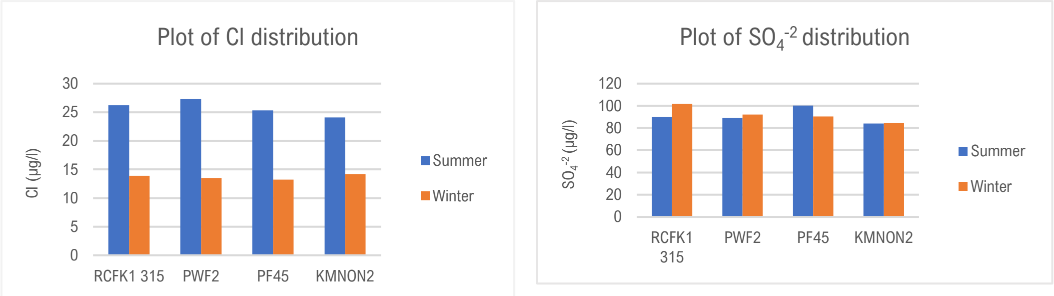


d) TDS seasonal variation



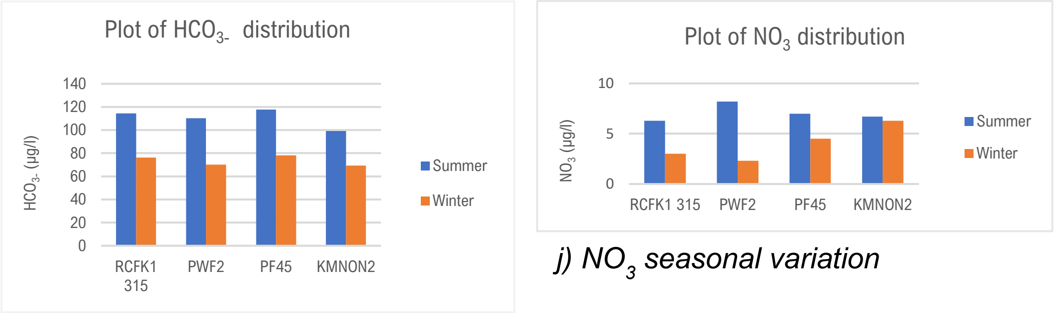
e) Ph seasonal variation

f) Ph seasonal variation



g) Cl seasonal variation

h) SO_4^{-2} seasonal variation



j) NO_3 seasonal variation

i) HCO_{3-} seasonal variation

Figure 11. Plots of seasonal variations for various groundwater parameters

5.2.1 Physiochemical properties of water samples

From pH variation in Table 1, it can be deduced that the recorded pH values are of alkaline in nature and above (typically above 8.0) in both winter and summer season except for PF45 which was acidic in summer (6.9) and RCFK1 315 which had a pH of 7.3 in summer and 7.9 in winter. The other samples had pH ranged from 8.1 to 8.9 which is alkaline and falls within the WHO (2011) permissible pH range of 6.5 - 8.5. The concentrations of ions and TDS of the groundwater samples are within the permissible limits for domestic use as stipulated by DWAF (1996). The concentration of anions occur in the order of HCO3->SO4-2>Cl->NO3- in summer and SO4-2> HCO3-> Cl->NO-3 in winter. The cations occur in the order

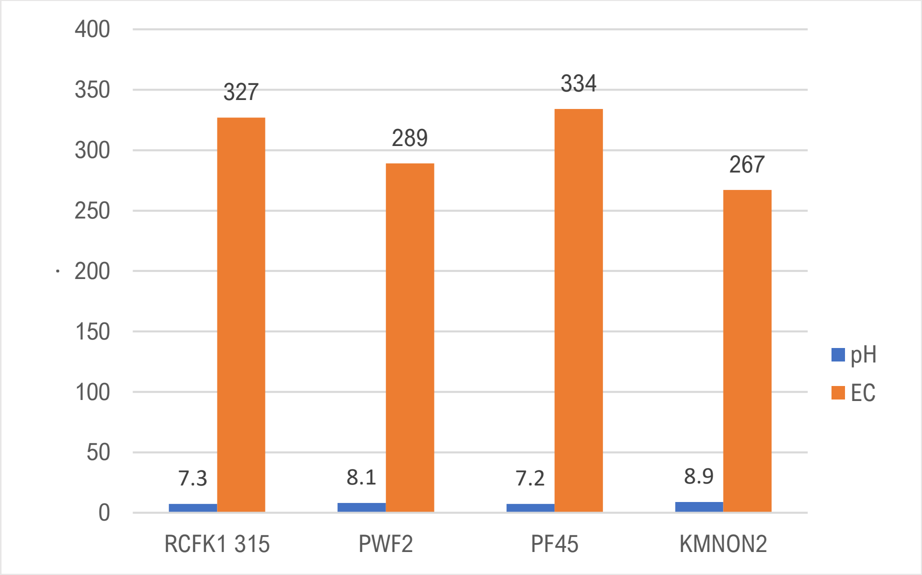
Ca2+> Mg2+> Na+K in summer and Na+K>Ca2+ >Mg2+ in winter. The highest recorded concentration of SO4-2 was 109.3 µg/l at PWF2 and corresponds to the low pH of the groundwater. Liu et al., (2021) depicted similar trends of anions and cations in groundwater around Dagushan iron mine in Northeast China. The variation of TDS is slight between the dry and wet season. The EC ranged between 267–334 mS/m in summer season with 50 % exceeding the permissible levels and 230-321 mS/m in winter with 50% exceeding the permissible levels of 300 mS/m. Patel et al., (2014) discovered similar EC variations between in winter and summer season and the inversely proportional relationship with pH.

Table 1 Selected concentrations of various parameters in groundwater samples

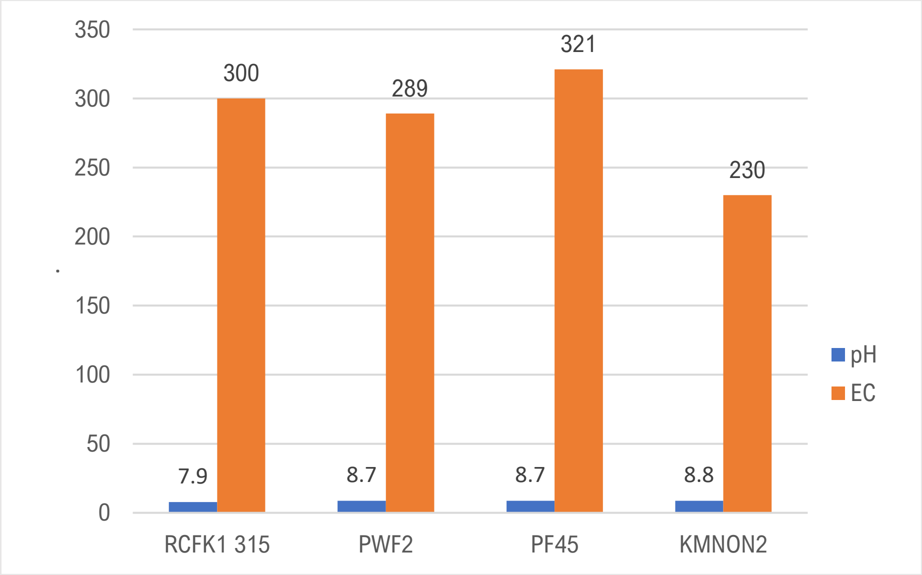
Sample ID	**Season**	**pH**	**EC**	**Ca^{2+}**	**Mg^{2+}**	**Na^++K^+**	**$HCO3^-$**	**SO_4^{2-}**	**Cl^-**	**NO_3^-**	**TDS**
RCFK1 315	Summer	7.3	327	42.5	14.3	12.4	114.5	89.8	26.2	6.3	334.2
PWF2		8.1	289	45.5	17.2	14.2	110.2	88.9	27.3	8.2	340.2
PF45		6.9	334	44.3	15.2	13.3	117.8	109.3	25.3	7.00	320.1
KMNON2		8.9	267	43.8	14.8	13.4	99.2	84.2	24.1	6.7	330.4
RCFK1 315	Winter	7.9	300	12.4	9.8	29.2	76.2	101.7	13.9	3.00	314.2
PF45		8.7	289	7.7	6.8	18.2	70.1	92.3	13.5	2.3	320.2
PWF2		8.7	321	10.4	8.2	23.8	78.2	90.3	13.2	4.5	344.1
KMNON2		8.8	230	9.5	7.6	19.2	69.4	84.3	14.2	6.3	310.4
Recommended limits		6.5-8.5 [a, b]	300 [a, b]	100 [a, b]	30[a]	*	200[a]	150[a]	250[a]	45[a]	500[a]

[a]-world health organisation (2011), [b]-Department of water Affairs (1996), *-not established.

The highest recorded concentration of SO_4^{-2} was 109.3 mg/l at PWF2 and corresponds to the low pH of the groundwater. Liu et al., (2021) depicted similar trends of anions and cations in groundwater around Dagushan iron mine in Northeast China. The variation of TDS is slight between the dry and wet season. The EC ranged between 267–334 mS/m in summer season with 50 % exceeding the permissible levels and 230-321 mS/m in winter with 50% exceeding the permissible levels of 300 mS/m. Patel et al., (2014) discovered similar EC variations between in winter and summer season and the inversely proportional relationship with pH Figure 12.



a) Summer pH vs EC



b) Winter pH vs EC

Figure 12. Plots showing the relationship between pH and EC in summer and winter seasons.

The alkaline pH values are in line with association of the geological formations of the area, which is rich in alkali minerals such as carbonate minerals. The subtle linear trend in pH values in both seasons indicates that there is leaching of effluents from the tailings dump to the groundwater (Table 1). Patel, et al. 2014 however, stated that hydrogeochemistry of groundwater near a haematite iron ore mine in Chukru India was influenced by drainage from tailings dumps. Patel, et al. (2014)

recorded near neutral to alkaline pH values (7.33 to 8.22) close to the tailings dumps and a slight decrease (6,9 to 7,2) were observed further away. The study by Patel, et al., (2014) attributed the pH of the studied groundwater to the dominant carbonate species is HCO_3^- from calcite dissolution.

High alkaline pH values were also recorded by Verma et al. (2012) in groundwater near the Dhobil iron ore mine at West Singhbhum in Jharkhand State, India. According to Verma et al (2012) the tailings samples were rich in Ca, Mg, Na and K which contributed to marginally alkaline pH of the surface and groundwater between 7.2 to 7.6. A study by Jahanshahi & Zare (2015) in the iron ore mines of Golgohar in Iran, concluded that alkaline leachate generated in tailings dumps, was due to insufficient sulphide minerals in the iron ores and the presence of high concentration of $CaCO_3$.

Seasonal pH variations around Iron ore mine, Chitradurga, Karnataka showed high pH values in groundwater samples varied between 6.8 to 7.9 (winter) and 6.85 to 8.5 (summer) (Priyanka, et al., 2017). These observations are similar to the current study, with pH values varying between 7.9 to 8.8 in winter and 7.3 to 8.9 in summer. Naicker et al., (2013) stated that increased EC is associated with decreased pH, observation which were made by this study and Patel et al., (2014). These observations are different from the ones from groundwater near Bukit Ibam iron mine in Malaya (what is now peninsular Malaysia) which had low pH indicative of acid drainage generation from the tailings (Madzin, et al., 2017).

Dlamini et al. (2013) also reiterated that iron ore tailings pose a threat to groundwater pollution due to presence of acid generating minerals. Pilbara iron ore mines also show high pollution risk to groundwater tailings dumps due to presence of sulphide minerals (Green & Borden, 2011). Worth noting, the values of SO_4^{-2} anions of the groundwater were having a significant negative correlation with pH (r=-.074) at $p < 0.05$ in both seasons Table 2. SO_4^{-2} has a strong positive correlation between with HCO_3^- (r=99) (Table 2). A study by Liu et al. (2021), drew similar coincidence when reported high SO_4^{-2} and high pH of 8,3. The Mg^{2+} anions were found to have positive significant correlation (r=9.8) with Ca^{2+} similar to study by Siddik, et al. (2022). The values of Cl^-, showed weak negative correlation with Mg^{2+}

(r=-0.007) and pH (*r*=-0.55), while NO_3^- was also weakly correlated with Mg^{2+} (*r*=-0.06).

Table 2. Correlation coefficients between measured parameters in groundwater from the study area

	pH	**EC**	**Ca^{2+}**	**Mg^{2+}**	**Na^++K^+**	**$HCO3^-$**	**SO_4^{2-}**	**Cl^-**	**NO_3^-**	**TDS**
pH	1									
EC	-0.17	1								
Ca^{2+}	-0.53	0.3	1							
Mg^{2+}	-0.53	0.3	0.98	1						
Na^++K^+	0.27	-0.71	-0.53	-0.53	1					
$HCO3^-$	-0.71	0.28	-0.06	-0.79	-0.67	1				
SO_4^{2-}	-0.74	0.9	-0.78	0.96	0.08	0.99	1			
Cl^-	-0.55	0.39	0.41	-0.3	0.42	-0.4	0.39	1		
NO_3^-	-0.23	0.3	0.3	-0.06	0.52	0.64	0.29	-0.074	1	
TDS	0.04	0.43	0.39	0.41	-0.27	0.42	-0.31	0.39	0.33	1

5.2.2 Hydrochemical types

The trilinear Piper diagram was plotted to classify the hydrochemical types of the groundwater which is influenced by chemical equilibrium between major cations and anions (Piper, 1944). The trilinear Piper diagrams for both summer (Figure 12) and winter (Figure 13) seasons were plotted to observe the differences in water classification between the two seasons.

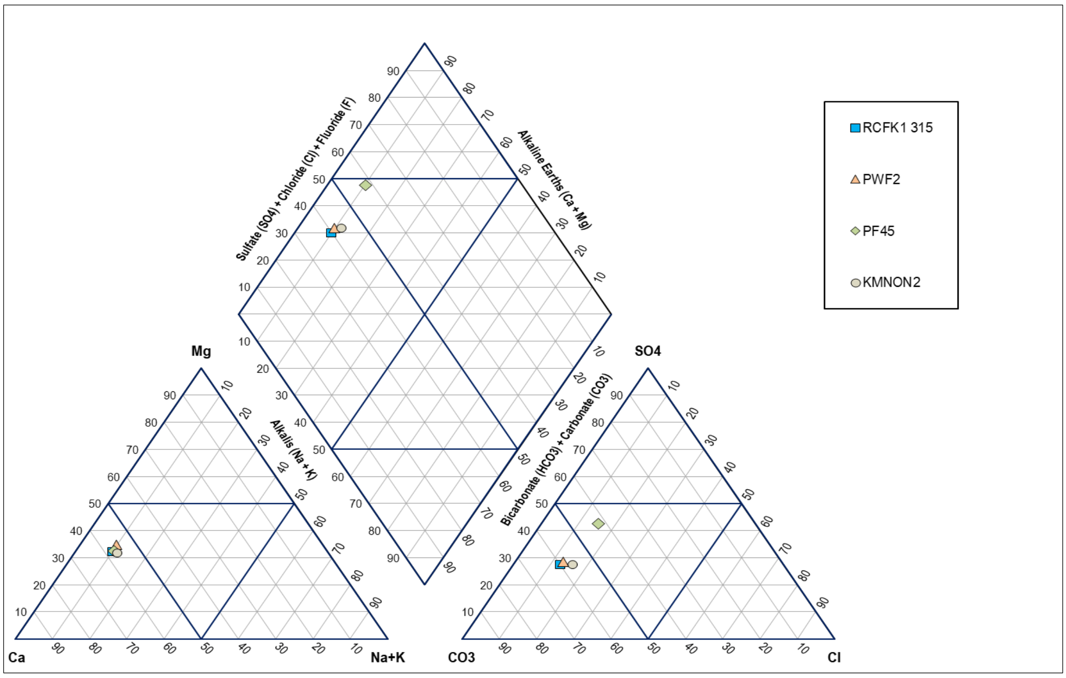


Figure 13. Trilinear Piper Diagram showing the hydrochemical nature of the groundwater in summer.

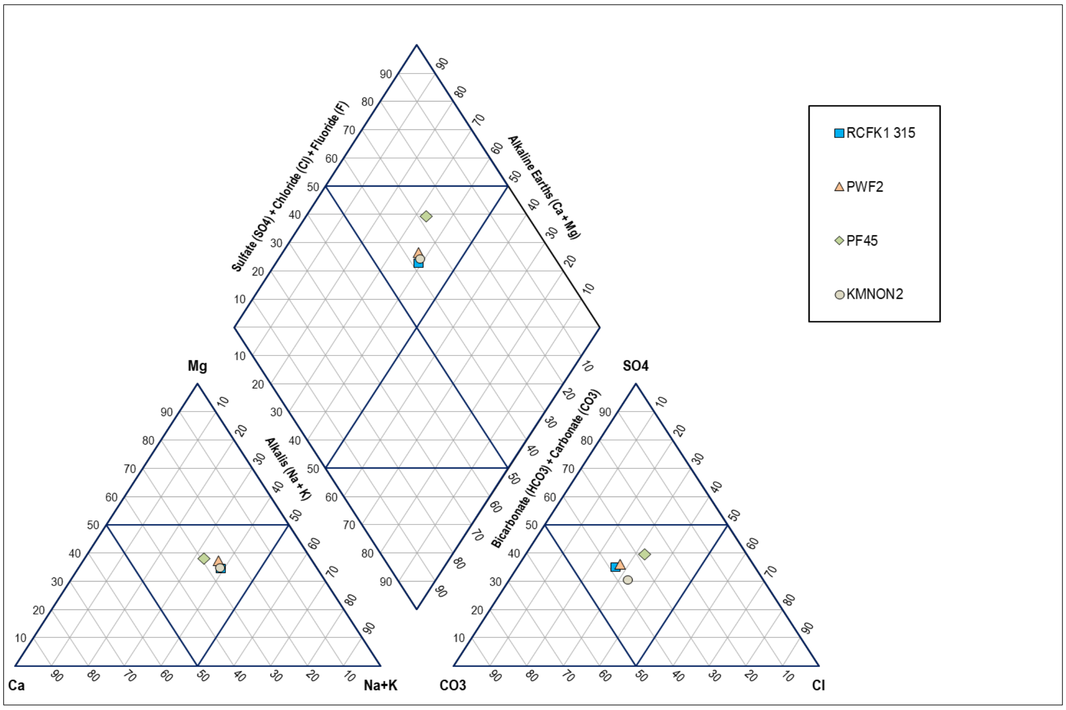


Figure 14. Trilinear Piper Diagram showing the hydrochemical nature of the groundwater in winter.

The hydrochemical nature of the groundwater varied between the summer and the winter periods. From the cations diagram, all the groundwater samples are classified as Ca–type in summer and as non-dominant in winter. From the anions diagram, the groundwater samples belong to the 'HCO_3 type' and as non-dominant in winter. The pH values of groundwater are influenced by the nature of the carbonate species in solution (Patel, et al., 2014). As presented in Table 1, the pH (7.3 to 8.9) of groundwater indicates the domination of HCO_3. Similar trends in groundwater nature indicate similar hydraulic connection and influence which is clearly geological. Gradiner (2003) reported similar trends of dominance of alkaline earth metals in groundwater near Harmersley Yandi Iron Ore Mine in Australia.

5.2.3 Iron

The Fe concentration in groundwater samples varied between 5 021 µg/l and 6 380 µg/l in summer and 20 542 µg/l and 24 952 µg/l in winter. These values are way above the desirable limit of 300 µg/l stipulated by the WHO (2003). The high Fe concentration in the groundwater is attributed to the geology of the area which is rich in iron and manganese (Sumner & Beukes, 2006). Evidently, there is a notable increase in the concentration of Fe during the summer compared to the winter season. This suggests a higher dissolution of precipitated Fe which is likely due to the increased water availability after rainfall. Coetzee et al. (2013) stated that ferric oxides in carbonate aquifers precipitates owing to the high pH formed during dissolution of carbonates. When the water subsequently evaporates or moves away, the iron may precipitate out of the solution. This observation further substantiates the leaching process from the tailings dump material. Similar observations in variation of iron between the rainy season and dry season were made by Singh and Kamal (2017) in the Goa mining region of India, where poorly managed iron ore tailings dump are the most likely source of Fe and other PTEs into the groundwater (Singh and Kamal 2017; Madzin et al., 2017). However, this is influenced by other factors which include particle size distribution of the tailings dump material, rate of oxidation of sulphide minerals, mainly pyrite and water availability.

Khumani Iron ore mine is situated in an arid area with low rainfall, and high evaporation rates (Atlas Weather, 2023). Due to climatic conditions such as low rainfall and the nature of the confined aquicludes in the area, it is unlikely for iron to leach from the tailings dumps into the groundwater. However, a study by Qing-xiang (2008), revealed that stabilities of subsurface aquicludes are often compromised by cracks due to subsiding gradient as a result of weight above the surface which can lead to percolation of water bearing Fe.

5.2.4 Other PTEs

High concentrations of other PTEs (example, Mn, Cu, Zn, Al, Pb, Co, and Ni), were measured from the groundwater samples around the tailings dump (refer to Table 1). The concentration of these PTEs also varied between the summer and winter season as shown in Table 2 below.

Table 3. Trace elements of groundwater samples collected around the tailings disposal facility.

Sample ID	Season	Al µg/l	As µg/l	B µg/l	Ba µg/l	Be µg/l	Bi µg/l	Cd µg/l	Ce µg/l	Co µg/l	Cr µg/
RCFK1 315	Summer	230,0	12,6	99,4	623,2	1,2	0,7	1,9	18,5	3,8	47.3
PWF2		222,5	11,4	82,4	599,7	0,8	0,4	1,9	27,4	4,25	45,1
PF45		204,5	9,4	100,2	600,7	0,9	0,1	1,2	14,1	4,5	48
KMNON2		243,6	15,6	97,7	612,8	1,3	0,2	0,8	6,3	2,7	38,1
RCFK1 315	Winter	288,7	22,5	150,6	722,3	2,4	0,9	2,3	41,9	25,2	70,7
PF45		308,2	10,5	183,3	700,8	3,3	1,3	2,2	30,8	16,3	55,9
PWF2		292,5	32,4	167,9	698,5	1,5	0,8	2,3	34,6	20,9	59,8
KMNON2		312,0	20,5	155,3	732,8	1,8	0,4	1,9	39,2	17,6	63,5

Sample ID	Season	Cs µg/l	Cu µg/l	Fe µg/l	Ga µg/l	Ge µg/l	Hf µg/l	K µg/l	La µg/l	Li µg/l	Mg µg/l
RCFK1 315	Summer	0,2	31,9	6380	10,2	1,2	1,5	8077	12,5	12,1	5037
PWF2		0,3	39	6212	11,2	1,9	1,6	9276	10,7	11,3	5052
PF45		0,3	32,8	5021	12,9	1,8	1,2	8229	9,5	16,2	5102
KMNON2		0,3	33,2	6221	13,3	1,6	1,2	7029	10,2	17	5013
RCFK1 315	Winter	0,4	60,1	22330	15,1	2,8	3,4	1679	21,6	37,3	1419
PF45		0,5	56,1	23098	18	2,4	2,5	3651	39,1	46,62	1196
PWF2		0,6	60,3	24952	19,1	3,7	2,9	2731	27,3	33,4	1009
KMNON2		0,8	66,6	20542	17,4	3,5	2,2	1122	23,4	34,6	1287

Sample ID	Season	Mn µg/l	Mo µg/l	Nb µg/l	Ni µg/l	Pb µg/l	Ti µg/l	U µg/l	V µg/l	Zn µg/l
RCFK1 315	Summer	21,7	3,1	3,5	23,2	13,6	634	1,7	25,6	50,9
PWF2		33,3	2,4	4,6	25,2	19,2	838	1,2	30,6	48,7
PF45		25,4	3,2	5,7	13,3	15,2	706	1,3	30,5	63,2
KMNON2		41,7	3,9	3,2	24,4	14,3	717	1,1	34,4	61,3
RCFK1 315	Winter	404	6,8	10,1	34,7	70,8	2011	3,5	52,6	172,9
PF45		555	5,3	5,8	37,9	55,6	2055	1,7	50,5	208
PWF2		532	6,1	8,2	42,4	66,8	1957	2,7	54,7	222
KMNON2		422	7,6	8,7	50,5	69,4	2200	2,9	51,9	216

The concentrations of these PTEs were higher in winter compared to summer seasons. All these PTEs are associated with the mineralogical and geochemical characteristics of the aquifers in the area. The groundwater samples exceeded the permissible concentrations stipulated for As, Ba, Cd, Ni and U in both summer and winter seasons. Considering the WHO standards (2011), all the groundwater exceeded limits for As, B, Ba, Cd, Cu, Mn, Ni, Pb, Cr, U, and Zn. These findings are similar to the study by Kumar et al. (2017) of high concentrations of PTEs which included Cu, Cr, and Pb in groundwaters of Joypurhat district in Bangladesh. The seasonal variations suggest increase in groundwater recharge during rainfall season, thus increasing water volume and dilution factor of PTEs. Naicker et al., (2003) reported different view from this study as they alluded to PTEs enrichment of groundwaters in the Witwatersrand during rainfall seasons.

5.2.5 Rock–water interaction

PHREEQC software version 2.18 was used to define the saturation index (SI), of groundwater samples which estimate the saturation states for the selected minerals as shown in Table 3 below. Minerals which dissolve quickly when in contact with water, example, gypsum and carbonate, quickly reach a state of equilibrium.

Guidance for *SI* for state of equilibrium;

SI= 0, at equilibrium*; SI<0,* under-saturation state; and *SI > 0,* super-saturation, mineral phases precipitates.

Table 4. Saturation indices of groundwater in the study area

Sample ID		Oxides				Carbonates					
	Season	Gibbsite	Goethite	Hematite	Manganite	Smithsonite	Calcite	witherite	Dolomite	Siderite	Cerussite
RCFK1 315	Summer	6.5	13.5	29.1	-2.3					1.3	
PWF2		7.3	12.6	27.2	-2.3					2.3	
PF45		7.2	13.1	28.3	-2.3					1.8	
KMNON2		6.8	13.2	29.3	-2.3					2.4	
RCFK1 315	Winter	5.5	15.4	33.1	2.9	2,7	3,7	1,2	6,8	3.1	6,1
PF45		5.3	15.4	30.4	3.1	3,1	2,9	1,8	7,2	3.3	5,8
PWF2		6.1	16.2	34.6	2.9	2,6	4,2	3,9	6,6	4.3	6,4
KMNON2		5.2	15.8	29.7	1.8	2,2	3,4	4,2	6,9	3.9	5,3

Sample ID		Sulphates						Halides
	Season	Anhydrite	Alunite	Jarosite-K	Gypsum	Melanterite	Barite	Sylvite
RCFK1 315	Summer	1.2	17.3	18.4	1.2	-2.4	7.5	-2.3
PWF2		1.4	16.9	18.5	1.1	-3.1	7.5	-2.4
PF45		1.6	17.5	18.6	1.1	-2.4	6.7	-1.9
KMNON2		1.2	17.3	18.7	1.5	-2.8	7.8	-1.7
RCFK1 315	Winter	1.6	9.4	19.6	1.4	-5.2	7.2	-3.6
PF45		2.1	10.2	20.4	1.2	-4.7	7.7	-3.4
PWF2		1.9	9.8	17.8	1.4	-5.1	8.2	-4.4
KMNON2		1.5	9.6	20.6	1.4	-6.1	6.6	-3.8

Saturation indices (SI) data shown in Table 3, show that all the groundwater samples were saturated with oxides mainly gibbsite, goethite and haematite in both winter and summer season. The groundwater was only super-saturated with manganite in winter and was below zero in summer. Carbonate minerals (smithsonite, calcite, witherite, dolomite and cerussite) were all at state of equilibrium in all samples in the summer season and were super saturated in winter. Siderite was the only carbonate in all the groundwater samples which was super-saturated in the summer season. This variation can be attributed to seasonal changes in environmental conditions, such as temperature and precipitation patterns, influencing the dissolution rates of carbonate minerals in the groundwater. Further investigation is needed to fully understand the mechanisms driving these seasonal fluctuations in mineral saturation levels. All the sulphate minerals were super-saturated in both seasons except for melanterite which was under saturated in both seasons. The groundwater samples were under-saturated with halides (mainly sylivite) in both seasons.

5.3 Mineralogical and Geochemical Composition of Tailings Disposal

The study involved the analysis of the vertical and lateral distribution of PTEs in the various sampling points in the tailings dump. Also presented are the results of leaching tests which were compared to the regulated leaching concentration thresholds as stipulated in NEM: WA No.59 of 2008. Results of ABA conducted on the tailings dump samples are presented pH-NNP and AP-NP graphs in order to classify the drainage type.

5.3.1 Major elements geochemistry

The chemical composition of major oxides and PTEs are shown in Table 4. All the tailings dump samples showed a uniform trend in concentration of major oxides which was: SiO_2> Fe_2O_3> Al_2O_3> MgO> CaO> TiO_2>FeO>MnO>NaO>SrO> K_2O> P_2O_5. Dauce et al. (2019) reported similar trends in oxide concentrations in tailings sample from Quadrilátero Ferrífero with grades of 30.3 wt.% Fe and 55.4 wt% SiO_2. The concentration of SiO_2 varied between 62.3 to 82.4 wt.%. The oxides of Al varied between 12.3 to 14 wt. 6%, and Fe varied between 6.6 to 8.3 wt.%. MnO was the fourth highest oxides ranging between 2.3 to 3.2 wt.%, followed by CaO which ranged between 1.8 and 2.1 wt.% and TiO_2 which ranged between 1.4 to 1.9 wt%. The concentration of K_2O, P_2O_5 and Cr_2O_3 were all below 0,5 wt.%.

Table 5. Major oxides (wt %) in tailings deposits samples

Sample	SiO2	Fe2O3	FeO	MnO	SrO	Al2O3	MgO	CaO
Comp1aA	46,2	20,5	4,2	0,9	0,18	12,3	3,8	4,8
Comp1aB	44,3	18,4	4,6	1,9	0,2	13,5	6,7	4,3
Comp1bA	43,2	18,5	3,4	0,6	0,4	13,6	4,8	4,4
Comp1bB	48,5	19,3	3,3	0,4	0,5	14,1	3,7	3,4
Comp1cA	46,5	18,9	2,4	0,8	0,6	10,8	4,1	4,6
Comp1cB	46,7	22,1	2,7	1,3	0,4	11,9	4,2	3,9

Comp2aA	51,5	17,7	2,1	0,8	0,7	9,1	6,2	4,8
Comp2aB	49,9	18,5	2,6	1,2	0,9	11,2	4,3	3,4
Comp2bA	50,9	18,2	1,3	0,9	0,3	9,2	5,4	5,5
Comp2bB	49,7	21,2	2,1	1,9	0,5	10,1	3,5	4,1
Comp2cA	50,1	18,8	2,1	0,2	0,18	8,4	5,6	5,1
Comp2cB	54,2	19,7	2,3	1,2	0,3	8,8	3,7	3,6
Comp3aA	49,4	20,4	2,2	0,2	0,4	14,16	2,8	2,1
Comp3aB	47,8	20,6	2,9	0,8	0,3	14,5	3,9	3,5

Sample	**Na2O**	**K2O**	**TiO2**	**P2O5**	**LOI**	**Sum**
Comp1aA	0,7	0,1	3,7	0,18	1,2	98,76
Comp1aB	0,5	0,4	3,7	0,15	1,2	99,85
Comp1bA	0,5	0,4	3,8	0,16	1,2	94,96
Comp1bB	0,7	0,5	3,9	0,2	1,2	99,7
Comp1cA	0,9	0,15	4,1	0,2	1,2	95,25
Comp1cB	0,5	0,5	4,1	0,19	1,2	99,69
Comp2aA	0,4	0,2	4,2	0,16	1,2	99,06
Comp2aB	0,8	0,3	4,3	0,17	1,2	98,77
Comp2bA	0,6	0,5	4,1	0,2	1,2	98,3
Comp2bB	0,8	0,4	3,5	0,15	1,2	99,15
Comp2cA	0,8	0,5	3,6	0,14	1,2	96,72
Comp2cB	0,7	0,3	3,7	0,15	1,2	99,85
Comp3aA	0,8	0,6	3,8	0,16	1,2	98,22
Comp3aB	0,4	0,3	3,5	0,2	1,2	99,9

The high oxides of Fe_2O_3, MnO and CaO in the tailings dump samples is an indicative of the ore deposits of the Asbestos Hills Subgroup which are mined at Khumani (Beukes & Gutzmer, 2008). From the bar graph displayed in Figure 14, the occurrence of oxides in the tailings showed a similar trend in all the samples.

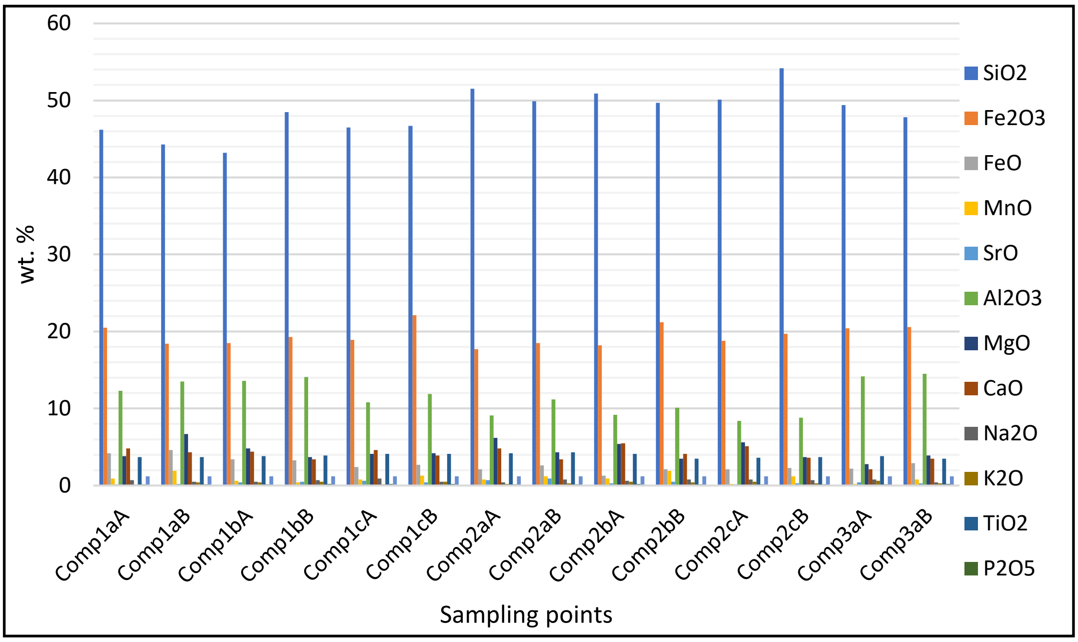


Figure 15. Major oxides in tailings dumps

5.3.2 Trace element concentrations.

The concentrations of PTEs are presented in Table 5. The tailings dumps are characterized by relatively high concentration of Mn, Fe, Zn, B, Ni, Ba, Mo, Co, and Pb and relatively low Cu, Cd, As, and Hg. The concentration of Mn varied between 550 ppm and 1402 ppm at 0 to 1 m depth (Comp1aA, Comp1bA, Comp1cA, Comp2aA, Comp2bA, Comp2cA, Comp3aA), and 902 to 2.760 ppm at 1-2 m depth (Comp1aB, Comp1bB, Comp1cB, Comp2aB, Comp2bB, Comp2cB, Comp3aB). Zn varied between 69 ppm and 344 ppm at the depth of 0 to 1 m and 108 to 344 ppm at 1 to 2 m depth. The vertical concentration trends of selected PTEs including Zn, As, Cu, Ni, Cr, Co, and Pb are indicate a clear distinct difference between PTEs concentrations in the upper subsamples (0 to 1 m) (Comp1aA, Comp1bA, Comp1cA, Comp2aA, Comp2bA, Comp2cA, Comp3aA), and the lower subsample (1 to 2 m) (Comp1aB, Comp1bB, Comp1cB, Comp2aB, Comp2bB, Comp2cB, Comp3aB. Concentrations of PTEs in all the samples were significantly higher than in lower horizons from the upper horizons ($P < 0.05$). These trends indicate that PTEs from the exposed surfaces of the tailings dumps are leached to lower horizons. The high concentration of the PTEs in the tailings is of a concern as these PTEs are most likely leached into groundwaters under certain conditions. The investigated tailings dumps are clearly a potential source of PTEs. A study by

Hattingh et al., (2003) discovered high concentration of Fe, Mn, Co, Ni and As in aquifers near a TSF owing to leaching of these PTEs from a mine waste.

Table 6. Elemental concentrations (µg/l) *in TSF.*

	Comp 1a-A	**Comp 1a-B**	**Comp 1b-A**	**Comp 1b-B**	**Comp 1c-A**	**Comp 1c-B**	**Comp 2a-A**	**Comp 2a-B**
As	0.9	2.1	0.7	1.2	5.2	9.3	0.2	6.7
B	150	120	150	150	120	150	150	120
Ba	62.5	88.3	67.8	90.2	55.3	63.8	45.6	102
Cd	2.4	4.7	1.4	12.3	0.9	3.7	2.8	6.6
Co	88.2	109	104	112.5	72.3	88.3	88.6	78.3
Cr	6.5	6.1	6.2	8.8	4.5	4.4	5.3	10.2
Cu	16	22	14.9	20.1	10.6	18.3	17.9	28.4
Fe	6680	7021	19858	21310	12782	25768	10483	19591
Hg	0.8	1.5	0.3	2.3	1.1	2.6	1.5	1.2
La	0.5	1.2	0.6	0.8	1.2	2.1	0.2	3.2
Li	10.9	11.1	12.1	21.1	2.1	3.4	11.2	20.2
Mn	1000	1920	902	1109	850	2001	689	925
Mo	40	33	39.7	40.8	28	34.7	42.8	62.1
Ni	93	83.4	87.4	103	75.4	120	62.1	90.6
Pb	22	19.7	29.6	34.5	12.3	18.9	10.7	19.5
Sb	1.31	0.11	1.69	0.45	2.79	0.19	0.93	0.06
Se	20.75	30.27	20.78	20.29	30.76	10.08	20.96	11.09
Sr	1.19	0.59	3.17	0.43	1.63	0.16	2.22	0.31
Ti	5.66	10.23	11.31	24.05	4.61	20.07	3.64	38.1
V	3.05	22.34	7.94	30.37	1.14	40.11	0.57	20.06
Y	0.3	0.2	0.81	0.08	1.09	0.09	0.87	0.09
Zn	266	300	254	344	320	288	266	412

	Comp 2b-A	**Comp 2b-B**	**Comp 2c-A**	**Comp 2c-B**	**Comp 3a-A**	**Comp 3a-B**
As	4.9	5.8	Nd	2.2	0.6	8.3
B	150	150	120	150	150	120
Ba	62.9	109.4	55.3	78.9	50.9	63.4
Cd	1.2	1.7	Nd	1.4	1.2	2.9
Co	55.2	80.2	42.1	88.7	33.2	69.6
Cr	6.3	10.9	4.2	12.3	2.1	13.4
Cu	14.4	18.9	17.3	23.5	10.7	28.8
Fe	11115	16083	11770	15981	15272	17021
Hg	0.4	1.2	Nd	Nd	Nd	Nd

La	1.4	0.3	1.2	0.6	0.6	0.4
Li	12.8	31.2	1.3	7.9	4.4	10.5
Mn	1402	2400	466	2760	550	1450
Mo	26.1	78.3	12.9	54	20.1	49
Ni	55.3	88.7	34.6	109.2	48.6	66
Pb	11.2	15.6	9.3	22.9	10.9	28.7
Sb	1.77	0.14	0.4	0.9	0.1	0.4
Se	21.71	30.1	20.3	31.3	12.3	23.3
Sr	1.93	0.43	1.22	1.31	2.93	3.43
Ti	11.98	22.46	10.4	9.3	12.98	34.46
V	23.01	10.36	12.2	15.4	14.8	22
Y	0.1	0.02	0.1	0.3	0.4	0.9
Zn	108	206	172	355	69	209

5.4 XRD

The main mineral phases identified by XRD, shown in Figure 15, detected showed a uniform decreasing trend of quartz, haematite, goethite, magnetite, siderite, calcite, dolomite, K feldspar, plagioclase, talc, clinochlore, anatase and pyrite.

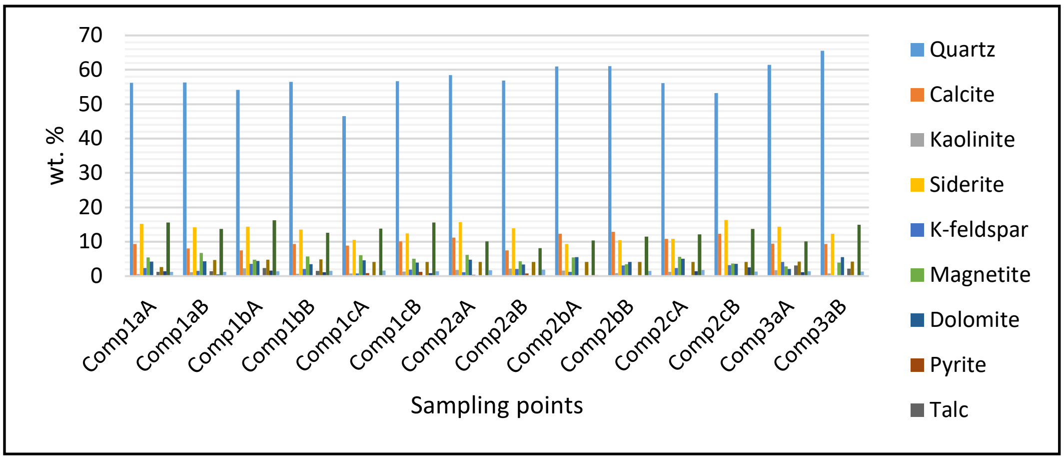


Figure 16. Minerals in the Khumani Mine TSF

The main mineral phases identified by XRD, shown in Figure 15, detected showed a uniform decreasing trend of quartz, haematite, goethite, magnetite, siderite, calcite, dolomite, K feldspar, plagioclase, talc, clinochlore, anatase and pyrite

Quartz is the dominant mineral in all the tailings dump samples varying between 53.2 and 65.5 wt.%. Haematite is the second most dominant mineral in the samples varied between 23.9 to 34.6 wt.%. Goethite and siderite were also detected within a range between 6.8 to 11.8 wt. % and 4.5 to 8.1 wt. % respectively. Calcite ($CaCO_3$), which is a strong buffer, was also detected in all the samples. Pyrite and talc were found in impurity amounts in some samples. Pyrite minerals (FeS_2) were detected in Comp1cA, Comp1cB, and Comp2aA which may influence the occurrence of acid mine drainage. Due to the presence of buffer minerals such as calcite and talc any acid drainage formed is likely to be neutralised, however. Other detected minerals include kaolinite and apatite can be found in the pores of goethite.

The presence of clay minerals, particularly kaolinite, in the tailings dump samples suggests a robust capacity to absorb PTEs. This phenomenon contributes to a reduction in the leachability and mobility of these elements. However, kaolinite has only a limited cation exchange capacity, and adsorbed ions can potentially be re-released as conditions in the tailings change over time (Schroth & Sposito, 1997). According to González-Valoys et al. (2021), clay minerals make a suitable surface area for absorption/adsorption of the PTEs especially Pb and Zn. Roselli et al. (2015) argued that the cation exchange capacity of kaolinite is limited when compared to bentonite and smectite and that it is likely to release PTEs when condition such as water volume changes in the TSF

5.5 Acid Base Accounting

The ABA results for all collected tailings dump samples are presented in Table 6. From the tailings pH values, all samples were characterised by neutral to alkaline pH (7.2 to 9.5) except for Comp1c A, Comp1cB and Comp2a-B which had pH values of 6.3, 6.9 and 6.9 respectively. All the samples were characterised low pH sulphur content varying between 0.01 to 0.2%.

Table 7. Result of ABA test of tailings dump samples.

Sample ID	Tailings pH	% Reactive S	NP kg/t CaCO3	AP kg/t CaCo3	Net NP (NP-AP)	NPR (NP/AP)	Interpretation
Comp1a-A	7.9	0.04	124.4	31.3	93.1	3.97	Acid neutralising
Comp1a-B	8.3	0.02	126.2	33.4	92.8	3.78	Acid neutralising
Comp1b-A	8.2	0.03	120.5	30.7	89.8	3.93	Acid neutralising

Comp1b-B	7.8	0.05	128.9	28.8	100.1	4.48	Acid neutralising
Comp1c-A	6.3	0.2	113.8	32.3	81.5	3.52	Acid neutralising
Comp1c-B	6.9	0.1	138.2	33.2	105	4.16	Acid neutralising
Comp2a-A	7.2	0.06	129.8	31.8	98	4.08	Acid neutralising
Comp2a-B	6.9	0.06	133.2	32.2	101	4.14	Acid neutralising
Comp2b-A	8.1	0.03	124.5	29.9	94.6	4.16	Acid neutralising
Comp2b-B	9.5	0.01	129.7	28.9	100.8	4.49	Acid neutralising
Comp2c-A	9.4	0.01	128	30.4	97.6	4.21	Acid neutralising
Comp2c-B	8.7	0.03	131.4	31.3	100.1	4.20	Acid neutralising
Comp3a-A	8.5	0.02	128.6	29.3	99.3	4.39	Acid neutralising
CompAa-B	6.6	0.2	130.2	32.8	97.4	3.97	Acid neutralising

The NNP values ranged between 81.5 to 105 kg/t $CaCO_3$ with NP to AP ratio > 2. According to Perry (1998), material with NP to AP ratios greater than 2 produces alkaline drainage. In the current study, all the ABA results showed net alkaline water. The presence of pyrite in Comp1c 0.9 to 1.2 wt. %, Comp2a of 0.4 to 0.8 wt. % and 1.3 to 1.5 wt.% at Comp2c is compensated by the high calcite and dolomite equivalent, which was above 7.5 wt. % resulting in a positive net neutralisation potential (Figure 16).

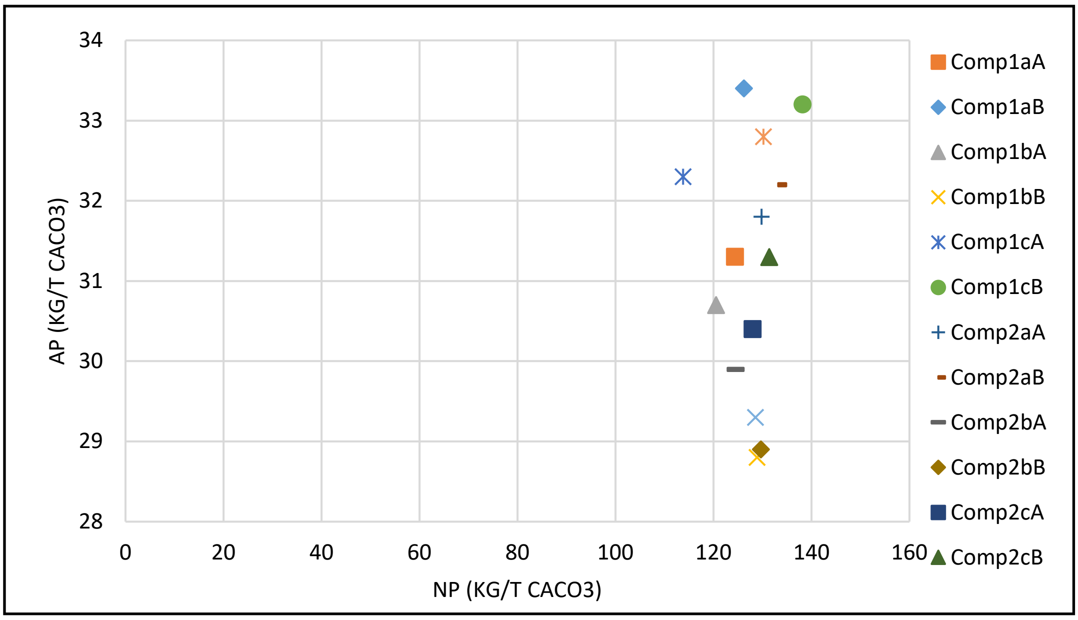


Figure 17. Relationship between AP and NP

Similar findings were made by Dold and Fontbote, (2002) in tailings from Punta del Cobre belt, northern Chile with 7.1 wt.% calcite and 3.5 wt.% pyrite. Dold and Fontbote, (2002) further revealed that tailings from Ojancos with about 3 wt.% calcite and 4 wt.% pyrite have high potential to generate acid. The high NP (113.8 to 133.2 kg/t $CaCO_3$) is indicative of the geological formations of the area which is associated with carbonate rocks (Beukes & Gutzmer, 2008). The ABA results shows that the generated alkaline drainage will likely leach considerable concentration of PTEs in tailings dump thus posing greater threat to groundwater resources (Figure 17). Similarly, Lusunzi, (2023) revealed that tailings from Nestor mine though alkaline in nature but have severely enriched the groundwater and surface water resources with PTEs.

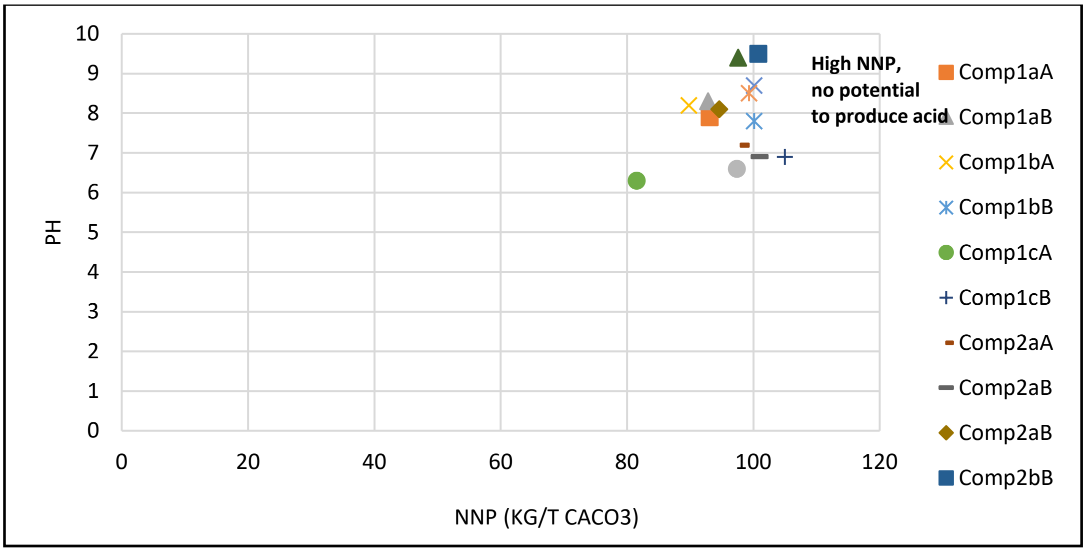


Figure 18. Relationship between pH and NNP

5.6 Summary

5.6.1 Water hydrogeochemistry

The analysis provided valuable insights into the composition and characteristics of groundwater in the region, highlighting potential areas of concern and emphasizing the importance of monitoring and management strategies.

- The groundwater was characterised by near neutral to alkaline pH owing to the geological formation of the area.

- High concentration of $CaCO_3$ was found in all the groundwater samples, and the waters were classified as Ca–type in summer and as-non dominant in winter.
- As, Fe, Mn, Cu, Zn, Al, Pb, Co, and Ni were found to exceed the permissible limits of DWAF (1996) in winter.

5.6.2 Tailings mineralogical and geochemistry

The analysis of the mineralogical and geochemical properties of the tailings from Khumani Mine provided valuable insights into the nature of the tailings and their implications for environmental management and remediation strategies.

- The tailings contained high concentrations of Mn, Zn, B, Ni, Ba, Mo, Co, and Pb and relatively low Cu, Cd, As, and Hg in the tailings dump with minerals of quartz, haematite, geothite, magnetite, siderite, calcite, dolomite, K feldspar, plagioclase, talc, clinochlore, and anatase.
- Tailings were classified as non-acid producing with NP to AP ratio > 2.

6 CONCLUSION AND RECOMMENDATIONS

6.1 CONCLUSIONS

It can be stated that this study has shown that the hydrogeochemistry of groundwater around the tailings dump has been influenced by the Khumani Mine TSF despite some of the groundwater sampling points occurring up-slope of the TSF. The main findings of the study are summarised below:

6.1.1 Climatic conditions

The climatic conditions of the study area are typical of arid regions where the rate of evaporation exceeds precipitation. Key characteristics of the area include:

- Low rainfall of approximately 161mm, resulting in limited water availability for chemical reactions in the tailings dumps, such as the leaching of potentially toxic elements (PTEs) and the oxidation of sulphide minerals.
- The oxidation of sulphide minerals is primarily driven by bacteria, water availability, and oxygen.

The hypothesis was that the scarcity of rainfall in the region, which usually serves as a solvent for chemical reactions and a conduit for PTEs, would inhibit the leachability and mobility of PTEs. However, the high concentrations of PTEs, including Fe, Pb, and As, in the groundwater samples suggest that there is vertical movement of these elements from the tailings into the groundwater reserves.

6.1.2 Water hydro geochemistry

The water hydrogeochemistry of the study area, focused on key parameters such as pH, metal ion concentrations, electrical conductivity, Piper Plots classification, priority potentially toxic elements (PTEs), and saturation index (SI) data. Understanding these aspects is vital for assessing the quality and suitability of groundwater for various uses and identifying potential risks associated with PTEs and mineral saturation levels.

- The groundwater was characterised by near neutral to alkaline pH in both summer and winter seasons. The concentration of metal ions was high in summer season compared to winter season but were still within DWAF

(1996) guidelines. EC was found to exceed the 300 mS/m limit in 50% of samples in both summer and winter.

- From the Piper Plots all the groundwater samples are classified as 'Ca–type' in summer and as non-dominant in winter and the groundwater samples belong to the 'HCO_3 type' and as non-dominant in winter.
- Chemical elements As, Fe, Mn, Cu, Zn, Al, Pb, Co, and Ni are priority PTEs of concern. These PTEs exceeds the permissible guideline concentration stipulated by DWAF (1996).
- SI data are showing that all the groundwater sample were saturated with oxides (gibbsite, goethite and haematite), and sulphates (Anhydrite, alunite, jarosite-K, gypsum and barite) in both winter and summer season. Carbonates minerals (smithsonite, calcite, witherite, dolomite and cerussite were all in a state of equilibrium in all samples in the summer season and were super saturated in winter. The groundwater samples were under-saturated with halides mainly sylvite in both seasons.

The hydrochemistry of the groundwater reflects characteristics typical of confined aquifers, as indicated by the saturation of oxides and sulphates in both seasons. However, the exceedance of As, Fe, Mn, Cu, Zn, Al, Pb, Co, and Ni which are also high in the tailings, suggest that there might be cracks on the subsurface of the aquicludes which resulted into percolation of the alkaline rich drainage enriched in these PTEs.

6.1.3 Tailings mineralogical and geochemistry

The analysis of the tailings from Khumani Mine shed light on the nature of the tailings and their potential implications for environmental management and remediation strategies.

- Khumani Mine mines iron ore and a representative sample taken from the tailings dump showed haematite and goethite as the main iron ore minerals.
- The ICPMS results showed high concentrations of Mn, Zn, B, Ni, Ba, Mo, Co, and Pb and relatively low Cu, Cd, As, and Hg in the tailings dump. Vertical trends of PTEs indicated that concentrations of PTEs were lower at the exposed surfaces (0 to 1 m) compared to the lower horizons (1 to 2 m). This is indicative of minor oxidation and subsequent leaching of PTEs at the exposed surfaces which is reduced in lower horizons.

- The XRD results showed dominance of quartz, haematite, geothite, magnetite, siderite, calcite, dolomite, K feldspar, plagioclase, talc, clinochlore, and anatase. Talc, pyrite, and clay minerals (kaolinite) were also identified.
- The presence of kaolinite minerals presents adsorption sites for trace elements which further inhibits their mobility due to the low cation exchange capacity of kaolinite.
- The ABA indicates that all the samples were characterised as low tailings pH indicative of content of $CaCO_3$, and low sulphur content varying between 0.01 to 0.2 %, showing net alkaline water with positive NNP values and NP to AP ratio > 2.

The conclusion drawn is that the leaching of PTEs from the tailings dump is high. The alkaline nature of the drainage formed has a potential to leach PTEs and the presence of kaolinite present limited cation exchange capacity for adsorption PTEs. Further studies are required to determine the condition of the aquicludes which are most likely cracked due to high groundwater withdrawals or/and weight of above ground.

6.2 RECOMMENDATIONS

Based on the findings and analyses presented in this study regarding the hydrogeochemistry, mineralogical composition, and geochemical characteristics of tailings from Khumani Mine, the following recommendations are proposed for effective management and mitigation of potential environmental impacts:

- This study has shown that the minerals in the TSF have enriched the on groundwater with PTEs such as As, Fe, Mn, Cu, Zn, Al, Pb, Co, and Ni. The climatic conditions, and the physical nature of the physical nature of the TSF material (PSD) was found not to inhibit vertical migration of PTEs. Therefore, the TSF material cannot be discarded in an unused pit without further treatment or lining to prevent contamination of groundwater resources.
- The mineralogical and geochemistry of the tailings material showed that the material is rich in alkalis which are buffer minerals for acid generation

and showed reduced mobility of PTEs, making the material suitable for disposal without lining. However, care must be taken to ensure the material is not exposed to water. That is, the subsurface of the backfilled site must be lined with impermeable material such as bentonite and topsoil with vegetation be stabilised.

- Vertical trends showed high migration of PTEs from the exposed surfaces to underlying horizons. Therefore, when backfilling is completed, it is recommended that the backfill be stabilised with topsoil and grass covers on the surface to inhibit wind and water erosion and oxidation of exposed surfaces.

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