University of Venda
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UNIVERSITY OF VENDA

SCHOOL OF ENVIRONMENTAL SCIENCES

DEPARTMENT OF MINING AND ENVIRONMENTAL GEOLOGY

# GEOCHEMICAL AND MINEROLOGICAL CHARACTERIZATION OF GOLD MINE TAILINGS FOR THE POTENTIAL OF ACID MINE DRAINAGE IN THE SABIE-PILGRIM'S REST GOLDFIELDS

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## Declaration

I, **Rudzani Lusunzi**, hereby declare that the dissertation for the Master of Earth Sciences in Mining and Environmental Geology, hereby submitted by me, has not been submitted previously for a degree at this or any other university, that is my own work in design and execution, and that all reference material contained therein has been duly acknowledged.

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Rudzani Lusunzi Date

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## Publications

1. Rudzani L, Gumbo JR, Yibas B, Novhe O, (2017). Geochemical and Mineralogical Characterization of Gold mine tailings for the potential of acid mine drainage in the Sabie-Pilgrim’s Rest Goldfields, South Africa. Page 272-275. Proceedings 9th International Conference on Research in Chemical, Agricultural, Biological and Environmental Sciences (RCABES-17). ISBN 978-81-934174-6-1 http://earet.org/proceedingspdf.php?id=53

2. Lusunzi Rudzani, Jabulani Ray Gumbo, Bisrat Yibas, Obed Novhe (2018). Acid Base Accounting (ABA) of mine tailings for the Potential of Acid Mine Drainage in the Sabie-Pilgrim’s Rest Goldfields, South Africa. Conference Proceedings 11th International Conference on Acid Rock Drainage and IMWA Annual conference. I.S.B.N. xx

## Abstract

This study entails geochemical and mineralogical characterization of gold tailings of Nestor Mine and Glynn's Lydenberg Mine of the Sabie-Pilgrim's Rest goldfields. A total of 35 samples were collected and were analysed for chemical composition (XRF and ICP-MS), mineralogical composition (XRD). In addition, acid-base accounting (ABA) techniques had been conducted to predict the potential for acid mine drainage. Seepage from Nestor tailings dump and water samples from the adjacent Sabie River were also collected and analysed by means of inductively coupled plasma mass spectrometry (ICP-MS) and immediate constituent (IC) - analytical techniques. The study revealed that Sabie-pilgrim's rest goldfield is characterized by both acid generating and non-acid producing tailings, and this is attributed to variations in the mineralogy of source rocks. Gold occurred within the Black Reef Quartzite Formation in the Nestor Mine and within the Malmani Dolomite in the case of Glynn's Lydenburg Mine. Mineralogy and bulk geochemical analyses performed in this study showed a clear variation in the chemistry of Nestor Mine and Glynn's Lydenburg Mine tailings. Predominant oxides in Nestor mine tailings samples are $SiO_2$ (ranging from 66.7-91.25 wt. %; followed by $Fe_2O_3$ and $Al_2O_3$ (in range of 0.82-15.63 wt. %; 3.21-12.50 wt. % respectively); $TiO_2$ (0.18-10.18 wt. %) and CaO (0.005-3.2 wt. %). Also occurring in small amounts is CaO (0.005-3.2 wt. %), $K_2O$ (0.51-2.27 wt. %), MgO (0.005-1.46 wt. %), $P_2O_5$ (0.029-0.248), $Cr_2O_3$ (0.013-0.042 wt. %) and $Na_2O$ (0.005-0.05 wt. %). The samples also contain significant concentrations of As (137-1599 ppm), Cu (34-571 ppm), Cr (43-273 ppm), Pb (12-276 ppm), Ni (16-157 ppm), V (29-255 ppm), and Zn 7-485 ppm). In the Glynn's Lydenburg Mine tailings $SiO_2$ is also the most dominant oxide ranging between 47.95 and 65.89 w%; followed by $Al_2O_3$ (4.31 to 16.19 wt. %), $Fe_2O_3$ (8.48 to 11.70 wt %), CaO (2.18 to 7.10 wt. %), MgO (2.74 to 4.7 wt. %). Occurring in small amounts is $K_2O$ (1.12-1.70 wt. %), MnO (0.089-0.175 wt. %), $P_2O_5$ (0.058-0.144 wt. %) and $Cr_2O_3$ (0.015-0.027 wt. %). Arsenic (As), is also occurring in significant amounts (807-2502 ppm), followed by Cr (117-238 ppm), Cu (10-104 ppm), V (56-235 ppm), Ni (45-132 ppm), Pb (13-63 ppm) and Zn (90-240 ppm). Nestor Mine tailings associated with Black Reef Formation mineralization have net neutralizing potential (NPR) <2, hence more likely to generate acid; and their acid potential (AP) ranges 1.56 to 140.31 $CaCO_3$/ton and neutralizing potential (NP) range from -57.75 to -0.3 $CaCO_3$/ton. Glynn's Lydenburg Mine tailings dump which is associated with dolomite mineralization, however, was not leaching acid. Based on acid-base accounting results, these tailings have more neutralizing potential (ranging between 57.6 and 207.88 $CaCO_3$/ton) than acid potential (ranging between 7.5 and 72.1 $CaCO_3$/ton); and their NPR>2, hence unlikely to produce acid. This is confirmed by paste pH which was in the ranges between 7.35 and 8.17. Tailings eroded from Nestor Mine tailings dump were also found to be characterized by high content of metals and oxides, namely, As, Cu, Ni, Pb, V, and Zn with $SiO_2$, $Fe_2O_3$ and $TiO_2$. The tailings were observed eroded into the Sabie River where AMD related precipitate (yellow boy) was also observed, indicating further oxidation downstream. Field observations, onsite analyses of water samples and laboratory results revealed that Nestor Mine tailings storage facility discharges acid mine drainage with considerable amounts of Al, As, Cu, Fe, Mn, Zn and $SO_4$ and very low pH exceeding the limit as per South African water quality standards. High concentrations of these metals have toxicity potential on plants, animals and humans. Upon exposure to oxygen and water, tailings from Nestor Mine are more likely to generate acid mine drainage that can cause detrimental effect to the environment and the surrounding communities. Potential pollutants are Fe, Mn, Al, As, Cr, Cu, Ni and Pb. Tailings from Glynn’s Lydenberg showed no potential for acid mine drainage formation.

**Key words**: Acid Base Accounting, Acid Mine Drainage, Mine Residues Deposits, Net Acid Neutralizing Potential, Net Acid Potential, Tailings Storage Facility

## ABBREVIATION

| | |
|---|---|
| ABA | Acid Base Accounting |
| ALD | Anoxic Limestone Drain |
| AMD | Acid Mine Drainage |
| AP | Acid Potential |
| CEC | Cation Exchange Capacity |
| ICP-MS | Inductively Coupled Plasma Microscopy |
| NP | Neutralisation Potential |
| NAP | Net Acid Potential |
| NNP | Net Neutralizing Potential |
| SAPS | Successive Alkalinity Producing Systems |
| SRB | Sulphate Reducing Bacteria |
| TSF | Tailings Storage Facility |
| RAPS | Reducing Alkalinity Producing Systems |
| XRD | X-Ray Diffraction |
| XRF | X-Ray Fluorescence |

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# Chapter 1: INTRODUCTION

## 1.1 Background

Mining is one of the most important economic activities in South Africa. In contrast to its economic benefit, different kinds of mine residue deposits (herein referred to as tailings mine dumps) associated with extraction and processing of metals accumulated along centuries constitute potential environmental pollution sources. In Mpumalanga Province, Sabie-Pilgrim's Rest Goldfield had been producing gold since 18th century generating wastes in the form of tailings and waste rocks. According to Cartwright (1961) gold was first discovered within the Sabie-Pilgrim's Rest area in 1872 and mined as alluvial workings and shortly thereafter, by underground mining of primary and secondary mineralisation in the oxidised zones of both concordant and discordant reefs. Engineering News (1997), reported that in 1996 alone about 377 million tons of mine waste were produced accounting for 81% of the total waste stream in South Africa.

Metals can be introduced into the aquatic ecosystem in the form of particulate through erosion of mine residue deposits or the direct discharge of tailings in rivers as reported by Nriagu, (1990). AMD prediction is of paramount importance in predicting the release of dissolved metals from both active and past mining operations. Waste rock dumps, ore stockpiles, tailings deposits and mine pit itself are some of the sources of AMD generation from mining operations (Kleinman et al., 1981; Oberholster et al., 2013). According to Antmann and Luoma (1991) leachate from mining complexes and waste rock deposits may drain into nearby aquatic ecosystems and once in streams, metals can be transported considerable distances downstream. Elevated levels of metals (e.g. lead, copper, iron, zinc) contained in acid mine drainage have a direct impact on ecosystems and water quality, thus impacting the environment and potentially human health (Williams et al., 1982).

Geochemical characterization of mine waste impoundments is important for rehabilitation, or remediation, and to protect the surrounding environment. Surface to subsurface sampling is entailed for effective geochemical characterization, though it can be labour or cost intensive if not properly planned. Metals in mine waste impoundments are mostly hosted by acid-generating sulphide-rich minerals such as pyrite ($FeS_2$) or adsorbed onto surfaces of weathering products of such sulphide-rich minerals. Such minerals are unfortunately difficult to detect or identify by using current remote sensing techniques including multispectral or even hyperspectral data. However, it had been shown that certain sulphide-rich minerals, particularly pyrite, weathers to a series of iron-bearing sulphates, hydroxides and oxides (Swayze, 2000).

Though the true scale of environmental pollution due to mine water discharge is difficult to assess accurately, in 1989, it was estimated that ca. 19300 km of streams and rivers, and ca. 72,000 ha of lakes and reservoirs worldwide has been seriously damaged by mine effluents (Johnson, 2000).

Acid mine drainage (AMD) is a concern in certain regions of South Africa because of decades of intensive mining (McCarthy, 2011). Engineering News, (1997) reported 377 million tons of mine wastes containing large amounts of acid producing sulphide minerals such as pyrite were produced in 1996 alone in South Africa. Rosner et al., 1998 identified more than 270 million tons of tailings dumps related to gold mining and covering a total of about 180 km$^2$ in South Africa of which majority are situated either in highly urbanised areas or close to valuable agricultural land. Increased operating costs of deep underground mines since the 1970s have encouraged some companies to shift focus on reclamation of existing tailings dumps to recover gold still available in economically viable quantities. Only those portions of tailings dam with high gold grade are reclaimed and as a consequent on-going acid generation and contaminant remobilization from remaining low-grade tailings will continue to degrade the environment. A contaminated footprint of the former tailings materials remain after reclamation process and continue to affect the environment (Rosner et al., 1996).

According to Hobbs et al. (2008), Witbank Coalfield mines are known to release AMD to the Olifants River with little being documented on their threat to Crocodile catchment and only gold mines at Barberton are suspected danger to Crocodile River.

Mining is currently inactive in many parts of the Sabie-Pilgrim's Rest goldfield and there is a considerable amount of mine residues deposits that have been generated from past mining activities. The area is characterised of tailings impoundments of different ages and sizes. Nevertheless, few or no environmental studies had been carried out on new or old mine wastes. The present study focuses on the Nestor and Glynn's Lydenburg Gold Mine tailings storage facilities in the Sabie area. The geochemical and mineralogical study of Sabie-Pilgrim's Rest Goldfields will help to understand and predict the potential of acid mine drainage occurrence and develop remediation and/or management program. The type and extent of pollution in the unsaturated zone determine the type and extent of rehabilitation approach that would be required for safe land use and the prevention of groundwater contamination. Large-scale pollution of land from the tailings dumps in the Sabie-Pilgrim's Rest goldfield poses a serious threat to human health and the environment, including surface and groundwater, forestry as well as agricultural practices. The issue of control of water pollution has reached primary importance in both developed and developing countries. The prevention of pollution at source, the precautionary principle and the prior licensing of wastewater discharges by the competent authorities have become key elements of successful policies for preventing, controlling and reducing inputs of hazardous substances, nutrients and other water pollutants from point sources into aquatic ecosystems (Enderlein, 1996). However, mining commenced in the Nestor and Glynn Lydenburg of Sabie-Pilgrim's Rest prior to any environmental regulations guidelines for sustainable mining in South Africa.

## 1.2 Research Problem

According to Cartwright (1961) gold mining at Sabie-Pilgrim's Rest dates over a century and this activity started way back in 1872 and prior to mining there was no baseline data. No comprehensive study exists of the environmental risks posed by gold mining in the Sabie-Pilgrim's Rest in particular with regard to impacts from acid mine drainage, radionuclides and metalloids resulting from mine residue deposits on the surface water resources, ecosystems and human health. Large-scale pollution of land from mine residue deposits, particularly tailings, in the Sabie mining area poses a threat to human health and the environment, including surface and groundwater as well as forestry and agricultural activities.  In the Sabie-Pilgrims Rest Goldfield, Epigenetic gold mineralization occurs in concordant and discordant gold-quartz-carbonate-sulphide veins of the Transvaal Sequence within the Black Reef

Formation where Nestor TSF is located as Well as Oaktree Formation of the Malmani Subgroup where Glynn's Lydenburg TSF is located. The Nestor TSF is located on the shore of Sabie River just about 300 m up-stream and weathered tailings from the storage facility were observed eroded into the river with evidence of yellow boy observed under Klein-Sabie Bridge flowing down-stream to join the Sabie River.

The Council for Geoscience is currently assessing the impact of South African mining on the Komati/Crocodile Catchments. During the field investigation, tailings dumps in the old mining sites of Sabie were leaching acid. The Nestor tailings dump is currently leaching acid and the leachate is characterised by low pH 1.84, the paddocks water had pH of 2.6 with water under Sabie Bridge having a low pH of 3.7. Yellow boy and white precipitates like salts were observed and they are washed towards Sabie River. This is posing a very serious threat to Sabie River as it was observed that the leachate and mine dump sediments are discharged directly in to Sabie River, especially during and after heavy rainfall.

### 1.3 Justification

Knüppe (2010) identified industrial activities, mine drainage, domestic effluent and agricultural runoff as sources of water pollution worldwide. While surface water has become a less reliable source of clean water because of industrial activities, mine water, domestic effluent and agricultural runoff, groundwater becomes an alternative source of clean water to accommodate fast growing need for water resource in South Africa (DWAF, 2004).

Accurate prediction of Acid Mine Drainage from mines is a critical requirement permitting long and short-term operation which is beneficial to both the mining industry and government. It is very important to undertake detailed geochemical and mineralogical characterization in the Sabie-Pilgrim's Rest Goldfield with the view of establishing the presence and quantity of acid-forming minerals and neutralising minerals within mine residues. This would provide a sound understanding on potential/occurrence of acid mine drainage within the areas study area. The results of this study will be of interest to Council for Geoscience (CGS), an institution involved in geological research in South Africa and other research organisations, in the context of understanding the potential of AMD in Sabie-Pilgrim's Rest Goldfields. The results may also help the academic community in the further understanding of the Goldfields, and government departments (Department of Mineral Resources, Department of Water Affairs and Sanitation) in order to make informed decisions which will help in management/mitigation measures to be taken in order to deal with the problem.

The Nestor Mine are engaged in active reclamation of tailings storage facilities as observed during preliminary site visit by the Council for Geoscience AMD task team in February 2012. This large scale reclamation of tailings storage provides a perfect opportunity to study tailings dams' profiles and characterize their oxidation profiles. Cross-sections and full natural profiles can be observed and studied from the exposed tailings storage facilities which would be cost-effective compared to drilling and also overcome difficulties encountered during drilling of deep holes on tailings dumps. Nestor Mine TSF in the Sabie-Pilgrim's Rest Goldfield represents one of the oldest tailings dumps within the goldfield from which gold had been extracted since 1872 as reported by Cartwright (1961). Its proximity to the Sabie River and Sabie Village only 1.5 km away and Sabie town makes this study relevant. On the other hand, Glynn's Lydenburg Mine TSF is located a kilometre west of Sabie town and it had been covered with grass.

The study is essential because it will help to understand the extent of water pollution from Nestor and Glynn's Lydenburg Mine tailings storage facilities. The type and the extent of pollution in the unsaturated zones determine the type and extent of rehabilitation that would be required for safe land use and the prevention of surface and groundwater contamination. The findings from the present study will further assist the Department of Water and Sanitation (DWS) in understanding the potential impact on the water resources in the vicinity of Sabie and in structuring water quality management approach.

## 1.4 Objectives

### 1.4.1 General Objectives

The main objective of this study is to characterise the quality and quantity of the potential leachate from gold tailings storage facilities and mine water in the Nestor and Glynn's Lydenburg Mine in the Sabie-Pilgrim's Goldfields. This will enable the characterization of existing and/or potential sources of water pollution and development of appropriate management/mitigation measures. The two respective tailings storage facilities have unique mineralization. Mineralization in Glynn's Lydenburg Mine took place within Malmani Dolomite while in Nestor Mine mineralization took occurred within the Black Reef Formation.

### 1.4.2 Specific Objectives

The specific objectives were:

- To determine the mineralogy and the geochemistry of tailings materials
- To characterise the quality and quantity of the potential leachate
- To determine the quality of seepage water and compare with the adjacent Sabie river water
- To map oxidation zones for the mine residues deposits;
- To determine heavy metals content of the tailings.

## 1.5 Hypothesis

- Oxidation of sulphide minerals from Nestor and Glynn's Lydenburg tailings storage facilities can generate acid mine drainage (AMD).
- Potential metal contaminants of leachate can be determined from Sabie-Pilgrims Rest.
- Malmani dolomite can act as buffer for potential acid generated from Glynn's Gold Mine Tailings Dump.
- Oxidation and phreatic water surfaces can help in prediction in the prediction of acid mine drainage from Nestor and Glynn's Lydenburg Mine Tailings Dumps.

## 1.6 The Study Area

### 1.6.1 Location of the study area

The study area is located in the Sabie area of Mpumalanga Province, South Africa. Figure 1 shows the location of both the Nestor Mine Tailings Dump and Glynn's Lydenburg Mine Tailings Dump.

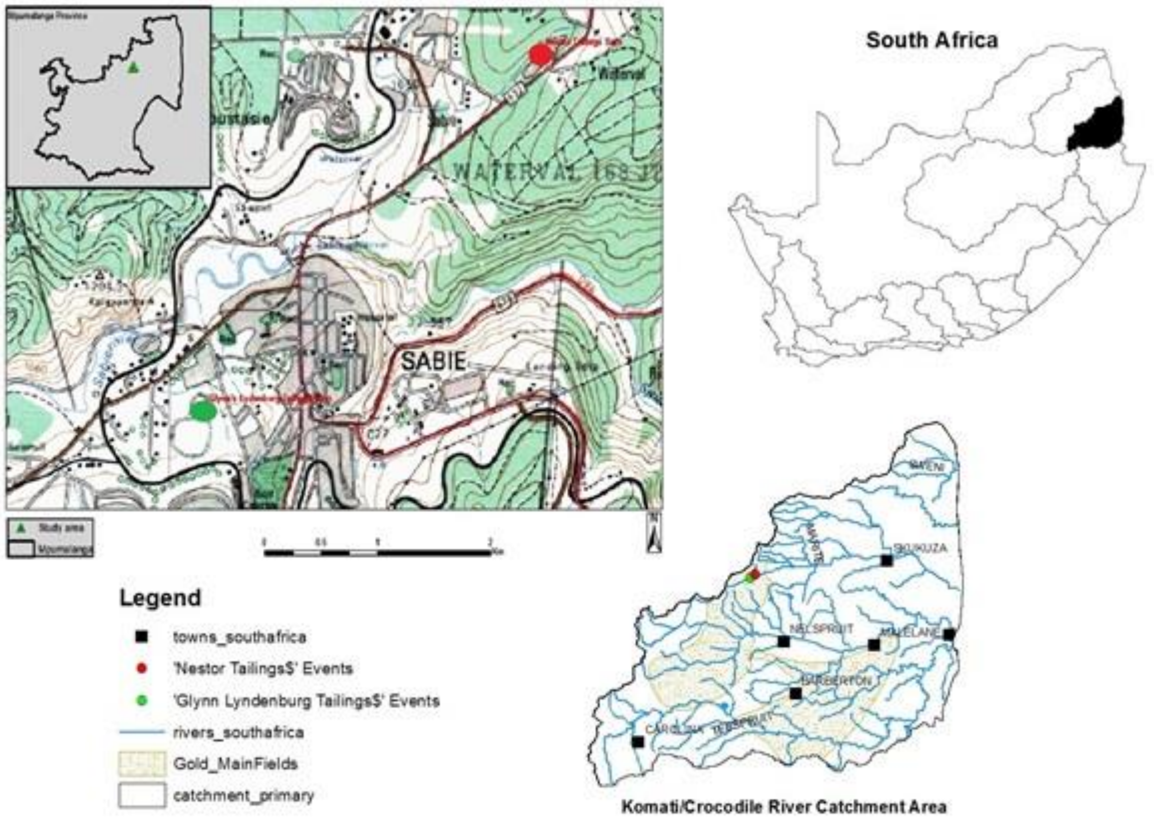

Figure 1 Location of the Study Area

### 1.6.2 Climate of the study area

The annual mean rainfall varies between 2000 mm in the escarpment to around 450 mm in the Lowveld towards the border between South Africa and Mozambique recorded in the catchment area (Water Research Commission, 2001). The rainfall is concentrated in summer months which are from November to March. Within the Sabie catchment, cyclonic activities are also recorded occasionally. The rate of evaporation varies from 1700 mm in the east to 1400 mm in the west and summer values are higher than winter values in the Lowveld (Heritage et al., 2001). Sabie river reaches peak flows in summer with low flows being experienced at the end of winter dry season, although no flow conditions have never been recorded (Water Research Commission, 2001).

### 1.6.3 Hydrology and Topography of the area of study

In terms of water management areas as designated by Department of Water Affairs, the study area falls under the Sabie River Catchment within the Inkomati basin which is the international drainage basin occupied by South Africa, Mozambique and

Swaziland (Figure 1). The water management area extends over several parallel river catchments which all drain in a general easterly direction, and flow together at the border with Mozambique or within Mozambique to form the Inkomati River, which discharges into the Indian Ocean immediately north of Maputo (Deacon, 1996). The study area is surrounded by forestry, with timber plantation and rural communities. The Sabie River Catchment covers an area of 7069 km$^2$, of which 6347 km$^2$ falls within South Africa. The main stream of the catchment is the Sabie River, acting as tributaries are the Sand and the Marite Rivers respectively, while the Mac River is a tertiary drainage (Deacon, 1996).

Topographically, the Sabie Catchment has been divided into two regions which are the Middleveld and Lowveld region. The western portion of the catchment is occupied by the Middleveld region which is characterised by an undulating topography which is more mountainous in the west. On the other hand, the Lowveld region is characterised by flat to gently undulating topography except in the east in the vicinity of Lebombo Mountains. The Sabie River catchment has no large flood plains, wetlands or swamps (Deacon, 1996).

At an altitude of 2200 m west of the catchment, the Sabie River rises in the Drakensberg Mountains, north of the Long Tom pass. The Sabie River has a total length of about 230 km to its confluence with the Inkomati River in Mozambique (Deacon, 1996).

# Chapter 2: Literature Review

## 2.1 Geological Setting of Sabie-Pilgrim's Rest

Sabie gold mining area forms the southern part of the Sabie-Pilgrim Rest Goldfield, situated in Mpumalanga province, South Africa. This Goldfield is very much important in so far as the history of gold mining in South Africa is concerned. Gold was discovered in 1872, initially recovered by alluvial diggings along the Sabie River and later by underground mining (Cartwright, 1961). Some of the major mines operated in the Sabie-Pilgrim's Rest Goldfield area include: Nestor Mine, Rietfontein, Gylnn's Lydenburg, and Elandsdrift Gold Mine under the ownership of Transvaal Gold Mining Estates (TGME) (Figure 2) (Oosterhuis, 2002).

The Sabie catchment is underlain by a wide variety of lithologies, comprising sedimentary, intrusive and extrusive igneous and metamorphic rocks (WRC, 2001). The youngest rocks in the catchment are the sedimentary and the volcanic Karoo sequence formed 280-190 Ma, followed by the Timbavati Gabbro Intrusion 1.450 Ma), the Transvaal Sequence (2.300-2.220 Ma) and Archean Basement Complex of metamorphic gneiss and migmatite and intrusive granites being the oldest (3.300-2.800 Ma) (Johnson et al., 2006). Dolerites dykes, diabase and gabbro are also fairly dominant in the lower reaches of the Sabie catchment.

Gold mineralisation occurs within the Malmani Subgroup, part of Chuniespoort Group of the Transvaal Sequence. In addition, Oosterhuis (2002) also reported the occurrence of gold mineralisation within the Black Reef formation and the underlying basement granite in the Sabie area (Figure 2).

The stratigraphic succession, younging upwards (Figure 3), includes Achaean basement granite, as well as minor Godwan Group and Wolkberg Group clastic sediments that uncomfortably overlie the basement rocks (Oosterhuis, 2002). The protobasinal Wolkberg Group forms the lowermost part of the Early Proterozoic Transvaal Supergroup and lies uncomfortably on the Archean Nelspruit batholith which comprises a large composite body of granodiorite-adamellite which contains local small pegmatites but is then barren of mineralization (Robb et al., 1983).

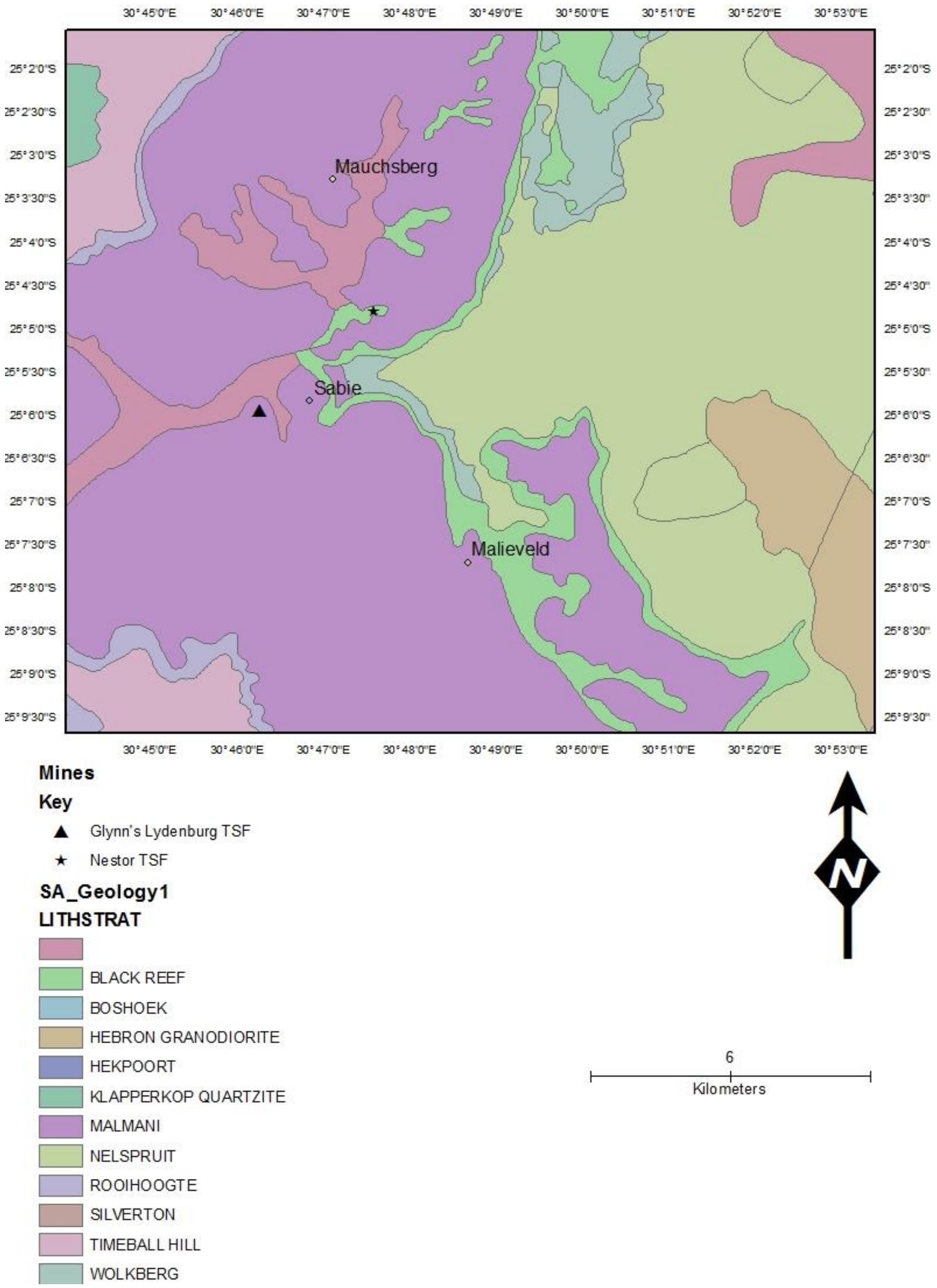

Figure 2 Generalised geology of Sabie (1:1 000 000 digital Metallogenic Map)

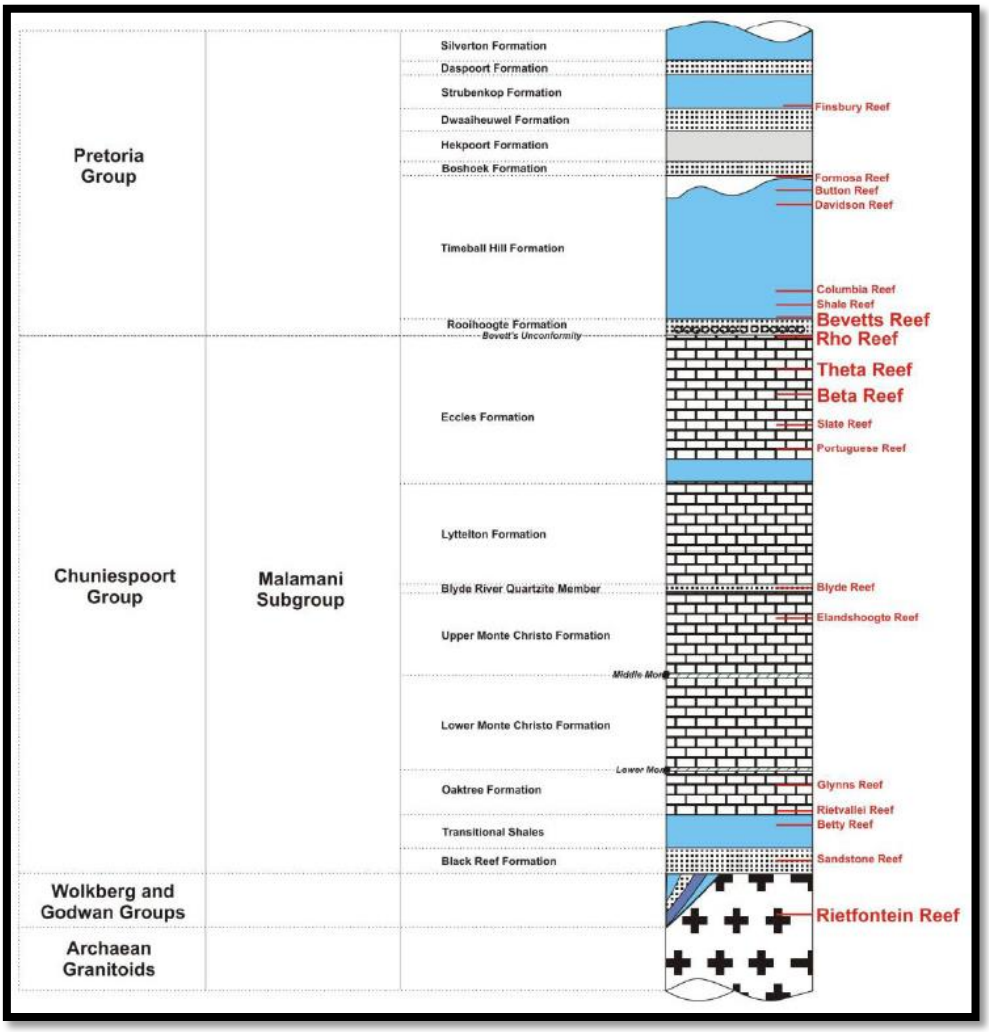

Figure 3 Stratigraphic succession of Sabie-Pilgrim's Rest showing major reefs (Ward and Wilson, 1998)

The Transvaal Supergroup is separated from the Wolkberg Group by an angular unconformity. The Black Reef Quartzite Formation forms the base of the Transvaal Super group which marks a major regional unconformity. The siliclastic sedimentary rocks of the Black Reef Formation which form the main part of the escarpment in the area and consisting of feldspathic quartzite with interlayered lenses of grit and conglomerate disconformably overlie the Wolkberg Group. This formation is in turn overlain by the Chuniespoort Group, comprised of the lower Malmani Dolomite Subgroup, the Penge Iron Formation and the upper Deutschland Subgroup. The Malmani Subgroup consists of four Formations, namely, the Oaktree, Monte Christo, Lyttelton, and Eccles Formations and is a host to the majority of gold-bearing quartz veins. Variations in chert content and algal structures found in the dolomite are the basis of formational divisions within the Malmani Subgroup (Button, 1973; Clendenin, 1989). Clendenin (1989) and Tyler (1989) recognised successive regressive and transgressive sedimentary cycles in the Malmani Subgroup. Iron- and manganese-rich dolomite, carbonaceous shale, and quartzite comprise the Oaktree Formation while the Monte Christo formation is characterized by oolitic carbonate rocks (Button, 1986). In the Sabie-Pilgrim's Rest Goldfield siliclastic sediments composed of quartzite and/or shale mark the base of the overlying chert-poor Lyttelton Formation, which is composed of dark-coloured quartz arenite (Tyler, 1989). This unit grades upward to the upper dolomite and chert zone of the Eccles Formation (Button, 1973). In the eastern Transvaal developed the Pretoria Group and it is approximately 7,000 to 8,000 m in thickness (Button, 1973; 1986). The Pretoria Group overlies the Deutschland Subgroup. The Pretoria Group consists of alternating shale and quartz arenites, with minor conglomerates, granulestones, and interlayered volcanic units (Button, 1973).

Numerous basic dykes and sills of different ages, principally of Bushveld Igneous Complex age, with some post-dating the Complex, have intruded into the Transvaal Supergroup in the Sabie-Pilgrim's Rest area, and increase in frequency upward in the stratigraphy (Sharpe, 1981; Tyler, 1989). Pre-Bushveld dikes-sills and syn-Bushveld dikes-sills of pyroxenitic composition has been distinguished by Sharpe (1981) and Willemse (1959). The Pre-Bushveld diabase intrusions are intersected by gold-mineralized quartz veins such as that in Olifantsgeraamte mine, whereas the pyroxenitic syn-Bushveld dikes-sills crosscut mineralization such as that of Frankfort mine. Greenschist facies metamorphism had occurred to the pre-Bushveld dikes-sills prior to the emplacement of the Bushveld Complex (Sharpe, 1981). These intrusions had locally metamorphosed the Transvaal sedimentary and volcanic rocks (Button, 1986).

Mafic dyke emplacement, postmineralization normal faulting, and limited graben development have occurred parallel to the northeasterly trending lineaments which are evident within the Sabie-Pilgrim's Rest goldfield (Anderson, 1992) and bedding in the goldfield dips between 4 degrees and 15 degrees to the west. Vein emplacement is controlled by low angle, southward-verging bedding-parallel simple shear thrusts (Harley and Charlesworth, 1992).

## Gold mineralization

The recent publication in this regard includes: Ward and Wilson (1998) reported that the Epigenetic gold mineralisation occurs in concordant and discordant gold-quartz-carbonate-sulphide veins. Although the mode of mineralisation has been a controversial subject, many recent authors (Tyler, 1985; Meyer et al., 1986; Harley, 1983; Ward and Wilson, 1998; Oosterhuis, 2002) believe that the mineralization is of hydrothermal origin. According to Boer et al. (1995) the hydrothermal deposits of the Sabie-Pilgrim Rest Goldfield are unusual in terms of their geological setting and geochemical characteristics, and do not correspond to the known genetic models for typical mesothermal deposits. They thought to be associated genetically with the Bushveld Complex (Oosterhuis, 2002). Along a north-northeasterly direction, normal faulting, minor graben development, and the emplacement of several dyke swarms have taken place throughout the goldfield. In the alignment of some of the stoped-out areas in the mine workings of Glynn’s Lydenburg Gold mine this dominant structural trend is also reflected which are elongated parallel to the north-northeasterly trend (Fowler, 1968; Harley and Charlesworth, 1992).

Within the Transvaal Drakensberg goldfield, epigenetic gold mineralization occurs as concordant and discordant veins in the variety of host rocks. The mineralization had been suggested to be coeval to the emplacement of the Bushveld Complex by preliminary dating (Boer et al., 1995). The flat reefs or bedding-parallel veins have been linked to water sills that resulted from high fluid pressures of deep-seated magmatic source possibly related to intrusive Bushveld Complex and in this case, the clustering of deposits around Sabie-Pilgrim’s Rest goldfields may reflect the position of deep-seated mineralising intrusions (Harley and Charlesworth, 1992).

The Sabie-Pilgrim’s Rest Goldfield is located near the eastern margin of the Bushveld Complex and the two had been suggested to be genetically linked. Chaney and Twist (1991) suggested that the Bushveld Complex covered the Goldfield during the time of mineralization and that folding and multiple periods of erosion has reduced the extent of the complex and enclosing strata. The goldfield of Sabie-Pilgrim’s Rest is further intersected by two concentric structures along which feeder sites to the Bushveld Complex, namely, Losberg and Uitkomst, are arranged (Sharpe et al., 1981). Insights into the source of fluids in the mesothermal gold deposits and the nature of hydrothermal systems around large mafic intrusions can be provided by the Sabie-Pilgrim's Rest Goldfield since layered basic igneous complexes are not commonly thought to be associated with hydrothermal gold deposits.

## 2.2 Acid Mine Drainage (AMD)

Acid mine drainage (AMD) is the legacy of the past mining activities and continues in the current mining operations and it do affect the environment negatively. Forster and Solomons (1988) indicated that acid mine drainage from the mining environments forms when ore and waste materials containing sulphide minerals such as pyrite are exposed to water and oxygen. Water and oxygen must both be available in order for pyrite to oxidise where water doesn't only serve as a reactant, but also as a reaction medium and product transport.

Sulphide minerals from mine wastes can generate acid through oxidation and produce high concentrations of dissolved sulphate and metals (Ritchey, 1989). When the acid solution comes in contact with other minerals in the tailings, a serial of chemical reactions occurs. The presence of carbonate in the system may neutralise the acid generated by sulphide minerals oxidation (Lin, 1997). Secondary and tertiary minerals may also be produced (Jambor, 1994). Blowes and Jambor (1990) and Johnson (2000) indicated that the mobility of metals released from sulphide oxidation is thus affected by the formation of these minerals. Metal content, mineralogy and physico-chemical conditions determine the potential of environmental pollution by metals and metalloids from tailings impoundments (Al et al., 2000).

Mine residue deposits are materials remaining after the process of separating the valuable fraction from the uneconomic fraction (gangue) of an ore, such as tailings, slimes, waste rocks/overburden, slags. Tailings are distinct from overburden, which is a waste rock or material overlying an ore or mineral body that are displayed during mining without being processed (USEPA, 1994a). Elements and compounds uncovered by mining and mineral processing have the potential to change the receiving environment to its impairment as they were not part of the ecological system in such forms or concentrations. Minerals such as sulphides are formed at high temperatures and pressures at geological depth and are present in most mining and mineral processing wastes. Exposure to the surface and aerobic surficial conditions and minerals processing of sulphidic minerals result in mineral breakdown which release elements from their mineralogical bindings which may not be easily absorbed by unfamiliar ecosystems without impact. It is precisely because these elements were not part of overlying ecosystems before mining that they may pose threats to ecosystems and communities post-mining (Franks et al., 2011).

There are factors that play role in acid generation, the physical nature of the material is the fundamental factor especially particle size of the material. Particle size affects the surface area exposed to oxidation and weathering (Robertson and Broughton, 1992; Lapakko, 1987). Based on Jennings et al. (2008) technical report there is large difference in weathering rates based on particle size, the smaller particle size (~0.25 mm) are responsible for approximately 80% of both silica dissolution and sulphide oxidation, and larger particle size expose less surface area however on the other it may allow water and air to penetrate deeper into the unit, exposing material to oxidation and ultimately producing more acid. The relationships between particle size, surface area and oxidation play a prominent role in acid formation, the oxidation reactions will be discussed in the section 2.2.1. (Jennings et al., 2008; Robertson and Broughton, 1992) When material weathers with time, the particle size is reduced, exposing more surface are and changing physical characteristics of the unit (Robertson and Broughton, 1992).

The silica solution and Sulphide oxidation are responsible for neutralization and generation of acid respectively. Particle size, minerals present, extent of liberation and surface morphology are relatively proportional to surface are in acid generation. As the particle size is reduced, the balance of available sulphide and silica mineral surface area may change due to change in the relative amounts of these minerals present or in their specific surface area (Lapakko, 1987). Changes in amounts of surface areas may occur due to preferential reduction in particle size (Robertson and Broughton, 1992; Lapakko, 1987). Lapakko (1987) concluded that a particle size reduction may result in preferential enhancement of acid-generation or acid-neutralizing mineral surface areas, and this will in turn affect the drainage pH. Thus, it is possible that one particle size fraction of given rock, and not by another (due to variation in relative contents and availabilities of sulphide and silica minerals) will generate acid.

The permeability and pore size are also affected by small particle diameter and particle size, both of which influence the volume of extraction fluid held in pore spaces of granular materials and amount of time that is retained by material (Lapakko et al., 1998). The other components that affect the rate of acid generation include the type of sulphide mineral present including crystal form, type of carbonate mineral present, mineral surface area, available water and oxygen and bacteria (Lapakko et al., 1998; U.S. Environmental Protection Agency, 1994a).

### 2.2.1 Reactions for AMD

There are three general types of acid release from mine waste (Lapakko, 2002; Lapakko et al., 1998) In contrast according to The Lehigh Environmental Initiative at Lehigh University there are four reactions that represent chemistry of pyrite weathering to form AMD, the forth reaction is an overall summary reaction 1. The three reactions are the Iron sulphide oxidation, dissolution of soluble iron sulphate minerals and less soluble sulphate minerals of the alunite series dissolution (Jennings et al., 2008; Lapakko, 2002; Lapakko et al., 1998).

According to Jennings et al. (2008) the reaction between pyrite, oxygen and water produces a solution of ferrous sulfate and sulphuric acid as shown below in reaction 2, This oxidation process in undisturbed natural systems it occurs at the slow rate over geologic time period and the Ferrous iron can further be oxidized producing additional acidity (Nordstrom and Southam, 1997) . The oxidation (prior to mining) of sulphide minerals and the formation of sulphuric acid is the function of natural weathering processes (U.S. Environmental Protection Agency, 1994a).

$4FeS_2 + 15O_2 + 14H_2O \longrightarrow 4Fe(OH)_3 + 8H_2SO_4$… …………….............(1)

$2FeS_2(s) + 7O_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$………………..…………...(2)

Further oxidation of $Fe^{2+}$ (ferrous iron) to $Fe^{3+}$ (ferric iron) takes place when there is sufficient oxygen dissolved in the water or when water is exposed to atmospheric oxygen (Jennings et al., 2008; Lapakko, 2002), this reaction (3) occurs more slowly at lower pH values(U.S. Environmental Protection Agency, 1994a).

$2Fe^{2+} + ½O2_{+}\ 2H^{+} \longrightarrow 2Fe^{3+} + H_2O$ ……………….……………….(3)

If the ferric iron is in contact with pyrite, dissolved pyrite reaction occurs as shown in equation 4. Reaction 5 the Ferric iron precipitates as hydrated iron oxide. The dissolution of pyrite reaction (5) generated more acid (Jennings et al., 2008; Lapakko, 2002; Lapakko et al., 1998; Ferguson and Erickson, 1988).

$2Fe^{3+} + 6H_2O \rightleftarrows 2Fe(OH)_3(s) + 6H^{+}$ ...………………………………(4)

$14Fe^{3+} + FeS_2(s) + H_2O \longrightarrow 2SO_4^{2-} + 15Fe^{2+} + 16H^{+}$…………………… …(5)

Reaction 2, the oxidation of pyrite to form dissolved ferrous iron, sulphate and hydrogen can occur abiotically or can be bacteria catalysed by *Thiobacillus ferrooxidans and Thiobacillus thiooxidans bacteria* (Ferguson & Erickson, 1988). Reactions (3, 4, 5) can be accelerated or catalysed by the presence of bacteria: *Thiobacillus ferrooxidans*, without the influence of the bacteria the oxidation rate of ferrous iron in an acid medium would be slow to provide significant AMD, and therefore the final stage of AMD formation process occurs when the catalytic bacteria has become established (Jennings et al., 2008; Ferguson & Erickson, 1988). Reactions 3 and 4 represent the first or initial stage in three-stage AMD formation process and it is relatively slow. Stage 1 persists under pH > 4.5 surrounding conditions, transitional stage 2 occurs as Fe hydrolysis (reaction 4) is slower and pH declines, Stage 3 consist of rapid acid production and dominant where pH are acidic, where $Fe^{2+}$ is more soluble (Ferguson & Erickson, 1988).

U.S. Environmental Protection Agency (1994a), Ferguson & Erickson (1988) identified primary, secondary and tertiary factors that control the acid drainage. Primary factors include the production of acid, such as the oxidation reactions. The primary factors are sulphide minerals, water, oxygen, ferric iron, bacteria as catalysts in oxidation reactions and generated heat. The rate of iron sulphide oxidation and acid production depends on the solid-phase compositional variable, availability of oxygen and water. It is often reported that reactivity increases in the order Pyrite > Pyrrhotite>Marcasite (Ferguson & Erickson, 1988; Lapakko, 2002).

Secondary factors control the product of the oxidation reaction such as reactions with other minerals that consume acid and also secondary factors neutralize acid or react with other minerals.  Secondary factors can either neutralize the acid generated by sulphides of change the effluent character by addition of metal ions. The most common neutralizing minerals are calcite and dolomite. Metals occurring in dissolution include aluminium, manganese, copper, lead and zinc (Ferguson & Erickson, 1988; U.S. Environmental Protection Agency, 1994a).

Tertiary factors are physical aspects of the waste management unit that influence the oxidation reaction, migration of the acid and consumption (U.S. Environmental Protection Agency, 1994a). The physical characteristics of the material are tertiary factors affecting acid drainage however physical nature of material such as particle size, permeability are important to the acid formation potential (U.S. Environmental Protection Agency, 1994a).

Acid mine drainage is a worldwide challenge not only in South Africa. In Europe, AMD continues to emanate from mines established during Roman Empire prior to 467 AD (CSS, 2002). A survey done in 1994 by Canadian Mine Environment Neutral Drainage (MEND) of metal-mine and industrial-minerals tailings showed that of the 7 billion tons of tailings and 6 billion tons of waste rock, 1.9 billion tons of tailings and 750 million tons of waste rock were potentially acid generating (MEND, 1995). Acid mine drainage had been released from the abandoned Britannia copper mine in British Columbia into local waters for many years reducing fish populations (Barry et al., 2000).

Ferguson and Erickson (1988) estimated that 7 000 km of streams in United States of America (USA) were affected by acid mine drainage while USEPA (1995) also showed that between 8 000 to 16 000 km in total of the streams in USA were draining acid water (AMD). Mendez (1978) reported reductions of benthic fauna in West Virginia stream severely affected by acid mine drainage. Nearly 300 abandoned metal mines have affected some streams in Boulder River watershed in Montana emptying all fish near mine sources (Faraq et al., 2003).

In September 2002, acidic mine water started discharging from an abandoned mine shaft in the Mogale City/Randfontein area of the Western Basin, South Africa as a result of flooding of mines within this basin to a level that allowed water to flow out to the surface. This was promoted mainly by cessation of underground water pumping which led to voids becoming flooded (DWAF, 2010). Significant trace elements concentrations of As, Cr, Ni, Pb and Zn were found on gold mine tailings dumps in the East Rand from the study conducted by Rosner (1996). Discharging of mine water is of concern to the environment as the water is characterized by elevated concentrations of salts, metals and radionuclides. A similar situation of acid mine drainage discharging has also developed in Central Basin (Johannesburg area) and Eastern Basin (Springs-Nigel area). A study conducted by Oelefse et al. (2009) on mine residues on the West Rand of the Witwatersrand basin had revealed that the gold tailings dumps were leaching acid mine drainage.

Acid mine drainage problems are also experienced in other gold mining areas, including Free State, Klerksdorp/Orkeney/Stilfontein/Hartebeesfontein (KOSH), Far West Rand and Evander Gold Mining areas of Mpumalanga and KwaZulu Natal and the O’Okiep Copper District. In the mid- 1990’s acid water started discharging from the Middleburg Colliery which is located northwest of the city of Witbank. The resultant acidified water contributed to large volumes of acid mine drainage on the upper reaches of the Olifants’ River catchment upstream of Lake Loskop where pollutants from upstream settle (Oberholster et al., 2010).

### 2.2.2 Acid producing minerals

In mine acid environment, there is a complex of sulphide (Table 1) and sulphate mineral assemblages that weathers in response to oxidation (Jennings at al., 2000) and there are many natural occurring bacteria, which play a major role in sulphide mineral oxidation reaction (Gleisner and Roger, 2002). The sulphides minerals in Table 1 are the primary acid forming minerals in acid mining environment; there response to oxidation depends on the surface area of the mineral, particle morphology and crystallinity  (Gleisner and Roger, 2002).Pyrite and (or) pyrrhotite is the most ubiquitous sulphide mineral in all sites of acid forming environment, it is responsible for acid discharge from underground coal and metal mines, surface mine spoils and tailing disposal areas (Udayabhanu and Prasad, 2010; Gleisner and Roger, 2002; Jennings at al., 2000) .

Jennings at al. (2000) conducted experiments on Acid production from sulphide minerals using hydrogen peroxide weathering. From their finding, pyrite is commonly the mineral that will generate acid upon weathering, some sulphide mineral such as chalcocite, galena that may be found in acid mine environment may not generate acid. Galena did not generate acid under experimental conditions, the pH was 4.07. The minerals that are found to be acid forming are in the order of their response to oxidation: pyrite> marcasite> pyrrhotite> arsenopyrite>chalcopyrite> and sphalerite (Gleisner and Roger, 2002; Jennings at al., 2000). Table 1 below lists sulphides mineral according to response to oxidation, i.e. pyrite is easily oxidised during acid generation than pyrrhotite (Udayabhanu and Prasad, 2010; Gleisner and Roger, 2002; Jennings at al., 2000; Plumlee, 1999).

Table 1 Common Sulphides known (inferred) to Generate Acid when oxidizing (Plumlee, 1999)

| Mineral | Formula |
|---|---|
| Common sulphides known (inferred) to generate acid with oxygen as oxidant: | |
| Pyrite, marcasite | $FeS_2$ |
| Pyrrhotite | $Fe_{1-x}S$ |
| Bornite | $Cu_5FeS_4$ |
| Arsenopyrite | $FeAsS$ |
| Ernagite/Farmitite | $Cu_3AsS_4$/$Cu_3SbS_4$ |
| Tennantite/Tetrahedrite | $(Cu, Fe, Zn)_{12}As4S_{13}$/$(Cu, Fe, Zn)_{12}Sb_{13}$ |
| Realgar | $AsS$ |
| Orpiment | $As_2S_3$ |
| Stibnite | $Sb_2S_3$ |
| Common sulphides that may generate acid with ferric iron as oxidant: | |
| All of the above plus: | |
| Sphalerite | $ZnS$ |
| Galena | $PbS$ |
| Chalcopyrite | $CuFeS_2$ |
| Covellite | $CuS$ |
| Cinnabar | $HgS$ |
| Millerite | $NiS$ |

| | |
|---|---|
| Pentlandite | (Fe, Ni)$_9$S$_8$ |
| Greenockite | CdS |

Sulphate minerals found in the acid mine drainage are the secondary minerals that generate acid. The precipitation of pyrite and pyrrhotite provides a source of Fe and acidity that leads to precipitation of sulphates minerals. Upon oxidation, hydrolysis and evaporation sulphates minerals form efflorescent salts. The other common minerals that form efflorescent salt are barite, anhydrite, gypsum, anglesite, and jarosite (Gleisner and Roger, 2002; Jennings at al., 2000). The Metal-sulfate such as melanterite salt leachates indicates the chemical composition with low pH value and high contents of dissolved solids and characteristics of acid drainage. In most cases goethite and jarosite are the common secondary sulphate minerals observed in acid mine drainage (Hammarsstrom et al., 2005).

### 2.2.3 Neutral producing minerals

Minerals that have the ability to neutralize can be gathered in two groups, namely, those providing carbonate to acidic water and those providing hydroxide to acidic water. Some minerals belong to both groups and some minerals may be considered neutralizing under some site-specific conditions and aid generating under other conditions (Morin et al., 1988).

Carbonate minerals include, amongst others, calcite and aragonite ($CaCO_3$), siderite ($FeCO_3$), rhodochrosite ($MnCO_3$), dolomite ($CaMg(CO_3)_2$), and ankerite ($CaFe(CO)_2$). Each of these minerals releases cation and carbonate to the water upon dissolution, with the carbonate participating in aqueous reactions. However, each mineral has different extent to which it can neutralize acidity and pH before a solubility limit is reached and dissolution ceases. Site-specific conditions as concentrations of various cations and anions in the water (speciation) and the aqueous pH determine neutralizing capacity (Morin et al., 1988). From one field study of natural neutralization by in-situ calcite, it was found that siderite formed as calcite dissolved, thereby removing some of the carbonate from the solution before it can participate in aqueous neutralizing reactions (Morin et al., 1988).

Hydroxide minerals include various combinations and hydroxide such as gibbsite ($Al(OH)_3$), boehmite (AlOOH), basalumite ($Al_4(OH)_{10}SO_4$), amorphous ferric hydroxide ($Fe(OH)_3$), goethite (FeOOH), and potassium jarosite ($KFe_3(SO4)_2(OH)_6$. Like carbonate minerals, the neutralizing capacity of each mineral is dependent on such site-specific factors as concentrations of various cations and anions and aqueous pH. Solubility of these minerals varies with the degree of crystallinity. The abundant numbers of minerals in this group and geochemical and site-specific complications in their behavior cause great difficulty in understanding acid neutralization by these minerals (Morin et al., 1988). The complexity in delineating the occurrence of aluminum-hydroxide-bearing minerals based on the chemistry of water in contact with these minerals has been demonstrated by Nordstrom (1982).

By using the concept of an equilibrium pH, a mineral's neutralization capacity can be expressed in simplistic manner. This values expresses the pH to which the acidic water would be neutralized by a mineral and, because of site-specific factors, a mineral can be expressed to have a different equilibrium pH at each site of acid drainage, although a definable range can be expected amongst many sites. Based on speciation and mineral-solubility calculations with data from six published field investigations and one laboratory study (Morin, 1988), the ranges of equilibrium pH for several mineral suites are listed in Table 2 below:

Table 2 Ranges of equilibrium pH for several mineral suites

| Range of Mineral Suite | Equilibrium pH |
|---|---|
| Calcium-based carbonates | 5.5-6.9 |
| Iron-based carbonates | 5.1-6.0 |
| Aluminium-hydroxide-bearing minerals | 4.3-5.0 |
| Iron-hydroxide-bearing minerals | 3.0-3.7 |

Minerals are assumed to dissolve to equilibrium from the preceding discussion. Some period of time is required to reach equilibrium in reality and, if acidic water quickly moves out of contact with a neutralizing mineral, the concepts of chemical equilibrium, solubility limits, and equilibrium pH are no longer applicable. Time-dependent kinetics may be necessary to describe and predict mineral dissolution and aqueous chemistry in waste-rock piles where water movement can be rapid (Lasaga and Kirkpatrick, 1981; Pearson and McDonnel, 1975). Kinetics of dissolution of siderite, calcite and dolomite have been examined by Evangelou et al. (1998), in excess hydrochloric acid and found that the dissolution essentially followed a first order equation simplified to:

$\ln [XCO_3] = -K_t + \ln [XCO_3^0]$

Where: t = elapsed time

$[XCO_3^0]$ = initial amount of carbonate mineral

$[XCO_3]$ = amount of carbonate remaining at time t

Values of K where found to be 27.64, 6.75, and 0.23 $hr^{-1}$ for siderite, calcite and dolomite, respectively. These values indicated the following temporal trends in dissolution (Table 3).

Table 3 Kinetics if dissolution of siderite, calcite and dolomite (Evangelou et al., 1998)

| Percent of Complete Dissolution | Elapsed time (hours) | | |
|---|---|---|---|
| | Siderite | Calcite | Dolomite |
| 10% | 0.0038 | 0.016 | 0.46 |
| 50% | 0.025 | 0.10 | 3.01 |
| 90% | 0.083 | 0.34 | 10.0 |

These results show that significant dissolution will occur within several hours. However, the values of K are dependent on such factors as mineral impurities, the acid initiating dissolution, and the speciation of acidic water and thus values will be site-specific.

According to Blowes et al. (2003) mine water typically has low pH and high concentration of sulphate, iron, and other metals. When neutralizing capacity of waste rock exceeds its acid generation capacity potential, the resulting pH is neutral. Consequently, the concentration of sulphate will be high with low concentration of iron in the mine waters. Further pyrite oxidation under neutral conditions is limited as iron precipitates as oxyhydroxides on the surface of sulphides such as pyrite

(Nicholson et al., 1990) and also absorbs released metals (Blowes et al., 1998; Romero et al., 2006). The neutral pH can impact on bacteria. When neutrophilic bacteria are most common instead of pyrite, pyrite oxidation will be slowed down even further (Blowes et al., 1998).

Various minerals including calcium- and magnesium-bearing carbonates, oxides, and hydroxides of calcium, magnesium, and aluminium, some silicate minerals, and some phosphates impart acid neutralization (Sherlock et al., 1995). Dissolution rate is influenced by factors such as pH, temperature, mineral composition, crystal size and shape, redox conditions and the concentration of "foreign" ions like metals. Because of their faster dissolution rate, carbonate minerals have considerable high neutralizing capacity than other neutralizing minerals (Sherlock et al., 1995).

## 2.3 Environmental Hazards of acid mine drainage

Dumping of wastes in the form of mine tailings creates serious environmental and health problems to the communities living next to abandoned mines and mine tailings (Miller, 1992). Brnich and Mallet (2003) showed that mine tailings are rich in metals and semi-metals are the potential sources of acid mine drainage. According to Ogola (1995), the scale of mining together with mining methods and chemicals used to recover the valuable minerals determine the degree of impacts to both the environment and human health. The absence of vegetation cover on exposed mine tailings contributes to erosion and sedimentation (Wright et al., 2004).

Acid mine drainage contaminated water often contain elevated concentrations of metals that can be toxic to aquatic organisms and the stream might become barren of most living creatures (Kimmel, 1983).Acid mine drainage is a pollutant. Even after mining has ceased, acid generation and discharge continues especially in a high rainfall locations. This acid act as hazard to the environment, as a result it is unsuitable for the use of animals, plants, human beings and aquatic life (Udayabhanu and Prasad, 2010; Paula and Babcock, 2013). The impact of acid mine drainage is not restricted to the local areas at the source but can also affect area at distance if the acid water is allowed to get discharged into the main water stream, the South Africa example of this scenario is pollution arising from gold mines of the Central and Western basin in Vaal river as a result of the inflow from Klip River and Blesbokspruit (Paula and Babcock, 2013; McCarthy, undated).

The Acid contribution to surface water may cause environmental damage. Metals/metalloids such as arsenic, copper, silver and zinc may leach, the contamination to the water may result and cause water to be unsafe for drinking (Udayabhanu and Prasad, 2010; U.S. Environmental Protection Agency, 1994). In ground water, acid mine drainage is diluted and possibly chemically reduced but there is a possibility that there is a risk of drinking water contaminated and be detrimental to human health. Leached metals are more harmful to the aquatic life and also to Wildlife. Wildlife impacts begin as early as the mine starts operations, especially the habitat destruction occurs at that time (Paula and Babcock, 2013).

According to Udayabhanu and Prasad (2010), the acid mine drainage has direct effect on fish, high acidy may affect fish reproduction, and fish growth rate. The acid water death is very tragic kind of death to the fishes, acid water increase permeability of fish gills to water and lack of oxygen to the cells leads to anoxia and ultimately death. Sulphide mining includes dust emission from the mine this has been an issue to the air quality (Paula and Babcock, 2013). A human who ingests high level of arsenic and lead may experience neurological effects and impairments of the circulatory system (Paula and Babcock, 2013). Paula and Babcock (2013) conducted studies using Agency for Toxic Substance and Disease Registry (ATSDR) and come to conclude that people who spend their lifetime near soils containing arsenic concentrations due to acid mine drainage might ingest enough arsenic to incur skin cancer. Plants growing in contaminated soil display uptake of lithophile elements and there is a potential for the transfer of elements such as Uranium into the grazing animals (Lottermoser and Ashley, 2006).

In Spain, some 600 m$^3$ of acid water was deposited over the Banks of Guardiamar River during flood with metal and sulphide rich sediments (USEPA, 2002). Nordstron and Alpers (1999) reported that millions of fish had been killed from mining related activities in U.S. during the past century. In 1989, large fish kill was also reported by Munshower et al. (1997) from acid, metalliferous tailings and efflorescent metal salts flushed in Montana’s Clark Fork River.

A study was conducted of distribution of fish in Pennsylvania streams affected by AMD. At pH 4.5 to 5.5 fish were found to be severely affected with a complete loss of fish in 90% of streams having waters of pH 4.5 and total acidity of 15 mg/L (Cooper and Wagner, 1973). Warner (1971) reported more species of insects and algae were found in unpolluted West Virginia streams (pH>4.5) compared to those streams polluted by acid (pH 2.8 to 3.8).

From the Auditor General of South Africa’s reports 5906 abandoned mines were officially listed in South African with 1730 being ranked as high risk as of end May 2008 (AGSA, 2009). The report showed that contamination of surface water and groundwater metals as one of major risks associated with abandoned mines.

DWAF (2007) reported the evident of water pollution caused by improper construction of gold mine dumps within the Olifants, Crocodile and Vaal catchments.

The Klip River on the West Rand of the Witwatersrand Basin has been negatively impacted by mine discharge generated by gold mines within the area and that has a negative impact on the quality of groundwater as most of these tailings dumps are on top of dolomite (Coetzee et al., 2007). Princess Tailings Dam has been identified as another source of contamination on Klip River Catchment through emanation of acid run-off, spillage and dust (Ngigi, 2009; Novhe, 2012). The Cradle of Human Kind World Heritage site located in Johannesburg had been impacted by the flow of acidic water (Abiye et al., 2011). Other sources of water pollution in the West Rand had been identified as industrial activities, urban runoff, informal settlement and sewer effluent (DWAF, 2009). Winde, 2006 argued that seepage from tailings storage facilities was likely to be the single largest source of water pollution in the West Rand of the Witwatersrand basin. Acid mine drainage from ownerless coal mines in the Olifants catchments creates tremendous environmental liability for South African government (Adler et al., 2007). From the study conducted by Driescher (2008), acid mine drainage was identified as one of the main sources of anthropogenic stressors on the aquatic environment of the upper Olifants River catchment. A mixture of acid mine drainage and increased nutrients levels present in the Olifants River System had affected phytoplankton communities (Oberholster et al., 2010), fish species (Watson et al., 2012) and crocodile population (Ashton, 2010).

## 2.4 Chemical contaminants related to acidified water

The earth’s crust is composed of major elements which are O, Si, Fe, Ca, Na, K, Mg, Ti, and P and trace elements which include Zn, Mn, Cu, Mo and B in minority, the trace element often inferred as  macro-nutrients which are essential for growth and development of organisms and play essential role for plants and man.  The large amount of quantity or excessive quantity of the macro-nutrients can be toxic (Ferguson & Erickson, 1988; Thornton, 1996; Lapakko, 2002). This section of the paper focuses on how each metal affects plants, animals and man, and their environments also studied the behaviour of each metal ( major and trace) in soil and sediments. The acid forming minerals releases the trace metals, major-metals of potential environmental concern for examples weathering of sphalerite leads to precipitation of Zn salts or to incorporation of Zn in solid solutions of $Fe^{2+}$ bearing minerals. Cd is released during Zn-rich efflorescent salts dissolution (Hammarsstrom et al., 2005). When oxidation process takes place, Heavy metals are mobilized and some become soluble (Aphane and Vermeulen, 2013; Ferguson and Erickson, 1988). The solubility, mobility of metals particles are depends on four main factors in terrestrial and aquatic environments i.e lowering of pH, Increased occurrence of natural or synthetic complexing agents which are capable of forming metal complexes that will increase metal mobility, Increasing salt concentrations and Changing redox conditions (Ferguson and Erickson, 1988).

### 2.4.1 Arsenic (As)

There are three oxidation states in which arsenic occurs, namely, (0), (III) and (V). Arsenic can exist as arsenite, As (III); arsenate (V) and as different complexes in solution. Arsenate salts are formed by inorganic arsenate with cation of calcium and iron. Soluble inorganic compounds are readily taken by living organisms and at elevated concentrations can exert toxic effects. The major two forms in which arsenic behaves as an anion are arsenates and arsenites. The type of inorganic arsenic species present in the aquatic environment is largely determined by pH and redox potential (Weast, 1979).

Arsenic and lead are more toxic to animals than plants they present the most insidious hazard to human health. Arsenic in plants functions as a constituent of phospholipid in algae and fungi, not known in animals. Its level of mammalian toxicity is high and medium to high for phytotoxity (Ferguson & Erickson 1988). Arsenate behaves similarly to phosphate in soils. It is absorbed by Fe, Mn and Al oxides and absorbs effectively at low pH, has low mobility in acid soils with high clay or oxide content (Ferguson & Erickson, 1988). When human beings are exposed to soil with arsenic high level, they are more likely to ingest soils and may experience gastrointestinal distress and change in liver (Paula and Babcock, 2013).

Metabolically, arsenic compounds are methylated to form monomethyl arsenic acid. Arsenic does not appear to accumulate at greater extent in animal tissues and tends to be involved in redistribution of copper, ultimately leading to a decrease in renal copper excretion. An increase in renal copper retention levels by 500% and five percent decrease in hepatic copper levels due to arsenic has been reported. An increase in hepatic iron concentrations and the resultant anemia reported too (Underwood, 1977).

### 2.4.2 Uranium (U)

Uranium is another toxic metal of concern, it contaminate the drinking water aquifers, degradation of aquatic ecosystems when released into ground water, surface water (U.S. Environmental Protection Agency, 1993). Fishes deaths have been reported by U.S. Environmental Protection Agency (1993) due to uranium contaminated water and drinking water not safe for consumption. Dewatering operation by underground water creates groundwater depressions that persist even after mining ceases, the surface disturbance or impact is not extensive as groundwater. Uranium contamination in groundwater is accompanied by overall chemistry of groundwater change (U.S. Environmental Protection Agency, 1995).

The use of abundant amounts of water to control dust or create slurry for the extraction of uranium during mining operation can contaminate large amount of water which then need to be disposed of. Tailings impoundments containing liquid material can leach contaminants into the soil and groundwater. Tailings dumps can also fail, releasing massive quantities of radioactive material into local waterways (Harding, 2008).

The major contributor to lung cancer seen in uranium miners is radon (Tomasek et al., 1994; Boice et al., 2008). Uranium mining operations frequently contaminate groundwater and surface water within its vicinity (Boice et al., 2008). Many compounds of uranium and decay products are soluble, toxic and radioactive. Uranium is principally toxic to kidney, particularly the proximal tubules in drinking water at level in excess of safe drinking water standard of 20 ppb (Craft el al., 2004), and it can also affect fertility, fetal growth and postnatal viability (ATDSR, 1999).

### 2.4.3 Iron (Fe)

Iron is the most abundant element in the earth's crust, Depending on the geology of the area and other chemical properties of the water body, iron may be present in natural waters in varying quantities. The two common states of iron in water are the reduced (ferrous, $Fe^{2+}$) and oxidized (ferric, $Fe^{3+}$) states (DWAF, 1996; Bartram and Balance, 1996). Ferric iron is found in solution only at a pH of less than 3. The organic or inorganic forming ion in the natural water system can enhance the solubility of both ferrous and ferric iron. Iron and manganese are naturally occurring in soils, can have deleterious effect on surface water (Vermont Department of Environmental, 2017; Bartram and Balance, 1996).

During the oxidation of pyrite in acid mine drainage, iron metals are release despite the fact that iron is an important micro-nutrient for all organisms and it is required in the enzymatic pathways of chlorophyll. Iron in excess quantities can be harmful to both plants and animals, it induces tissue damage and implicated in age-related macular degeneration (Gelfand et al., 2015; DWAF, 1996).

When iron metal is mobilized in groundwater and released to surface water it affect the associated aquatic habitat, it precipitates minerals which are deposited into lakes and streams. The extent at which iron dissolves in water is dependent on the availability of oxygen in water and to lesser extent to its degree of acidity. When the contaminated groundwater breaks to the surface, in the presence of oxygen, a rusty coat is formed which impacts the water quality, and there is loss of habitat for aquatic biota as exposed to the toxicity of iron metal (Vermont Department of Environmental, 2017; Bartram and Balance, 1997; Gelfand et al., 2015).

Wong et al. (2007) reported on iron toxicity as a potential factor to acid mine drainage, the iron excess is associated with retinal degeneration in the context of ocular siderosis, intraocular hemorrhage, and the hereditary diseases aceruloplasminemia and pantothenate kinase associated neuro-degeneration. Iron excess causes toxicity through generation of oxygen free radicals in organism cellular functionary. The excess iron in plants increases abundance of RNAs transcribed from short interspersed nuclear elements, which are inflammasome agonists (Wong et al., 2007; Gelfand et al., 2015).

### 2.4.4 Manganese (Mn)

Manganese is one of most abundant metals in nature, it is found in rocks, soils and waters and the Earths' crust consist of 0.1% of manganese (Pinsino et al., 2011b). Manganese in the nature is found in form of oxides, silicates, carbonates etc. Manganese content in water varies from 0.01-0.3mg/L (Nigam et al., 2015). There are three oxidation states of manganese in soil, namely Mn(II), Mn(III) and Mn(IV). In aquatic system the solubility of manganese increases at low pH and is mostly commonly in Mn(II) and Mn(IV) oxidation states. It precipitates out in sediments as Mn(IV) and re-solubilized as Mn(II) in water column. Manganese acts as constituent of the soil, its concentration range from 40 to 900mg $kg^{-1}$(Pinsino et al., 2011b; Nadaska et al., 2011).

Based on Pinsino et al. (2011a) manganese is considered an emerging contaminant because it is a real threat to human health and the environment. When discharged into the sea, it is toxic metal in marine environment, it decreases the fitness of organisms and in human excessive manganese induce neurological damage. Brain permeability of manganese is higher than that of zinc and iron and therefore it is very harmful to miners who are exposed to soil with manganese particles and the community close to the tailings (Pinsino et al., 2011a; Nadaska et al., 2011).

The manganese toxicity to the plants varies widely with the species. Toxicity include marginal chloroses and distorted development of the leaves, manganese causes disorders in some crops such as crinkles, the major factor is that manganese toxicity limit crop growth on acidic soils (Howe et al., 2005).

### 2.4.5 Copper (Cu)

Copper is another heavy metal that has an essential role as a nutrient for plants animals, and man. But if it is in excess in certain form it may be toxic to both plants and animals (Thornton, 1996). In Acid mine drainage, when chalcopyrite is oxidized, copper metals are released, copper has low mobility in reduced soils as the element is chalcophile and forms insoluble minerals such as $Cu_2S$ and CuS. The absorption increases with in increase with soil pH, in alkaline soils soluble $Cu^{2+}$ complexes are formed which are adsorbed to a lesser degree (Ferguson & Erickson, 1988).

Metals that most often exceeded standards or had increasing concentrations in groundwater or surface water are copper, cadmium, lead and mercury mostly about 63% of mines. Jennings et al. (2008) reported that the abandoned Britannia copper mine in Columbia has been releasing acid mine drainage into local water and fish abundance, distribution at contaminated and non-contaminated areas were studied. Laboratory outcomes confirmed that acid mine drainage from Britannia mine was toxic to juvenile Chinook and chum salmon (Jennings et al., 2008).

According to DWAF (1996) the copper toxicity decreases: in the presence of chelating agents, namely, humic acids, amino acids and suspended solids; with an alkalinity increase; and in the presence of other heavy metals such as zinc, molybdenum, sulphate, calcium or magnesium. Sodium nitrite and sodium nitrate decrease the toxicity of copper sulphate to aquatic life.

### 2.4.6 Zinc (Zn)

The heavy metals such as copper, selenium and zinc play an important role in maintaining the metabolism of the human being however excessive amount of zinc metals can be harmful to the human beings (Paula and Babcock, 2013; Zaidi et al., 2012). The elevated concentrations of Cd, Cu, and Zn in water column were associated with increased mortality of trout at sites in close proximity with acid mine drainage, the impact of the contaminated water caused hypertrophy, generation and necrosis of epithelial cells in the fish gills and many deaths were reported as due to the metals in the water column (Faraq et al., 2003).

According to Ferguson & Erickson (1988) the mobility of zinc in neutral soils are low, in alkaline soils the mobility of zinc higher and in anaerobic soils, the release of Zn

2+ from dissolved Fe and Mn oxides may at first increase Zn mobility, the mobility is restricted by the precipitation of exceedingly insoluble ZnS.

### 2.4.7 Aluminium (Al)

Having an abundance of 81 g/kg, aluminium is the most widespread metal in the earth's crust. Minerals of aluminium, particularly the silicates of aluminium are widespread and aluminium does not occur in elemental form. Bauxite, spinel and various aluminium silicates are some of the important minerals containing aluminium (Weast, 1979).

Aluminum present in only trace concentrations in natural waters occurs primarily as aluminosilicate minerals which are too insoluble. Al is relatively insoluble in neutral pH range. The concentration of Al in natural waters is almost near neutral pH (DWAF, 1996; Bartram and Balance, 1997).

In unpolluted water at a neutral pH the concentration of dissolved aluminium is 0.005 mg/l or less. The dissolved aluminium concentrations can rise to high values in acidic waters or where soluble aluminium complexes are present (DWAF, 1993). Aluminum is not bioaccumulated to a significant extent; certain plants can accumulate high concentrations of aluminum, e.g. tea leaves may contain up to 5000mg/kg. Because of its toxicity in aquatic organisms, aluminum does not bio concentrate in aquatic organisms to significant extent (Bartram and Balance, 1997). Like other heavy metals aluminum pose threat to the environment. Aluminium found in soluble form mainly in acid mine drainage waters and is a concern in waters affected by acid rain. It occurs toxic to hexahydrate (aquo) species, it toxicity depends on the chemical species involved (DWAF, 1993).

Waters and Webster-Brown (2013) studied Aluminum toxicity in streams affected by acid mine drainage, they used methods to predict Al toxicity in aquatic environments. Al concentration that is toxic to an organism depends not only on the type of organism but most trace metals in the waterway. Conductivity, pH, temperature, dissolved oxygen, and the presence of substance such as fluoride and side alter the toxic effect of Aluminum. Aluminum is toxic over the pH 4.4-5.4 the maximum toxicity is at pH5.0 – 5.2. Aluminum causes disruption of functionality of gills in *C. indistincta* (Chapman and Simpson, 2005). Soils with high and excess aluminum is said to be harmful to the human respiratory system, the respiratory effects include increases in granulomatous lesions in the lungs and increase the weight of the lungs (Bartram and Balance, 1997).

### 2.4.8 Nickel (Ni)

Nickel (Ni) is ranked of the 24th most abundant elements in the Earth's crust, comprising about 3% of the Earth's composition (Cempel and Nikel, 2005). In mining environment certain minerals such as gold, nickel and copper are associated to acid mine drainage problems that can cause long-term impairment to waterway and biodiversity (Akcil and Koldas, 2006). Nickel like other heavy metals is essential for at least several animal species; micro-organism and plants (Cempel and Nikel, 2005) and nickel may complex with cyanide and reduce the toxicity of cyanide at high pH level (DWAF, 1996).

Nickel is not a major concern compared to rest of other heavy metals especially in urban area however it may turn to be a problem if pH level in soil are reduced by use of soil liming in agriculture and mobilization as a consequence of acid mine(Cempel and Nikel, 2005).  Nickel is present in the soil, water and air in different form, it occurs predominantly as ion $Ni(H_2O)_6^{2+}$ in natural waters at the high pH levels 5-9 (Rathor et al., 2004). Similarly to Manganese the toxic symptoms of nickel include chloroses, chloroses is the main toxic symptom produced by nickel followed by necrosis. The other symptoms of nickel in plants are stunted growth of root and shoot, deformation and host of other growth abnormalities (Rathor et al., 2004; Howe et al., 2005).

When a Human is exposed to soil with high and excessive levels of nickel, they will have potential of pathological effects, among which includes skin allergies, lung fibrosis, cancer of the respiratory tract and iatrogenic nickel poisoning. Nickel may have other effects which modify toxic and carcinogenic effects of nickel due to its interference with heavy metals such as Fe(II), Ca(II), Zn(II) and Mg(II) (Rathor et al., 2004; Cempel and Nikel, 2005).

### 2.4.9 Sulphate

DWAF (1996a) defined sulphate as the oxy-anion of sulphur in the +VI oxidation state and forms salts with various cations such as sodium, calcium, manganese, barium and ammonium. Since most sulphates are highly soluble in water, sulphates tend to accumulate and give rise to progressively increasing concentration (DWAF, 1996a).

In unpolluted fresh water sulphate concentrations are typically less than 10 mg/l. The interactions of sulphate are governed by associated cations, usually sodium and magnesium (DWAF, 1996b). When acid mine drainage takes place concentrations of several hundred milligrams of sulphate per liter may occur (DWAF, 1996c). According to Kruger (2004), acid mine wastes and many other industrial processes such as tanneries, textile mills and other processes using sulphuric acid can discharge sulphates.

Sulphates and metals contained in acid mine drainage are the major source of natural water bodies contamination or pollution. Sulphate are not considered to be toxic at present however it affect the taste of water negatively and the sulphates concentration higher than 600mg/L which usually result in laxative affect (Luptakova et al., 2016; DWAF, 1996b). At the anaerobic condition sulphate produce sulphide which had toxic effects in the aquatic environments (Luptakova et al., 2016). The fish and plants deaths in aquatic environment are as a result of high levels of sulphide concentrations, hydrogen sulphide can also increase eutrophication in natural water bodies (Luptakova et al., 2016).

According to the Expert Team of the Inter-Ministerial Committee under the Coordination of the Council for Geoscience (2010) one of ways that acid mine drainage has impact on the environment is the reaction which produce acid mine drainage. The reaction result in high sulphate content in the resultant water that will remain high even after the acidity is neutralised. Therefore the water is unsuitable for domestic us, agriculture, some industrial uses and will increase the salinity of the receiving aquatic environment. It is therefore concluded that the associated high concentration of sulphate and iron also pose serious water quality problems if they enter the surface environment.

Although concentration of several hundred mg/l may occur where dissolution of sulphate minerals or discharge of sulphate-rich effluents rich from acid mine drainage takes place, typical concentrations of sulphate in surface water is 5 mg/l (DWAF, 1996b). By imparting a salty or bitter taste sulphate affects the portability of water. Ingestion of water with high concentrations of sulphate can cause acute health effects such as diarrhea (DWAF, 1996b).

### 2.4.10 pH

Chapman and Kimstach, (1992) defined pH as a measure of acid balance of a solution and it as negative of the logarithm to the base 10 of the hydrogen ion concentration, its scale runs from 0 to 14, that is from acid to basic. The pH 7 represent a neutral condition, pH is controlled by the balance between the carbonate, bicarbonate ions and carbon dioxide and natural compounds like humic and fulvic acids. Change in pH is a representation of certain effluents (Chapman and Kimstach, 1992). The natural waters have the pH that ranges from 6.0 to 8.5, mostly lower values occur in water with high organic content and water with higher pH values is mostly groundwater brines and salt lakes (Chapman and Kimstach, 1992). Gurdeep (1987) defined pH a reflection of the degree of acidity or alkalinity in the drainage, pH of the mine water is affected as the result of mining.

The rate of acid generation is primarily determine by pH (Akcil and Koldas, 2006), and it functions hand in hand with the available bacteria. For instance *A. Ferrooxidans* is most active in water with a pH less than 3.2; if this condition is not favorable the influence of bacteria on acid generation will be minimal. Another example is that acid tolerance is beneficial to the bacteria used in treatment, namely, sulphate-reducing bacteria survive in a wide range of pH conditions, but less active below certain pH (Doshi, 2006; Ferguson and Erickson, 1988).

The pH in conjunction with sulphate reflects that the lower the pH and more content of sulphate indicate that alkalinity produced from calcareous materials neutralizes acid in drainage. The pH in the water lowers principally from the formation of sulphuric acid and hydrolysis of oxidation product (Gurdeep, 1987). The relationship between the pH and sulphate are governed by the acid forming reactions which are oxidation of pyrite. The acid generated is the function of oxidation state of sulphide minerals (or iron metal); however, the oxidized iron precipitates at the base of drainage due to less solubility unless the pH is very low. When pH decreases, the rate of iron oxidized by oxygen also decreases however the rate of iron oxidation by bacteria increases at lower pH (Gurdeep, 1987; Ferguson and Erickson, 1988).

The pH values are affected by factors such as temperature, the concentrations of organic and inorganic ions, and biological activity. The availability and toxicity of constituents such as trace metals, non-metallic ions such as ammonium, and essential elements such as selenium are also affected by pH. The degree of dissolution of weak acids and bases can be affected by change in pH, thereby determining chemical species of many metals altering the availability and toxicity of metals in aquatic environment (DWAF, 1996b).

The pH value influences the taste of water, its acidity, chlorinating efficiency and the solubility of metal ions. Water may taste sour at low pH and high pH causes water to taste soapy (Kempster et al., 1980). People attaining water from a body which is exposed to acid rain tend to have deficiency in selenium due to solubility of elements as a result of lowering pH in water, (DWAF, 1996d).

### 2.4.11 Total Dissolved Solids (TDS)

The total amount of material dissolved in water is one of the major descriptors of its quality (Dallas and Day, 1993). DWAF (1996b) defined TDS as the total dissolved salts concentration is a measure of a quantity of all dissolved compounds in water that carry an electrical charge. Dallas and Day (1993) “the total amount of material dissolved in water is one of the major descriptors of its quality”.

The total dissolved solids concentration is a measure of all the quantity of compounds dissolved in water. The TDS concentration is directly proportional to the electrical conductivity (EC) of water; electrical conductivity being the measure of the ability of water to conduct an electrical current. Natural waters contain varying quantities of TDS as a consequence of dissolution of the minerals in rocks, soils and decomposing plant material.

The TDS concentrations of natural waters are therefore dependent at least in a part on the characteristics of the geological formations with which the water has been in contact (Dallas and Days, 1993). Because granite rock is composed of materials that do not ionize in water streams that runs through areas with granite bedrock tend to have lower conductivity. Higher conductivity is experienced in streams that receive runoff containing clay particles because of the presence of minerals in clay that ionize more readily in water. In water in contact with Precambrian shield areas and in water in contact with Paleozoic sedimentary rock formations the concentrations are much higher (DWAF, 1996a). TDS concentration also depends on physical processes such as evaporation and rainfall. Generally, TDS concentrations are low in rainwater, less than 1 mg/l and low in water in contact with granite, siliceous sand and well-leached soils less than 30 mg/l (DWAF, 1996a).

The effects of TDS are governed by the constituent's inorganic salts. The proportional concentrations of the major ions affects the buffering capacity of the water and hence the metabolism of organisms. Secondary effects include those on water chemistry, which in turn affect the fate and impact on the aquatic environment of other chemical constituents or contaminants (DWAF, 1996b). The effect of high TDS on aquatic organisms includes disruption of many physiological processes. Most organisms in the fresh water aquatic and semi-aquatic environment are adapted to osmotic conditions so they can excrete osmotically the salts they do not require. When the salts, indicated by TDS, in the water are very high (as in the case of most seepage and water affected by AMD), the organisms dehydrate. Physiological processes such as ion uptake and excretion in the plants and animals are disrupted, in this way death can occur (Pulles et al., 1996).

According to DWAF (1996a) some physiological effects which may directly relate to high concentration of dissolved salts include some effects on kidney function; effects of sodium on women with toxemia associated with pregnancy; adverse effects of sodium on certain cardiac patients and hypertension sufferers and laxative effects from mainly sodium sulphate and magnesium sulphate. When water with very high concentrations of TDS is used for bathing and washing purposes, excessive skin dryness and discomfort may result. Due to the portability of water saline water affect animal health and performance. The types of salts present in water and salinity level influence the taste of water. Certain salts such as magnesium sulphate are more harmful than sodium chloride or sodium sulphate (DWAF, 1996a).

### 2.4.12 Chloride (Cl)

Chloride in sea water is the major anion and in many inland waters particularly in South Africa. Chloride ions are essential components of living systems as they are involved in ionic, osmotic and water balance of body fluids. Chloride ions exhibit no toxic effects on living systems except where they have an effect by decreasing TDS (Dallas and Day, 1993).

Most chlorine occurs as chloride ($Cl^-$) in solution. It enters surface waters with the atmospheric deposition of oceanic aerosols, with the weathering of some sedimentary rocks, mostly rock salt deposits, and from industrial and sewage effluents, and agricultural and road run-off. High concentration of chloride can make water unpalatable and therefore, unfit for drinking or livestock watering (Chapman and Kimstach, 1992). Effluents containing ammonia, organic matter or cyanides convert chlorine into substances such as chloramines, which may be less toxic but more persistent than chlorine, thereby posing a long term threat to aquatic life. Chlorine can be described either being available, or residual. When present as chloramine it is referred to as combined. Chloramines slowly reach equilibrium with a low concentration of hypochlorous acid which accounts for their toxicity to fish (DWAF, 1996b).

The toxic effects of chlorine are usually irreversible. Free chlorine is more toxic but less persistent than combined chlorine. Chlorine itself does not accumulate, but chlorinated organic substances may bio-accumulate in aquatic organisms (DWAF, 1996b).

### 2.4.13 Nitrogen (Inorganic)

The term inorganic nitrogen incorporates all the major components of nitrogen [$NH_3 + NH_4^+ + NO_2^- + NO_3^-$] which are present in water. Both dissolved forms of inorganic nitrogen and those adsorbed on the suspended inorganic and organic material are available for uptake by algae and higher plants (DWAF, 1996b).

The common form of combined nitrogen found in natural waters is the nitrate ion ($NO_3^-$). During the process of dentrification, it may be biochemically reduced to nitrite ($NO_2^-$) usually under anaerobic conditions. The nitrite ion is rapidly oxidized to nitrate. Natural sources of nitrate to surface waters include igneous rocks, land drainage, and plant and animal debris. Municipal and industrial wastewaters which include leachates from waste disposal sites and sanitary landfills may enhance natural levels. The use of inorganic fertilizers in rural and suburban areas can also be a significant source (DWAF, 1996b).

Nitrate concentrations in freshwaters are usually very low, 0.001 mg/l $NO_2$–N, and rarely higher than 1 mg/l $NO_2$–N. High nitrate concentrations are usually indicative of industrial effluents and are often associated with unsatisfactory microbiological quality of water. Determination of nitrate plus nitrite in surface waters gives a general indication of the nutrient status and level of organic pollution (Chapman and Kimstach, 1992).

## 2.5 Prediction of acid mine drainage

According to Pope et al. (2010), mine drainage chemistry can be quantitatively predicted by investigating the geochemistry of rocks to be disturbed by mining. Kotelo (2013) indicated that characterization of the acid generating properties of mine wastes is troubled with uncertainty and deficiencies that create difficulties in evaluating and selecting suitable interventions for mitigating associated AMD risks in line with cleaner production and sustainable development principles. “There is no general method to predict long-term duration of acid generation or to predict when acid mine drainage will commence” (Skousen et al., 1998). Factors that influence AMD formation are highly variable depending on the mine site and geologic materials within the mine site. These factors include particle size, reactivity of NP and presence of oxidizers (Kuipers et al., 2006).

Commercial laboratories, research organizations and regulatory authorities have developed several AMD prediction techniques in Canada and United States. Generally, predictive techniques include static tests and kinetic tests (Duncan and Bruynesteyn, 1979).

### 2.5.1 Static predictive tests

Static tests are typically simple and inexpensive procedures to prove a preliminary assessment of the potential of a waste or other mine component to generate Acid Mine Drainage (AMD). They are primarily intended to examine the balance between the acid-producing and acid-consuming components of a sample (BC AMD Task

Force, 1989). Static tests do not provide definitive answers to all questions regarding the future behaviour of wastes and should not be used as such. They do however provide a means to classify wastes according to their potential to produce AMD and indicate the extent and type of further testing and evaluations that should be carried out. Static predictive tests serve as positive or negative indicators of theoretical potential for acid generation. These tests are useful in determining which geologic units have potential to generate acidity and are quick and comparatively inexpensive (Robertson and Broughton, 1992). When coupled with mineralogical and petrological data from test samples, certain static test procedures can provide some measures of neutralization rate (Mills, 1998).

The static predictive technique examines the balance between acid producing and acid consuming materials (Duncan and Bruynesteyn, 1979). Principal static prediction methods include paste pH, Standard ABA, Modified ABA, B.C. Research Initial Test. Other static acid mine drainage predictive tests include net acid production test and APP/S ratio (Ferguson, 1986).

#### *2.5.1.1 Paste pH*

According to Sobek et al. (1989), the main objective of carrying out this test is to determine the pH of a paste made from mixing the finely ground sample with water and indicate whether acid generation has occurred in the material prior to analyses. Paste pH is measured by a pH electrode in combination with a pH meter. Water is added to the sample to form a paste of a specific consistency. The electrode is placed into the paste and the pH value is directly read from the meter.

The following advantages and disadvantages for paste pH static tests have been summarised from Sobek et al. (1989):

Advantages of paste pH static test

- Simple and rapid method of determining the readily available acidity and alkalinity;
- Can be used in the field for initial screening of samples to assist in selection of samples for further laboratory evaluation.

Disadvantage of paste pH static test

Rates of acid and alkalinity generation are not predicted

### *2.5.1.2 B.C. Research Initial Test*

The aim of B.C. Research Initial Test is to provide a quantitative measure of the net acid production potential of a sample by comparing the maximum acid potential based on the stoichiometry of complete sulphur oxidation with the capacity of the sample to consume acid (Duncan and Bruynesteyn, 1979). Direct sulphuric acid titration is used from the neutral pH of the slurry containing the finely ground sample of a waste rock or tailing at a room temperature to an end point pH of 3.5 to determine the acid consumption for calculation of neutralization potential. The neutralization potential value obtained by acid titration is compared with theoretical acid potential, expressed in kg $H_2SO_4$/t (Duncan and Bruynesteyn, 1979). Acid potential is determined by analysing for total sulphur and calculating AP by assuming total sulphur conversion to sulphate (sulphuric acid) and a production of 4 moles of $H^+$ per mole of pyrite oxidized. Usually, the method only reports the final acid consumption to the end point pH (Bruynesteyn and Hackl, 1984). The end point of pH 3.5 is chosen as it is considered that this value represents the limit to biological oxidative activity. Therefore, if the theoretical acid production is not sufficient to below 3.5, then biochemical oxidation of the material will not occur, and formation of AMD is unlikely (Bruynesten and Hackl, 1984).

Bruynesten and Hackl (1984) summarized the following advantages and disadvantages of B.C. Research Initial Test:

Advantages of B.C. Research Initial Test

- Rapid and rapidly easy to perform;
- Can be used to screen large number of samples for further selective and more detailed evaluation;
- Sulphuric acid ($H_2SO_4$) titration of a sample down to pH 3.5 might provide a more realistic assessment of readily available neutralization capacity than the excess hydrochloric acid (HCl) addition method used in ABA.

Disadvantages of B.C. Research Initial Test

- Rates and extent of acid producing and neutralizing reactions are not determined;
- Calculations of acid production potential based on sulphur analysis can lead to overestimation of values;
- Does not indicate the pH to which the sample can neutralize during the extended contact with acidic water;
- More time consuming and costly than ABA.

### *2.5.1.3 Standard ABA Test*

Acid generating potential can be predicted from geologic formation using acid base accounting method. ABA has the ability to identify and quantify both acid-generating and neutralizing minerals in the geologic materials to be unearthed during mining operations (Skousen et al., 2002; Smart et al., 2002). Known as Sobek method (Sobek et al., 1978), this is a standardized EPA Protocol which was developed to characterize mine soil and overburden. Due to its simplicity and low cost analytical procedures are still widely used (USEPA, 1994b). This procedure is carried out with the objective to determine the balance between acid producing and consuming components of a mine waste. Standard ABA procedure is based on the addition of excess hydrochloric acid, heating to ensure complete reaction and titration of the consumed acid with sodium hydroxide to pH 7.0. Determination of the volume of normality of acid to be used in the digestion is based on so-called fizz test in which the carbonate content of a sample is estimated by observing the intensity of the reaction between a small quantity of the sample and strong hydrochloric acid. Determination of paste pH is also carried out (Sobek et al., 1978).

Sobek et al. (1978) summarized the advantages and disadvantages of using standard ABA test for the prediction of future mine drainage.

Advantages of Standard ABA Test

- Widely used and accepted method;
- Rapid and easy to perform

- Low cost, can be used to screen large number of samples for possible further selective and more detailed evaluation;
- Determines the maximum amount of neutralizing potential and acid potential available in the sample.

Disadvantages of Standard ABA Test

- Rates and extent of acid producing and neutralizing reactions are not determined;
- In using total sulphur analysis for calculation of AP, acid generating and none generating sulphur species are not differentiated, hence AP might be overestimated;
- Calculation of AP is based on one stoichiometry of reaction. Practically, the actual stoichiometry might vary significantly;
- Method does not indicate the pH to which the sample can neutralize during contact with acidic water;
- The boiling procedure might give overestimation of NP;
- Does not distinguish between reactive, readily available acid consuming minerals and less reactive species which might be important in the long term;
- Method does not indicate the pH to which the sample can neutralize during contact with acidic water.
- For some samples reproducibility of the NP determination is poor. In such cases, NP is often found to be affected by the quantity of acid added in the digestion stage.

#### *2.5.1.4 Modified ABA Test*

Various modifications of the original procedure have been developed that correct some of the disadvantages from the original method (Chotpantart, 2011). The objective in this method is still similar to the one of standard ABA procedure above. Neutralization potential and calculation of AP of a sample are still fundamental principles in modified ABA measurements. Net neutralizing potential (NNP) which is the difference between NP and AP allows classification of samples as potentially acid consuming or producing. Positive values for NNP imply that a sample is acid consumer and negative NNP values imply that a sample is acid producer. All values for NP, AP and NNP are expressed in units of tonnes $CaCO_3$ equivalent of the acid consumed (Lawrence, 1990).

The neutralizing potential is determined by titrating a sample with excess standardized hydrochloric acid at ambient, or slightly above (25-30ºC) ambient temperatures for 24 hours. A fizz test is performed for the amount of acid to be initially added to the test. Acid is added to maintain sufficient acidity for reaction as required during the acid-treatment stage. The unconsumed acid is titrated with standardized base to pH 8.3 after treatment to allow calculation of calcium carbonate ($CaCO_3$) equivalent of the acid consumed (Lawrence et al., 1989).

For calculation of acid potential, the sample is analysed for total sulphur and sulphate sulphur, and sulphide sulphur is calculated by the difference. Acid potential is determined from calculated sulphide sulphur analysis, assuming that total sulphur conversion of sulphide to sulphur and production of 4 moles of pyrite oxidized. In some cases, other sulphur species such as that associated with mineral barite (not distinguished in typical sulphate analysis) which do not contribute to the acid potential might be determined and correction made to the sulphide sulphur calculation (Lawrence et al., 1989).

The merits and demerits of Modified ABA procedure were summarized from Lawrence et al. (1989).

Advantages of Modified ABA procedure

- Rapid and easy to perform;
- Low cost, can be used to screen large number of samples for possible further selective and more detailed evaluation;
- Analysis of sulphur species allows a more realistic assessment of acid potential by using sulphide sulphur as the basis for calculation;
- Assessment of neutralizing potential is performed in the procedure, which can provide greater consistency of result and prevent overestimation of the value compared with the standard ABA procedure.

Disadvantages of Modified ABA procedure

- Rates and extent of acid producing and neutralizing reactions are not determined;
- Calculation of AP is based on one stoichiometry of reaction. Practically, the actual stoichiometry might vary significantly;
- Method does not indicate the pH to which the sample can neutralize during contact with acidic water.

### *2.5.1.5 Net Acid Production Test*

This static method of AMD prediction determine the balance between the acid producing and acid consuming components of a mine waste without need for sulphur analysis (Lawrence et al., 1988). Net Acid Production test uses the addition of hydrogen peroxide ($H_2O_2$) to oxidize sulphides contained in the test sample. All or part of the acid generated by the oxidation is consumed by the alkaline constituents in the sample. The net acid remaining after reaction is determined by titration to pH 7.0 to provide a direct assessment of the net acid production potential on the sample expressed as kg $CaCO_3$ equivalent per tonne of sample. This value can be compared with the Net NP from ABA (Albright, 1987; Lutwick, 1988; and Lawrence, 1988).

The following advantages and disadvantages of Net Acid Production Test are summarized from Lawrence et al. (1988):

Advantages of Net Acid Production Test

- Provide rapid and low cost assessment of the potential for acid generation;
- Can be used to screen large number of samples for further selective and more detailed evaluation;
- Sulphur analyses not required; method suitable for field use;
- Procedure might provide assessment of the readily oxidizable sulphur species.

Disadvantages of Net Acid Production Test

- Still in development stage and not proven as reliable method;

- Rates of acid generation not predicted;
- Alkaline components of the sample might interfere with the efficiency of pyrite oxidation by hydrogen peroxide.

#### *2.5.1.6 Alkaline Producing Potential/Sulphur (APP/S) Ratio*

Rapid indication of the potential of a sample of a mine waste to produce acid mine drainage without the need for kinetic testing is provided by this static acid mine prediction method (Capriccio et al., 1981). The method measures two components, namely, determination of the acid consumption of the sample (APP) and analysis of the sample for total sulphur content ($S_T$). The APP values obtained for number of samples from related geologic units, or primary mine components, are then plotted against corresponding ST values to provide an APP/S ratios plot. By comparing the plot with results simulated weathering (kinetic) tests such as humidity cells on the same samples, the relationship between weathering characteristics and APP/S ratio can be established. Future prediction of the behaviour of samples from same geologic units or mine components can then be made without the need for kinetic testing (Capriccio et al., 1981). Finely ground sample is treated with hydrochloric acid under milder conditions than employed for ABA in the determination of APP. The volume of base required to titrate the acid remaining after reaction to pH 7.0 is measured and compared with calibration curve prepared by performing the acid treatment procedure on $CaCO_3$ standards (Capriccio et al., 1981).

Capriccio et al. (1981) summarized the following advantages and disadvantages of APP/S Ratio test:

Advantages of APP/S Ratio Test

- The APP determination might provide a more realistic assessment of the available alkalinity in a sample by avoiding the digestion of minerals other than calcareous alkaline producing ones in the more extreme conditions of the NP determination in ABA;
- APP/S ratio plots in combination with corresponding weathering test data can be used to predict ARD potential of new rock samples without performing additional lengthy weathering tests;
- Low cost, can be used for screening of large number of samples.

Disadvantages of APP/S Ratio test

- Method developed to rank sedimentary horizons in coal deposits. Not widely used or proven for base metal and precious metal mine application;
- Rates and extent of acid producing and consuming reactions not directly determined, although correlation of APP/S ratio with weathering data base might provide some guidance;
- Use of total sulphur analyses may provide overestimation of acid potential and distort the APP/S ratio for some samples. The use of sulphide sulphur in the ratio might be preferred.

### 2.5.2 Kinetic predictive tests

Kinetic tests provide confirmation for AMD potential and attempt to predict drainage quality over time (Duncan and Bruynesteyn, 1979). Principal kinetic prediction methods include Humidity Cells, Columns and Lysimeters and B.C. Research Confirmation Test. Other kinetic methods that can be used for AMD prediction are Shake Flasks and Soxhlet extraction.

#### *2.5.2.1 Humidity Cell Tests*

In humidity cell tests, the aim is to model the processes of geochemical weathering of mining waste material. A weathering chamber is designed to provide a simple control over air, temperature and moisture, while allowing for the removal of oxidation products which are collected and monitored (Sobek et al., 1978).

The test procedure comprises subjecting a bed of a sample in a humidity cell to alternating cycles of dry air (3 days), moist air (3 days), and leaching (1 day). The leachates are then analysed for number of parameters including pH, redox (mV), acidity, alkalinity, sulphate, conductivity and dissolved metals by ICP. Generally, the test is run for ten weeks although a longer period might be required to establish the weathering characteristics of some samples (Sobek et al., 1978).

Various humidity cells designs have been used, ranging from simple plastic boxes to more elaborate designs which might enhance oxidation. Options in the operating protocol include the addition of bacteria, saturation (flooding) of a sample, temperature cycling, and use of humid air only between leaching stages, variable duration of the air/leach cycle and evaluation of control measures such as a function of time (Lawrence et al., 1990).

Sobek et al. (1978) and Lawrence et al. (1990) summarized the merits and demerits of humidity cell tests that follow below.

Advantages of humidity cell test

- Accepted method in Canada and the U.S.A.;
- Compares favourably with other prediction tests and folded data for reliability, can be used to calibrate other laboratory test procedures;
- Relatively simple to set up and operate;
- Models the wet/dry cycles of the environment;
- Rates of acid generation and sulphide oxidation can be determined;
- Temporary variations in acid generation rates can be determined;
- Effect of bacteria can be assessed;
- Provide an assessment of leachate water quality and dissolve metal flux that could be expected from a waste unit;
- Preliminary evaluations of the effect ARD control options such as blending of waste rock can be made;
- Fully saturated or submerged environment conditions can be evaluated.

Disadvantages of humidity cell tests

- Interpretation of results is sometimes complex;
- Tests might require a long time for completion and widely relatively high cost;
- Confirmation of ARD potential or determination of sulphide oxidation rates is often inconclusive due to the time required to deplete NP to levels which acid generation becomes measurable, even for samples where NP content is relatively low (such as >20 tonnes $CaCO_3$/1000 tonnes). Nevertheless, humidity cells do not permits tests to be carried out over extended periods of time. Pre-acidification of a sample can accelerate the NP depletion process but conditions created might not be realistic;
- Rates of acidity and alkalinity release might not be comparable or readily interpreted due to the differences in kinetics and equilibria of the acid

generating, acid consuming, and alkalinity generating reactions under laboratory and field conditions.

### 2.5.2.2 Columns and Lysimeters Tests

In order to model in the geochemical processes of weathering in the laboratory and to confirm or reduce uncertainty in the results of static prediction tests, columns and lysimeters kinetic tests may be performed. They are also carried out with the aim of determining the rate of temporary variation in acid generation and leachate water quality (Capriccio, 1981).

Larger scale weathering testing of mine wastes can be facilitated by columns or lysimeters. Columns are typically of glass, PVC, plexiglass, or other suitable inert plastic material and can range in size from 5 cm by 60 cm high, or larger for laboratory investigations, although intermediate sizes are more usual, such as 25 cm diameter by 120 cm high (Capriccio, 1981).

Lysimeter is a term synonymously used with columns. Ritchey (1989) defined lysimeter as a structure containing a mass of soil and designed to permit the measurement of water draining the soil. It consists of a basin having a closed sides and a bottom fitted with a drain. Quantities of material and/or artificial precipitation are measured, the seep percolates is measured and analysed, water of evaporation, and water taken to plants is weighed. Lysimeters can be constructed to permit the testing of material weighing from a few hundreds of grams up to several tonnes (Ritchey, 1989).

In basic protocol, columns or lysimeters are filled with test material and leached with a single pass of distilled water. The emerging leachate from the system is collected and analysed for parameters of interest. Numerous other test procedures alone and in combination are possible depending on the program objectives, including the following variations: Continuous single pass leaching with distilled water; Continuous leaching with an extractant other than distilled water (such as simulated acid rain, simulated or actual ARD); Recirculation of leachate; Internment extractant addition with either single pass or circulation flow (use of rest cycles); Maintenance of water table; Assessment of flooded disposal conditions; Upward flow of water through a sample; Assessment of bacterial effects; Assessment of rock blending; and

Assessment of covers (rocks, soil, plants) (Ritchey, 1989; Capriccio, 1981; and British Columbia AMD Task Force, 1989).

The advantages and disadvantages of columns and lysimeters kinetic tests below were summarized from Ritchey (1989); Capriccio (1981); British Columbia AMD Task Force (1989).

Advantages of columns and lysimeters kinetic tests:

- Accepted method in Canada and USA;
- Compares favourably with other prediction tests and field data for reliability;
- Relatively simple to set up and operate
- Larger scale of test allows larger particle sizes of waste to be evaluated;
- Can be used to model saturated and unsaturated waste deposition;
- Rates of acid generation and sulphide oxidation can be determined;
- Temporary variation in acid generation rates can be determined;
- Effects of bacteria can be assessed;
- Provides assessment of leachate water quality and dissolved metals flux that can be expected from a waste unit;
- ARD control options such as blending of waste rock can be evaluated;
- For larger columns and lysimeters, the evaluation of changes in mineralogy and effects of weathering with depth and determination of effluent quality profiles can be made.

Disadvantages of columns and lysimeters kinetic tests

- Interpretation of results is sometimes complex;
- Test might require a long time to completion (compared with humidity cells) and relatively high costs;
- Confirmation of ARD potential or determination of sulphide oxidation rates is often inconclusive due to the time required to deplete NP to levels which acid generation becomes measurable, even for samples where NP content is relatively low (such as >20 tonnes $CaCO_3$/1000 tonnes). However, columns and lysimeters tests do not permit tests to be carried out over extended

periods of time. Pre-acidification of a sample can accelerate the NP depletion process but conditions created might not be realistic;

- Rates of acidity and alkalinity release might not be comparable or readily interpreted due to the differences in kinetics and equilibria of the acid generating, acid consuming, and alkalinity generating reactions under laboratory and field conditions.
- Problems might be experienced with uneven solution application and application and channelling;
- Not practical for larger number of samples.

### *2.5.2.3 B.C. Research Confirmation Test*

This is a kinetic biological oxidation test designed to determine if sulphide oxidizing bacteria can produce more acid from oxidation of pyrite in the sample than can be consumed by an equal quantity of the sample. The test involves inoculating a pre-acidified (pH 2.0-2.4) pulp containing the test sample with an active culture of bacteria such as *T. ferroxidans* (Duncan and Bruynesteyn, 1979).

The pulp is monitored until stable, indicating the end of oxidation. An equivalent weight to the original sample is then added in two increments after24 hours and 48 hours and the pH is measured 24 hours after each addition. If the pH is above 3.5 at either point, the sample is classified as non-acid producer. If the final pH remains below 3.5 a potential for generation of acid mine drainage is indicated. Typically, the tests require 3 to 4 weeks for completion (Bruynesteyn and Hackl, 1984).

Like other AMD kinetic prediction procedures the B.C. Research Confirmation test has merits and demerits and they are summarized below from Bruynesteyn and Hackl (1984).

Advantages of B.C. Confirmation Test

- Relatively low cost;
- Has been widely used in Canada;
- Provides an assessment for the potential of biochemical oxidation.

Disadvantages of B.C. Confirmation Test

- Acidification procedure creates an unrealistic condition in that the inhibitory effects of the alkaline components of the waste on oxidation reactions are not evaluated, and the method does not allow evaluation or modelling of the initial ARD production stages in the upper pH ranges;
- The amount of generated acid in the test not correlated for the initial acid added to bring pH into the range suitable for inoculation. This can bias the results towards an acid classification;
- For samples with higher sulphur contents, the amount of a sample required by the test procedure might be too large, leading to incomplete oxidation of the variable sulphur due to inhibition of reaction by reaction products and low pH;
- Although the test is apparently simple, tests involving use of bacteria require experience and can have the problems of no optimum use of cultures, use of non-updated cultures, and difficulties of comparing results between different laboratories.

### 2.6 Management of acid mine drainage

The management of potentially acid generating wastes is an important environmental issue, and this has been and/or currently a priority in many countries affected by mine water pollution world-wide. According to AGSA (2009), the State of South Africa has inherited the environmental legacy of abandoned mines with cost of rehabilitation estimated at R30 billion and the amount excludes the treatment of AMD through the construction and operation of mine water treatment plants.

The Department of Water Affairs and Forestry (DWAF) has spent more than US $20 million over the last decade to investigate and clean up the historic pollution caused by abandoned or liquidated mines (Schwab ,2002),

The Australian and New Zealand Mineral and Energy Council (ANZMEC) baseline was published in 1995 to provide environmental guidelines for operating mines. These guidelines propose that acid generation should be predicted and incorporated in closure plan as required by the guideline (ANZMEC, 1995). According to Harries (1997) amounts to US $60 million had been estimated to manage AMD at operating mines in Australia. Major costs may arise later in mine life or after mine closure if proper waste management strategies are not followed. An estimate of US $100 000 per hectors was given by Australian Government for AMD discovered after mine closure (Harries, 1997). The Office of Supervising Scientist and the Australian Centre for Mine site Rehabilitation Research initiated the preparation of status report on AMD in order to better understand the impact of AMD in Australia and provide the basis for assessing long-term management options (Harries, 1997).

In 1989, acid mine drainage was identified as the main environmental problem facing Canadian mining industry. The Canadian Mine Environmental Neutral Drainage (MEND) was established by mines and provincial, territorial and federal government agencies. Mines were required to establish trust funds to cover the cost of the effect of AMD from mine wastes (MEND, 1995). The estimated cost of remediation in Canadian mine sites is three to four times (US $ 2 billion to US $ 5 billion) greater than Australian sites (Harries, 1997). In response to challenge presented by mitigation of AMD, 200 technology-based reports were generated to evaluate sampling, prediction, prevention, treatment and monitoring of potentially acid-generating materials and locations (MEND, 2001).

Mining of uranium in the former East Germany states of Saxony and Thuringa left environmental legacies which include AMD in some mines. Wismut Gmbh, a Fedaral-owned company was formed to address those impacts which entailed 1400 km of open mine workings, 311 million $m^3$ of waste rock, and 160 million $m^3$ of radioactive tailings located in densely populated areas (Wismut, 2008). In 1991, a fund of €6.2 billion was established under the Wismut Act passed by the Federal Parliament (Hagen and Jakubick, 2006). The Wismut rehabilitation programme has resulted in development of expertize and technologies in the local research institutions and local consulting groups. These can now be transferred to other areas and have been successfully applied in Central and Eastern Europe, Russia and Central Asia (Hagen and Jakubick, 2006).

In U.S.A. AMD from coal mines was identified impacting on the streams in the eastern states, with 7000 streams estimated to be affected (Ferguson and Erickson, 1988). USEPA (1995) estimated a total of 8000 and 16000 of streams to be affected by AMD. The National Abandoned Mine Land Programme under the Office of Surface Mining Reclamation and Enforcement (OSMRE) of the U.S. Department of Interior was established in USA to rehabilitated abandoned mines. A levy is collected on active coal mines and deposited into Abandoned Mine Lands (AML) fund (a trust administered by U.S. Treasury Office) (Office of Surface Mining, 2006). In Colorado and Montana, the U.S. Geological Survey had instituted additional programmes looking at hard-rock mining at a catchment scale.

Some of the known measures to manage acid mine drainage are summarised below:

### 2.6.1 Minimization of acid mine drainage

According to Skousen et al. (1998), there are two primary approaches of addressing AMD, namely, avoidance of mining sulphide rich deposits with high acid mine drainage potential and implementation of mitigation measures to limit potential AMD impacts. While the former is challenging as sulphide ores are mostly associated with the mineral resource of interest, selective handling and avoidance of sulphide ore and overburden is a strategy for minimising the risk of future acid generation.

Several methods that keep sulphides isolated from oxygen can be performed for mine waste isolation and avoidance of oxidising conditions.

Li et al. (1997) indicated that potentially acid-producing tailings can be disposed and stored under water with the objective of preventing contact between the minerals and dissolved oxygen. Shallow water covers may be used and covering the tailings with a layer of sediment organic material can improve its effectiveness by limiting oxygen ingress and affording some protection against the suspension of the tailings due to the action of wind and waves. An organic layer may also be incorporated in dry covers used for surface storage of reactive mineral. Clay is usually used for construction of a sealing layer, however, in areas of the world that experience acute wet and dry seasons, drying and cracking of cover can render it less effective than in temperate zones (Swanson et al., 1997). In Canada, subaqueous disposal of tailings and waste rock below water table is commonly practiced as a protocol for mine reclamation (Samad and Yanful, 2005).

Another approach for minimizing AMD production was suggested by Mehling et al (1997). The authors suggested blending of acid-generating and acid-consuming materials producing environmentally benign composites. A different on this approach is to add a solid-phase phosphates such as apatite to pyritic mine waste in order to precipitate iron (III) as ferric phosphate, thereby reducing its potential to act as an oxidant of sulphide minerals. However, this approach is temporary for inhibiting pyrite oxidation due to process of armouring of the added phosphate mineral (Evangelou, 1998). Soluble phosphate together with hydrogen peroxide can be applied as coating technology. The peroxide oxidises pyrite, producing ferric iron, which reacts with the phosphate to produce a surface protective coating of ferric phosphate (Evangelou, 1998).

Loos et al., (1989) indicated that various laboratory- and field-scale tests have been carried out to inhibit lithotrophic iron- and sulphur-oxidizing bacteria activities in mineral spoils and tailings since they have a fundamental role in generating AMD. Application of anionic surfactants such as sodium dodecyl sulphate (SDS) has been generally involved because they are highly toxic to this group of microorganisms. Nevertheless, this approach can be only short-term control of AMD problem and requires repeated application of the chemicals.

According to Benzaanoua and Bussiere (2002) backfill mining method can be used for minimisation of acid formation by backfilling mine workings using a mixture of tailings, Portland cement and other binders to create a waste disposal option that is both geotechnically stable and geochemically non-reactive since sufficient NP can be added to neutralise any future acidity. Sulphide minerals can be removed from waste products to create a beginning sand faction suitable to use a general backfill and companion low-volume concentrate requiring careful disposal by depyritisation of tailings. Small amounts of sulphide minerals that can be separated from non-acid forming silicate minerals using conventional mineral processing equipment to create a cleaned material with sufficient NP to improve any future acidity are contained in most mine tailings (Benzaanoua et al., 2000).

The measures described above are most effective when used in combination in most cases and when adapted to specific site situation (Kuipers et al., 2006). According to Edwards et al. (2000) thorough baselines studies of biological, hydrologic, and geochemical conditions characteristics of the unique site are required to provide a basis for long-term monitoring and provide an insight into a mechanistic processes involved in acid mine drainage evolution.

### 2.6.2 Treatment of acid mine drainage

Where acid mine drainage already exists, the common accepted management measure is water treatment for elevated metal levels and acidity. Depending on the treatment employed and unique site characteristics, the effectiveness and feasibility of water treatment is highly variable. Both active and passive treatment systems exists for treating acid mine drainage. These remediation technologies can be subdivided into the traditional treatment technologies and innovative treatment technologies. Some of the available technologies are summarised below:

#### *2.6.2.1 Traditional/active remediation strategies*

Active treatment can be defined as the improvement of water quality by methods which require on-going inputs of artificial energy and or (bio) chemical reagents (Younger et al., 2002). Different kinds of methods exist that are considered active, but the most prominent one is ODAS, which is –oxidation, dosing with alkali, and sedimentation (Younger et al., 2002). The process is similar to that of wastewater treatment plant. Sulphidization, biosedimentation, sorption and ion exchange, and membrane processes like filtration and reverse osmosis are among other traditional treatments common to wastewater treatment plants. The waters are removed from their course, treated and discharged (Younger et al., 2002).

Active treatment process involving addition of chemical-neutralising agent is the most widespread method used to mitigate acidic effluents (Coulton et al., 2003b). pH will raise, the rate of chemical oxidation of ferrous iron accelerated for which active aeration, or addition of chemical oxidising agent such as hydrogen peroxide is also necessary, and many metals present in the solution will precipitate as hydroxides and carbonates through the addition of alkaline materials to AMD. Production of iron-rich sludge that may contain various other metals depending on the chemistry of water treated will result. Several neutralising agents which include lime (calcium oxide), slaked lime, calcium carbonate, sodium carbonate, sodium hydroxide, and magnesium oxide and hydroxide have been used. These vary in cost and effectiveness. Traditional treatment technologies have high precision; for the most part of the engineered system can be altered to obtain desired discharge regardless of the changes in the incoming water characteristics. Another merit is that the land required to establish a plant for large flows is smaller than the space required for comparable passive treatment systems and also, the experience and information accompanying traditional wastewater plants are large which makes the expertise easier to find and with a higher confidence level in performance (Younger et al., 2002). Chemical treatment has disadvantages of high operating costs and problems with disposal of bulky sludge that is produced even though it can provide effective remediation of AMD (Coulton et al., 2003b).

There have been a variety of refinements aimed at improving the efficiency of the process and reducing the problems associated with the bulky sludge produced whereas active chemical treatment is in its basic concept a low technology approach to AMD remediation. Multiple-stepped addition of reagents accompanied by pH control can result in selective removal of some AMD components like arsenic and molybdenum (Aube and Payant, 1997). Aggregation of precipitates can be promoted by the use of different flocculating reagents thereby assisting their removal in settling pond. Alkali addition produces highly voluminous and water-rich iron-rich sludge which contains only 2-4% solids. Modifications to the technique which involve partial recycling of sludge into lime-holding tanks can produce a sludge that contains ca. 20% solids, which further improves to ca. 50% solids on dewatering (Coulton et al., 2003a). High density sludge process has major advantage of reduced disposal costs and storage of the final product.

#### *2.6.2.2 Innovative/Passive Treatment Methods*

Passive treatments are considered to be those that treat waters or solids using enhanced natural processes, in-situ and require minimal upkeep (Hedin et al., 1994; Younger et al., 2002). Some of the available technologies are summarised below:

##### 2.6.2.2.1 Limestone Drains

In Anoxic Limestone Drains, crushed limestone is packed in underground pathway that is created for acidic and potentially metal-laided water. ALDs typically have an outlet into a settling pond or wetland to allow metals an opportunity to precipitate and settle (Cravotta and Watzlat, 2002).

The objective of ALDs is to add alkali to AMD while maintaining the iron in its reduced form to avoid the oxidation of ferrous iron and precipitation of ferric hydroxide on the limestone or armouring which otherwise severely reduces the effectiveness of the neutralising agent. The partial pressure of carbon dioxide is increased within the drain, accelerating the rate of limestone dissolution and consequently increasing the concentration of alkalinity, which may reach up to 275 mg/l compared to open system which, in equilibrium, will produce 50-60 mg alkalinity/l (Kleinmann et al., 1998).

The use of ALDs is considered passive approach to mine water treatment since they require minimum maintenance once constructed. Mine water is contained to flow through a bed of limestone gravel held within a drain that is impervious to both air and water. The bed is generally constructed of plastic bottom liner and a clay cover. Various dimensions of the drain exists, from narrow which is 0.6 to 1.0 meter to wide, which is 10-20 m diameter, typically ~1.5-m deep and ~30 m in length (Kleinmann et al., 1998).

Evangelou (1998) summarised demerits of using ALD systems. Short-term performance of ALDs may be good in situations where the AMD contains significant concentrations of iron and aluminium, however, the build-up of hydroxide precipitates gradually decreases the drain permeability which may cause the failure of drain within six month of construction. Passage of AMD through an anoxic pond prior to anoxic limestone drain may be necessary to reduce dissolved oxygen concentrations to levels required to prevent iron oxidation and this problems are frequent where ALDs are used to treat aerated mine waters. Formation of ferrous carbonate and manganous carbonate gels within ALDs which may cause the incongruent dissolution of limestone gravel is another potential shortcoming.

Sasowsky et al. (2000) conducted studies in Big Laurel Creek at the East Fork Obey River in Tennessee and Silver Creek, Ohio and suggested that the armourning of limestone can be offset by incorporating sandstone into the drain. When acidic and metal contaminated water discharged onto both exposed limestone and sandstone the majority of metallic oxides precipitated on sand stone rocks, suggesting preferred precipitation media (Sasowsky et al., 2000).

Anoxic limestone drains are generally used as one component in association with aerobic wetlands and/or compost wetlands in passive treatment. ALDs have been reported to be the cause of dramatic improvements in terms of water quality draining through them to constructed wetlands that have been performing poorly (Kleinmann et al., 1998).

#### 2.6.2.2.2 Constructed Wetlands

Wetlands are part of passive AMD treatment technologies capable (USEPA, 2000). Two types of wetland are used to treat mine drainage, namely, aerobic and anaerobic/compost.

*Aerobic wetlands*

Constructed to treat mine waters that are net alkaline, Aerobic wetlands are the best treatment option if the metal of concern is iron. The main premeditative reaction that occurs within the aerobic wetlands is the oxidation of ferrous iron and subsequently hydrolysis of ferric iron produced, which is the net acid-generating reaction:

$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O \qquad (6)$$

$$4Fe^{3+} + 12H_2O = 4Fe(OH)_3 + 12H^+ \qquad (7)$$

To improve any insufficient alkalinity in the mine water, preventing significant fall in pH as a result of these reactions, anoxic limestone drain may be incorporated. Aerobic wetlands are relatively shallow systems that operate by surface flow in order to maintain oxidizing conditions. Macrophytes are planted for aesthetic reasons and filter and stabilize the accumulating ferric precipitates. They also provide additional surface area for precipitation of solid phase ferric iron compounds and minerals. Additionally, some aquatic plants may accelerate the rate of ferrous iron oxidation by causing oxygen flow from aerial parts to the root systems. Concentrations of oxygen and pH are important parameters in indicating how quickly iron oxidizes (Stumm and Morgan, 1981). Conversely, at pH <4, the rate of iron oxidation is effectively independent of pH. Chemical oxidation of ferrous iron will proceed rapidly because most aerobic wetlands operate at near neutral pH, although the presence of neutrophillic iron-oxidising bacteria that live at the interface of aerobic and anaerobic zones, such as *Gallionella ferruginea* and those that breakdown organically complexed iron, such as *Leprothrix species*, does imply that there, these contribute to oxidation in these passive systems (Johnson, 2002).

The removal of arsenic originating primarily from the oxidative dissolution of arsenopyrite (FeAsS) present in mine waste materials is the second major remediative process occurring in aerobic wetlands receiving AMD. Soluble arsenic present mostly as anionic AS (V) ($AsO_4^{3-}$) in mine waters may be removed mainly by adsorption on to positively charged ferric iron colloids and, in theory, by formation of scorodite ($FeAsO_4$). Novel strains of *Thiomonas*-like bacteria that oxidize arsenic (III) to arsenic (V), as well as oxidising ferrous iron and reduced sulphur compounds have been isolated from mine waters (Battaglia-Brunet et al., 2002; Coupland et al., 2003). These bacteria possibly contribute to arsenic removal in these waters and have a potential for use in fixed bed bioreactor systems for the precipitation of iron.

With other types of metals aerobic wetland alone is rarely successful. “Additional hydrogen ions released during metal hydrolysis reactions are buffered by net alkaline waters” (USEPA, 2000).

*Anaerobic wetlands/compost bioreactors*

The key reactions that occur in compost bioreactors used to mitigate acid mine drainage are anaerobic. The term compost bioreactor describes system’s installations. These systems are enclosed entirely below ground level and do not support any macrophytes, so that they cannot be described as wetlands. Aesthetic considerations dictate the use of macrophytes in constructed compost ecosystem. The ingress of oxygen into the anaerobic zones is through penetrating plant roots which is detrimental to reproductive processes. Compost bioreactors systems may be used to treat mine waters that are net acidic and metal-rich such as AMD from abandoned metal mines. The microbial catalysed reactions that occur within these systems generate net alkalinity and biogenic sulphide. The reductive reactions that occur within the compost wetlands are driven by electron donors that derive from the organic matrix of the compost itself (Kepler and McCleary, 1994).

Local availability and proven effectiveness determine the choice of bulky organic materials to be used.  Though in general, the compost are prepared by mixing relatively biodegradable materials such as cow or horse manure, or mushroom compost, with more intractable materials such as sawdust, peat or straw (Vile and Wieder, 1993). The slow biodegradation of intractable materials is presumed to act as long-term provision of appropriate substrates and ammonia for the indigenous iron- and sulphate-reducing bacteria (FRB and SRB) considered to have major roles in acid mine drainage remediation in compost wetlands (Vile and Wieder, 1993), and virtually, nothing is known about how the microbiology of anaerobic compost systems changes as the ecosystem ages, especially with substrate provision. Acid mine drainage quality in compost wetlands is improved by filtration of suspended colloidal materials and adsorption of metals by inorganic matrix.

*Composite aerobic and anaerobic wetlands*

For full-scale acid mine drainage treatment, passive bioremediation systems that utilizes a combination of aerobic and anaerobic wetlands have been used such as the Acid Reducing Using Microbiology (ARUM) system" (Kalin and Chaves, 1991). This system is composed of two oxidation cells within which iron is oxidised and precipitated and beyond these, AMD passes first through a holding cell and then through two ARUM cells within which alkali and sulphide are generated. Floating macrophytes such as cattails provide the organic materials that promote sulphate reduction in the ARUM cells. For AMD treatment in high latitude and subtropical locations, ARUM systems have been shown to be effective (Kalin and Chaves, 2001).

#### 2.6.2.2.3 Bioreactors

Passive bioreactors are lined trenches or pits that contain different materials, most commonly a mixture of cobbles, compost, other organic matter, and/or an alkaline agent. A tank may be set above containing any variety of materials such as those mentioned above used to establish appropriate microorganisms to precipitate metals and adjust pH (Zaluski et al., 2000).

#### 2.6.2.2.4 Successive Alkalinity Producing Systems

Basic elements of Successive Alkalinity Producing Systems (SAPS) also known as Reducing Alkalinity are organic mulch layer, limestone layer, and drainage system, including flushing system in some instances, a technology which was created in the early 1990's by Kepler and McCleary (1994). The reasoning is that mine drainage flows into the top of the cell creating a top layer of water which prevents the infiltration oxygen into the bottom layers, and water is also used in this way in tailings holding dumps. Dissolved oxygen will be removed by organic layer from water, anaerobic conditions further down support the establishment of sulphate-reducing bacteria. The likelihood of hydroxide precipitation is reduced by the reducing anaerobic environment that changes ferric iron ($Fe^{3+)}$ to ferrous iron ($Fe^{2+}$). These systems are sometimes referred to as Reducing Alkalinity Producing Systems (RAPS) since these units encourage reducing conditions and establishment of sulphate-reducing bacteria (SRB), a major contribution to water treatment (Younger et al., 2002). The water enters the limestone region at last, essentially devoid of oxygen preventing the armouring limestone. The water is usually directed to an aerobic settling pond or wetland to allow metals to form precipitates and further polishing upon parting the SAPS (Kepler and McCleary, 2003).

Because oxidation and reduction of iron (Fe) and aluminium (Al) leads to precipitates that can barricade the cell, many SAPS include flushing systems (Rees et al., 2001). Kepler and McCleary (2003) reported that the flushing systems generally operate by generating head differences that move water rapidly through the system.

SAPS require less to provide the same treatment and tend to be more competent than aerobic wetlands (Younger et al., 2002). Some maintenance is required by SAPS for periodic flushing and also to prevent or correct the development of the preferential flow paths possible in any of these passive systems (Kepler and McCleary, 2003; Rees et al., 2001). Driving head and freeboard are also required if preferential flow paths develop the water short circuits the system resulting in topographic relief requirements of greater than five meters (Younger et al., 2002).

#### 2.6.2.2.5 Permeable Reactive Barriers

Blowes et al. (2000) defined PRBs as barriers that react with specific chemicals of concern that are placed in the path of groundwater to flow through easily. Construction of PRBs involves digging of a trench or pit in the flow path of contaminated groundwater, filling the void with reactive materials, which can be a mixture of organic solids and possibly limestone gravel, that are sufficiently permeable to allow unimpeded flow of groundwater, and landscaping the disturbed surface (Banner et al., 1997). Solid organic matter like municipal compost, leaf compost, and wood chips/sawdust are used for PRBs designed to treat acid mine drainage with metals contamination (Blowes et al., 2000). Organic matter emboldens the propagation of sulphate-reducing bacteria that will reduce sulphate to sulphide and will result in the subsequent formation of insoluble metal sulphides (Naftz et al., 1999).

Alkalinities within PRB is generated by reductive microbiological processes and is further enhanced by dissolution of limestone and/or other basic minerals and remove metals as sulphides, hydroxides, and carbonates (Younger et al., 2003). The stability of metal sulphides is of paramount importance in the design of PRBs to treat AMD (Blowes et al., 2000). Sulphides have low solubility in anaerobic conditions and if oxidation were to occur, metals could be released from their metal sulphide form into the environment (Blowes et al., 2000).

In Shilbottle, northeast England, the largest PRB (180-m long, 3-m deep, and 2-m wide and consists of mixture of 25% horse manure and straw, 25% composted green waste, and 50% limestone) had been installed to remediate extremely acidic water emanating from a large pyritic shale waste dump (Younger et al., 2003).

Blowes et al. (2000) presented common problems of PRB performance as follows:

- Actual lifetimes of PRBs are considerable shorter due to the presence of other reactive substances in the environment, though barriers often have very long theoretical treatment lifetimes when only material and contaminants of concern are considered;
- Due to depletion of reactive component of the barrier chemical reactions can be slowed down;
- Precipitation of secondary reactive precipitate can reduce the reactive surface area;
- Physical clogging or preferential path flow.

#### 2.6.2.2.6 Biosolids

Biosolids are the nutrient-rich organic materials resulting from the treatment of sewage sludge. Sewage sludge becomes biosolids which can be safely recycled and applied as fertilizer to sustainably improve and maintain productive soils and stimulate plant growth. Biosolids are useful for mine lands reclamation and agricultural purposes (Murray et al., 1981; Sopper, 1993; Toffey 2003). Certain centralized standards such as Section 103C of Clean Water Act and state standards are to be met for the application of biosolids to land. Field experience of over twenty five years with biosolids demonstrated clear environmental benefits and negligible adverse effects according to Sopper (1993) and Toffey (2003).

Bastian (2003) indicated that biosolids are almost always applied with lime, either pre-mixed or in stages when reclaiming mine sites. The pH of soils will increase rapidly through the application of lime, however, for long term improvement of soils, the application of lime alone may not be sufficient as the pH will eventually decline as sulphur-bearing minerals are oxidized (Sopper, 1993). Nevertheless, in some cases biosolids application without lime raised the soil pH and decreased metals availability as reported by Sopper (1993).

Biosolids provide conducive conditions for microbial and plant growth by provision of carbon source and capacity for moisture retention and this is important for self-sustaining system establishment, hence they are advantageous over chemical fertilizers (Sopper, 1993).

Tailings sites treated with biosolids do not experience a reduction in total metals, but metals availability is reduced (Maxemchuk, 2002). Metals are immobilized through precipitation as carbonates, phosphates, sulphides, silicates and sorption by organic matter, and hydroxides (Sopper, 1993). Phyto-extraction, where vegetation are responsible for immobilizing metals or even remove metals from the soil takes place in some cases.

#### 2.6.2.2.7 Phytoremediation

Phytoremediation had been defined as the use of green plants and their associated microbiota, soil amendments, and agronomic techniques to remove, contain, or render harmless environmental contaminants (Wong, 2003). There are wide varieties of subcategories in the branch of phytoremediation and these include phytoextraction/phytomining, phytostabilization, rhizofiltration, and phytovolatilization.

Phytoextraction or phytomining if metals can be recovered can be defined as the uptake of contaminants by plant roots and translocation within the plants (EPA, 2000). For species selection, climate is a detrimental factor if there are limited plants that can do this. Plants must be hyperaccumulators for phytomining. There is about 300 species that hyperacummulate nickel, 26 cobalt, 24 copper, 19 selenium, 16 zinc, 11 manganese, one thallium and one cadmium (Brooks et al., 2003). Consideration of whether the resulting vegetation will be hazardous to local animals should be put in place, especially with the use of hyperaccumulators during the application of phytoextraction, this possibility varies from site to site (Wong, 2003).

Phytostabilization is defined as “immobilization of contaminant in soil through adsorption and accumulation by roots, adsorption into roots, or precipitation within the root zone plants and the use of plants and plant roots to prevent contaminant migration via wind and erosion, leaching and soil dispersion" (USEPA, 2000). Ideal plants to be used for this practice must be metal-tolerant, drought-resistant, fast growing crops that can also grow in nutrient deficient soils (Wong, 2003). This technology has advantages of being inexpensive, soils need not to be removed, ecosystem restoration is enhanced, and disposal of hazardous materials or biomass is not required (USEPA, 2000). Nevertheless, phytostabilization has setbacks that contaminants will remain in place and care must be taken to ensure that the vegetation continues to stabilize metals; extensive fertilization or soil modification may be necessary; plant uptake and translocation of metals must be prevented, root zones, root exudates, contaminants, and soil modification amendments must be monitored to prevent an increase in metal solubility and leaching; it may only be considered a temporary measure; stabilization might be due primarily to the effects of soil amendments, with plants only contributing to stabilization by decreasing the amount of water moving through the soil and by physical stabilizing the soil against erosion (USEPA, 2000). Biosolids application can be done with phytostabilization technique as it provides necessary fertilizing agents and assists in microorganism establishment.

Rhizofiltration involves the removal of contaminants in solution through adsorption or precipitation onto plant roots or absorption into the roots and this can be achieved by microorganisms associated with rhizosphere (USEPA, 2000; Wong, 2003). Plants are either aquatic plants or terrestrial plants on a floating platform since this technique is applied in water (USEPA, 2000). By removing plants themselves, contaminants can be physically removed. This technology has some demerits including a need for good control over pH, and a clear understanding and the chemical speciation and interaction of all species in the influent (USEPA, 2000). Additionally, there is a necessity for influent concentrations and flow rate control; plants may need to be grown and translocated to site, especially terrestrial plants; periodic harvesting and disposal are required, and laboratory results may not be achievable in the field (USEPA, 2000).

Phytovolatilization is the uptake and transpiration of contaminant by plant, with release of contaminant or a modified form of the contaminant to the atmosphere from the plant through contaminant uptake, plant mobilization, and plant transportation (USEPA, 2000). Phytovolatilization had been identified as a potential treatment for mercury and selenium contaminated soils (Caney et al., 1997; USEPA, 2000). If contaminants of concern will be transported in less-toxic forms, this process is beneficial, for example elementary mercury and dimethyl selenite gas. Uncertainty about metabolites, unhealthy plant accumulation, and uncertainty about other constituents at site are some of the disadvantages of phytovolatilization (Brooks et al., 1998; Wong, 2003; Madejon et al., 2003).

## 2.7 Control Technologies of AMD

Bell (1988) summarized the important parameters for acid generation control in waste rock as follows: reduce permeability of waste rock pile to air; prevent oxidation and associated exothermic reaction from significantly raising dump temperature; minimize leachate production and transport; and prevent the ingress of seepage to the more reactive portions of the dump such as at the toe of the dump.

Research to control acid generation process has focused on Biocidal Control of Bacteria, In Situ Neutralization, Alternative Dump Construction, Covers and Seals, and Underwater Disposal.

### 2.7.1. Biocidal Control of Bacteria

Bacterial population associated with acid generation have been controlled using anionic surfactants with some degree of success, mainly in coal mines (Dugan, 1975; Kleinmann and Erickson, 1983; Erickson et al., 1985; Shellhorn and Rastogi, 1985). Due to high solubility and easily degradable nature of anionic surfactants compounds, particularly under acidic conditions, their duration of effectiveness as a control method may be limited, although they have been proven biocidal agents. Erickson and Ladwig (1985) suggested that direct addition of anionic surfactants to the re-vegetated sites or sites subject to high rates of movement of water may be of the limited value. Unsatisfactory results have been reported by Patterson (1987) during field-testing of sodium lauryl sulphate at Equity Silver Mine. High solubility and the inability of the surfactants to penetrate the oxidation zones within the interior of the waste rock pile were attributed to failure of the product to maintain long-term control of acid drainage.

Several researchers (Schaitman et al., 1969; Erickson and Ladwig, 1985; Erickson et al., 1985; Onysko et al., 1984; Jiwik et al., 1989) have studied the effectiveness of chemical treatment methods to inhibit bacterial activity or coat particle surfaces and thereby reduce acid generation from waste rock. Organic and inorganic chemicals have been tested including: food preservatives such as sodium and potassium benzoate, potassium sorbate salts, sodium chloride, and low weight molecular organic compounds such as propionic, butyric acid and formate; detergents such as sodium lauryl sulphate, AJAX, and ALCONOX; sodium carbonate and potassium sulphate. As with all surface amendments, a disadvantage to use these compounds is the inability to provide control of acid generation reactions occurring at depth in waste rock pile. Additionally, the cost associated with reapplication of chemicals due to their solubility can be considerable. A cost effective way to utilize this technology has been suggested by Jiwik et al. (1989) by limiting use of bacterial agents to prevention of initiation of acid generation in waste rock until the rock can be deposited in a permanent manner. Application of bactericide to waste rock surfaces during dump construction can be done in such cases.

A marked specificity for *Thiobacillus* species have been shown by predatory organisms such as rotifers and protozoa. Provided suitable conditions prevail, use of these organisms can cause significant reduction in bacterial numbers over relatively short period of time (Christison et al., 1984). However, the predators organisms require a high cell density to induce feeding activity and once sated revert to a non-feeding encysted stage allowing the *Thiobacillus* population to recover. According to McCready (1987) predators are relatively large and cannot penetrate interslices less than 25 µm wide. As a result, the use of predators to control bacterial populations is not considered an effective acid generation control technology.

### 2.7.2. In Situ Neutralization

For acid generating rocks, addition of alkaline materials provides pH control. Methods of in situ neutralization include blending of acid consuming and acid producing wastes, placement of alkaline materials above or upgrading of acid generating rock, and the addition of alkaline material such as limestone in a collection trench downstream of the acid source (Capriccio et al., 1985). According to SRK (1989) the success of neutralizing compounds to control acid generation depends to a large extent on the movement of water through rather than around or over the system as well as characteristics of waste rock and proportion of excess neutralizing material. Limitations of alkaline trench method have been recognized by Capriccio and Geidel (1987) by recommending its use only in situations where the hydrologic system is well understood and amenable to manipulation. This approach is feasible as a preventative measure provided acid consuming materials are economically viable (Bell, 1988). However, as a treatment method this technique appears suitable only to mildly acid generating waste rock because the amount of neutralizing material required treating highly acidic waste rock could be prohibitive.

### 2.7.3. Alternative Dump construction

As a reactive waste management method, selective placement of reactive and neutralizing waste material when constructing or during reconstruction of dump have been carried out. The objective of this type of dump construction is to encapsulate the reactive waste within no-reactive material to prevent or control acid generation (Capriccio et al., 1985). The degree of thoroughness which can be achieved by mixing of alkaline and acid-generating material is of critical importance to success of this method. This type of dump construction is only feasible where there is sufficient volume of impermeable neutralizing material with reasonable haulage distance (Capriccio and Geidel, 1987).

The concept of selective placement for dump construction was used at Equity Silver Mines where an intermediate glacial till layer was placed within a waste rock pile during construction with monitoring program on place for provision of information on the long-term integrity of the restricting layer. A similar type of dump construction method has been proposed by Bell (1987) and it incorporates features such as placement of waste in a compacted layer to reduce pore space, placement of continuous horizontal and vertical barriers of compacted till, final capping of the waste pile with an impermeable material and finally vegetation.

### 2.7.4. Covers and Seals

In order to restrict water and oxygen access into reactive mine residues covers and seals are ideal. Bell (1988) listed the below requirements to effectively seal acidic mine residues:

- Top cover to prevent infiltration of rainfall and air diffusion;
- Side slope cover to prevent infiltration of water and the diffusion of advection of air;
- Stabilization on top and side covers to prevent erosion; and

- Resistance of the cover to cracking, root penetration, burrowing by animals and deterioration due to weathering and freeze/thaw effects.

Long-term control acid generating residues appear not to be provided through the use of top soiling and revegetation, although short term improvements have been documented (Bell, 1987; McCready, 1987; Schubert and Miller, 1982; Thurman et al., 1985). In revegetation trial conducted by Veldhuizen et al. (1987) on acid – generating base metal tailings, it was concluded that pyrite oxidation was not restricted and water infiltration was not significantly limited to reduce water flow from the impoundment by direct vegetation of reactive tailings.

A layered soil cover system as described by Ma~~u~~gnusson and Rasmuson (19834) may provide a more effective infiltration barrier, however simple soil covers afford a measure of control in infiltration of rainfall. This type of cover system consists of coarse and fine grained soils placed in layers and includes capillary barriers formed at the interfaces between the coarse and fine textured soils. The concept of engineered or composite covers is an extension of the layered soil covers. These covers utilize a layered system of various materials, namely, compacted glacial till, clay, limestone, top soil, mine tailings, sand and rock or gravel. Each of the layers performs specific function to restrict water and oxygen access and improve long-term stability. Erosion control is achieved by the first layer, typically provided by vegetation or coarse gravel or rip-rap. In order to provide a zone of moisture retention for vegetation support and to prevent desiccation and reduce oxygen diffusion, a second layer is placed. Medium to fine textured soils are generally used in this layer. The function of a third layer is to provide a section break to drain water away from the bottom, impermeable layer and prevent moisture loss from the infiltration barrier. The fourth layer serve as infiltration barrier and it therefore consists of relatively impermeable material such as clay, compacted till, or synthetic material.

At the Bersho Mine site in Sweden several composite covers have been tested on the waste rock piles (Sodermark and Lundgren, 1988). The consisted of a sealing layer of about 0.5 m depth beneath about 2 m of moraine as protection against freezing, desiccation and root penetration. The different sealing layers were tested, namely, Cefill, which is a product consisting of cement stabilized fly ash (5 to 10%

cement) with a water content of 30-40%. Cefill solidifies in 24 hours to form dense, hard-sealing layer; two types of clay, one dense and one semi-solid; and a bentonite-sand layer with approximately 10% bentonite. All three methods produced satisfactorily seals with oxygen transport expected to decrease by more than 99% as shown by the tests.

Synthetic covers include asphaltic and spray-on seals, concrete and flexible membrane liners. Asphalts, concrete and cementitious mixture may crack or heave, or be susceptible to chemical degradation, depending on site conditions. However, advantages of using these materials as surface sealants include their low permeabilities, load bearing strength and weatherability and ease of repair when uncovered. With respect to hydraulic conductivity of asphalt seals, there were some discrepancies noted. Bell (1987) found that an asphalt cap applied to a toxic waste dump was not an effective barrier due to unsatisfactory permeability characteristics. Northwest Geochem (1990) proposed field testing of cementitious mixture for use as surface sealants.

Provided they are installed correctly on a well prepared base, flexible membranes or geomembranes are effective impermeable covers. Nevertheless, there are disadvantages associated with geomembranes, namely, susceptibility to puncture during installation, limited longevity or liner integrity due to differential setting of the waste material, susceptibility of certain products to photochemical degradation and expense (Northwest Geochem, 1988). Capriccio and Geidel (1987) specified that to restrict subsurface recharge, the liner must extend to the base of the backfill. This manner of installation can be problematic. However, with proper installation of polyvinyl liner, substantial reduction if flow and acidity from acid generating waste-rock (Capriccio and Geidel, 1986). In limiting oxygen and water transport in acid generating waste rock, geomembrane used in combination with composite cover could prove to be very effective.

Two very recent additions to the list of potential sealant materials on acid generating waste rock dumps are geopolymers and wax blends. Geopolymers are compounds containing silica, phosphate and oxygen that bond to form a ceramic type product (SRK, 1989).

Frequent materials have been investigated for use as covers for acid generating mine residues deposits. Table 4 below lists the merits and demerits of several cover materials.

Table 4 Alternative Cover Materials (from Bell, 1988)

| Cover Material | Permeability to water (m/sec) | Advantages/Disadvantages |
|---|---|---|
| Compacted clay | $10^{-9}$ to $10^{-11}$ | Availability of large quantities problematic in many areas. Subject to erosion, cracking, root penetration. Good sealing if protected and maintained. |
| Compacted till | $10^{-7}$ to $10^{-9}$ | As above, but generally more permeable |
| Compacted top soil | $10^{-5}$ to $10^{-8}$ | As above, but less robust, more permeable. Questionable longevity |
| Peatland bog | $10^{-5}$ to $10^{-6}$ | Need maintenance in saturated conditions. Normally impractical for elevated waste dumps and side slopes |
| Concrete | $10^{-10}$ to $10^{-12}$ | subject to cracking, frost, mechanical damage |
| Asphalt | $10.^{-20}$ | As above |
| HPDE synthetic cover | Impermeable | Requires proper bedding and protective cover. Highly impermeable, lifespan unlikely to exceed 100 years. Subject to root and mechanical penetration |
| Wax blends | Impermeable | Relatively inexpensive, flexible, self-sealing, easily applied. Proper blending required for site specific conditions. Cannot be directly applied to uneven surfaces. |

### 2.7.5. Underwater Disposal

Bell (1988) and Northwest Geochem (1990) recognized that fluctuating water table within reactive waste rock as an ideal situation for acid generation and migration. Oxidation is restricted to zero level by disposal of reactive waste rock beneath the water table due to very low diffusivity of oxygen in water. Long term solution to the problem of acid generation is provided by underwater disposal of reactive waste rock (Pederson et al., 1990) provided the water table does not fluctuate and the material is kept flooded at sufficient depth all the time. However, if suitable natural bodies of water are not located short haulage distance away, the cost of constructing a facility to provide water cover may not be cost effective. Other drawbacks to underwater disposal of waste rock include concern over physical and chronic chemical impacts of waste rock disposal on the benthic population on natural water bodies. Diffusion of oxygen is limited under saturated conditions; however, a small amount of oxygen transfer continues to take place (Pederson, 1990).

## 2.8 Conclusion

The review has identified active and passive methods of managing acid mine drainage which is occurring on worldwide. Thus the environmental hazards arising from acid mine drainage are real and need to be tacked in order to minimise their impact on the aquatic environment.

## Chapter 3: Methodology

### 3.1 Sampling

Fieldwork and sampling have been conducted to quantify and characterise pollution that is likely/generated from the Nestor and Glynn’s Lydenburg Mine tailings storage facilities respectively, from 20 to 23 February 2015. Thirty tailings profile samples and five grab samples were collected at gold mines of both Nestor Mine and Glynn’s Lydenburg Mine which fall under Sabie-pilgrim’s Rest Goldfield of South Africa and located in Mpumalanga Province. The samples were obtained using both truck-mounted auger and handheld auger. Additional samples were collected from exposed sides of tailings dump.

Three handheld auger holes were drilled on tailings dam with samples collected at every 0.5 meter interval in  Nestor Mine while two handheld auger holes were drilled in the Glynn’s Lydenburg TSFs (Figures 4 and 5). For Nestor Mine tailings sample abbreviation NS was used, with the first sample NS01/1 taken at the depth of 0.02-0.5m, second sample NS01/2 at the depth of 0.5-1m, third sample NS01/3 at the depth of 1-1.5m and the fourth sample at the depth of 1.5-2 m and the same was done to the next other boreholes (NS01/1-4 and NS03/1-4) (Appendices). For Glynn’s Lydenberg Mine tailings abbreviation GL was used to represent samples GL02/1-4 and GL03/1-4 (Appendices).

In addition, Cross-sections and exposed profiles by reclamation processes of the tailings storage facilities and handheld auger (Figur 5) to the depth of two meters were used in Nestor Mine tailings storage facility to map and characterize the intensity and variations of oxidation in the tailings. For grab samples in Nestor Mine tailings storage facility, the upper layer was removed to at least 10 cm in order to take fresh sample and they were numbered NS 001-005 (Appendices).

Tailings storage facilities sampling were done by means of truck-mounted auger (Figure 6) in the Glynn’s Lydenburg Mine tailings storage facility wherein vertical profiles of up to ten meters were be drilled and samples were collected at each and every 1 meter interval and are represented by abbreviation GL001-010 (Appendices). In order to avoid contamination from one geo-environmental area to another, the drill rigs were washed and pre-contaminated prior collection of the next samples. Two additional handheld auger holes were drilled to the maximum depth of three meters for additional samples in the Glynn's Lydenburg tailings storage facility with samples collected per every 0.5 meter interval. The samples were preserved in polyethylene (PE) bags and later tested for various analyses.

Figure 4 Two meters handheld auger in Nestor Mine tailings storage facility

Figure 5 Handheld auger sampling in Glynn's Lydenberg Mine tailings storage facility

This together with logging of truck-mounted auger hole in Glynn’s Lydenberg Mine TSF up to ten meters depth and handheld auger to the depth of three meters was used to help to establish the oxidation zone depths and tracing of the unoxidized parts of the tailings storage facility (Figur 6). The collected samples were sent to Council for Geoscience laboratory, Pretoria for further analysis.

Figure 6 Truck-mounted auger sampling in Glynn's Lydenberg Mine tailings storage facility

The seepages from Nestor Mine TSF were also collected using two 100 ml plastic bottles at each site for metal loadings and anions analysis in the Council for Geoscience laboratory to assess the status of current acid mine drainage from the tailings storage facility. Water samples were also collected from Sabie River in pre-cleaned 100 ml plastic bottles and were filled completely, leaving no space between the contents and the lid. Samples collected for total metal analysis were acidified using Nitric acid and stored in a cooler box with ice while samples for inorganic constituents were stored in a cooler box and left untreated after collection as per USEPA (1986). Every attempt was made to minimize aeration during the collection and transfer of samples to reduce the loss of volatile chemicals.

## 3.2 Sample preparation and quality control

Also known as sample reduction, sample preparation is a process by which a sample is crushed and pulverized for analysis. Unfortunately, during sample reduction, contamination can never be avoided, but processes are utilized to keep the level of contamination to a minimum.

Severe geochemical testing programs can reveal whether wastes and materials produced by extractive operations of mining process are likely to release metals or other contaminants that could degrade the environment at or around a mine site. Testing programs aimed at determining the potential for acid generation and constituent release through weathering and leaching were performed on tailings samples collected from Glynn's Lydenburg and Nestor TSFs. Both onsite and laboratory analyses were carried out.

Size reduction to <75 µm was performed using a single swing mill (TM-SPR003) method. The milling pots used are made of carbon steel to minimize level of contamination.

The milling pot, puck, ring and lid were washed using distilled water and wiped with the paper towel with ethanol and then allowed to dry. The puck and the ring were put back into the pot after cleaning. A batch of 37 tailings samples was sent to the laboratory for preparation and analysis. Nestor Mine Tailings samples were 19 and made the first grid with 18 samples from Glynn's Lydenburg making the second grid.

- The first sample from the grid of Nestor Mine tailings, about 75 millilitres was transferred into the pot and the pot was closed and placed into the milling machine. After the closure of the milling machine cover, the labelled empty bottle was placed on top of the swing mill for sample identification.
- Time of six minutes was set on the machine which pulverized the sample for a set time and stopped automatically upon completion.
- The pot was then taken out and placed on the working table, and then transferred back to its labelled sample bottle.
- The pot, puck and the ring were then cleaned by milling a portion of quartzite and blown with compressed air and then wiped with paper towel wetted with ethanol.

For the next sample similar steps from the first bullet were performed.

For quality control, a batch of 37 samples was submitted to the laboratory for preparation. The first sample and the tenth sample were sieved using a small handheld sieve. Before sieving, the samples were weighed using a calibrated scale, and samples were sieved in small portions to avoid blocking of sieve pores. Two portions were then weighed and 95% of particles were found to be <75 µm. Also, one in ten samples was duplicated.

### 3.2.1 Water Sampling and onsite analysis

Water samples were collected from Nestor Mine tailings leachate accumulated next to the dump and from the adjacent Sabie River. Onsite analysis for pH, electrical conductivity (EC), Total Dissolved Solids (TDS), temperature and dissolved oxygen (DO) were done using Wissenschftlich-Technische Weskstatten (WTW) Multi parameters measurement meter, Multi 3340 from Germany. Three 100 ml bottles were used for water samples collection for alkalinity, anions and cations tests in the laboratory. The samples for anions and cations tests were flit with three drops of nitric acid added on cations bottle to preserve metals constituents while the alkalinity one was not flit. The samples were kept at cooler box with ice until submitted to the Council for Geoscience laboratory for analyses. The water bottles were labelled and abbreviated NO 001 for Nestor Mine leachate and NO 002 for Klein Sabie River water sample.

The water accumulated on the paddocks of the Nestor Tailings Dam had red-orange colour (Figure 19).

The analyses were in duplicate.

### 3.2.2 Laboratory analysis

#### 3.2.2.1 Static geochemical techniques

The following static laboratory analyses were performed: ABA, ICP-MS, IC, XRF and XRD.

Static Acid Base Accounting (ABA) is a screening tool used to determine the acid generating and acid neutralizing properties of geochemical material. The balance of these two properties is termed Net Neutralizing Potential (NNP) and is used to classify rock types to be mined in terms of acid generation potential (Usher et al., 2003). ABA was undertaken to determine the potential of the tailings to generate acid as well as their capacity to neutralise the generated acid. The NPR was calculated on the basis of modified methods of Sobek (Jambor, 2003), where neutralization potential (NP) and acidity potential (AP) were calculated from $C_{inorganic}$ and $S_{sulphide}$ expressed as $CaCO_3$/ton of waste material, respectively.

The ratio of neutralization potential (NP) to acid potential (AP) is presented in graphical interpretations (Fig.14) with the inference that geologic materials with an abundance NP are unlikely to generate acid drainage. NP: AP ratios <1 commonly produce acid drainage, NP: AP ratios >2 should produce alkaline water according to Skousen et al. (2002).

Below is the outlined procedure for various tests that form part of static ABA (Usher, 2003).

- **Initial pH**

This is referred to as the pH of the leachate before oxidation has occurred. The initial pH indicates the immediate acidic or basic characteristic of a sample and could also indicate if acid generation has already occurred (Usher et al., 2003). To measure this, 20 g pulverized sample was weighed and transferred into a 1 L bottle. 400 ml of de-ionised water was added into a 1 L bottle and put on the en-to-end shaker and the slurry/mixture was stirred and the sample was left to stand for 24 hours at which the initial pH of the fluid was measured.

- **Final pH (Net Acid Generating Test pH)**

Net Acid Generating test pH refers to the pH of the leachate after oxidation has occurred. A volume of hydrogen peroxide was added to 2 g of pulverized sample and the final pH was measured after a day.

- **Acid potential (AP)**

AP is a measure of the concentration of acid in the leachate after oxidation with hydrogen peroxide. The AP is expressed as kg/ton $CaCO_3$ required to neutralise the sample.

- **Determinants in the solution**

This is referred to as the concentration of determinants in the leachate after oxidation with hydrogen peroxide was recorded. These partial extraction results provide an estimate of the total number of kilograms of each determinant that may be leached by the weathering of a tonne of original sample.

- **Neutralizing potential (NP)**

Sulphuric acid was added to 2 g of a sample until the pH of a slurry/mixture was below 2.5 after 24 hours. The volume of sulphuric acid added was recorded. The acidified sample was then back-titrated with a known concentration of sodium hydroxide until the pH was stable after 24 hours. The volume of sodium hydroxide added was also recorded. Neutralizing potential was then calculated from the recorded volumes of sulphuric acid and sodium hydroxide required and expressed in kg/ton $CaCO_3$.

- **Net Neutralizing Potential (NNP)**

NNP was calculated from the AP and NP values (NNP=NP-AP). The more negative the NNP, the greater the potential of the sample to produce AMD. These NNP values are expresses as kg/tonne $CaCO_3$ per sample. Therefore, samples with a positive NNP have a capacity to neutralize AMD, whereas samples with negative NNP values may generate AMD.

It is important to note that although low positive NNP values represent samples that will have an overall positive neutralizing effect; these samples may produce AMD at some stage during the weathering process.

The samples were analysed by X-Ray Florescence spectrometry (XRF) analytical techniques for metal loadings and X-Ray Diffraction spectrometry (XRD) for mineralogical analysis.

Geochemical composition of samples was determined using X-ray fluorescence spectrometry (XRF) technique at the Council for Geoscience laboratory. With the exception of XRF, most analytical techniques for chemical composition of solid materials such as waste rock, tailings or spent ore require solubilisation of the solid material into solids form prior to analysis. Minor and major chemical constituents of rocks and minerals are commonly determined using XRF technique (Norrish and Chappell, 1967; Bertin, 1970; Johnson and Maxwell, 1981). By XRF analytical technique, the abundance of many elements that occur in concentrations of few parts per million can be determined and it an inferior technique for light elements, volatile elements, and many elements occurring at a concentrations of less than 10 ppm.

For XRF analysis, samples were air dried, crushed and milled to <75 µ. Tailings were analysed in a solid form by bombarding the sample with X-rays of known wavelength and energy. Emission of secondary florescence (photons) with energies and wavelengths characteristics of individual will be induced as a result of excitation by primary X-rays. The abundance of a given element is proportional to the number of photons intensity (U.S.EPA, 1986). For major element analysis, the milled sample (<75 µ fraction) was roasted at 1000 °C for at least 3 hours to oxidize $Fe^{2+}$ and S to determine the loss of ignition (L.O.I.). Glass disks were prepared by fusing 1 g roasted sample and 10 g flux consisting of 49.5% $Li_2B_4O_7$, 49.5% $LiBO_2$ and 0.50% LiI at 1150 °C. Quality control/Quality assurance was done by using in-house amphibolite reference material (sample 12/76). Also one in every ten samples was duplicated during sample preparation. For trace elements analysis, 12 g milled sample and 3 g Lico wax was mixed and pressed into a powder briquette by a hydraulic press with the applied pressure at 25 ton. The glass disks and wax pallets were analyzed by a PANalytical wavelength dispersive AXIOS X-ray fluorescence spectrometer equipped with a 4 kW Rh tube. In this study, both major and minor metals were analysed in the form of oxides ($SiO_2$, $Al_2O_3$, $Fe_2O_3$, MnO, $TiO_2$, MgO, CaO, $Na_2O$, $K_2O$, $P_2O_5$, and $Cr_2O_3$). Trace elements (Rb, Zr, Sr, Nb. Cu, Zn, Cr, V, Pb, Ga, Ni, As, Mo, Sn, Ce, U, Th) were also analysed.

For mineralogical identification of samples, X-ray diffraction technique was used at Council for Geoscience. XRD is used to identify minerals that are difficult to resolve with a petrographic microscope and to characterize crystal structures. Atoms or atomic layers in the crystal structure causes diffraction of incident beam of x-rays passing through it. XRD method measures these beam of diffracted x-rays (Hutchison, 1974; Bish and Post, 1989). The composition of clay minerals that are associated with many ore deposits is quickly and easily determined using the XRD analytical technique (Sobek et al., 1978). According to Sobek et al. (1978) analysing clay minerals, which have different sorptive properties, can provide a useful data that can be used in the design of waste rock and tailings piles, drainage covers, compacted liners, and remediation plans. Samples were scanned from 2 to 70° 2θ $Cu_{K\alpha}$ radiation at a speed of 0.02° 2θ steps size/0.5 sec, LYNXEYE detector and generator settings of 40 kV and 40mA. Phase concentrations were determined as semi-quantitative estimates using relative peak heights/areas.

Water samples were collected from seepage from Nestor TSF and water from the adjacent Sabie River. Three samples were collected from each site for different analyses. The first portion was filtered using 0.45 µm filters and was acidified using three drops of 3M Nitric acid for metal analysis. According to USEPA (1983), samples that must be delivered to the laboratory for analysis of their inorganic and organic constituents must be preserved to preclude precipitation of metal compounds or volatilization of organic compounds between the time of sample collection and analysis. The second portion was filtered using 0.45 µm filters and then analysed for anions. New filters were used at each seepage site as well as in the Sabie river water sampling in order to ensure that they do not become sources of contamination. The metal and anions analysis were done by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Ion Chromatography (IC) respectively in duplicate. The elements concentrations were compared to the South African water quality guidelines (DWAF, 1996).

Water samples were also analysed using ICP-MS. In ICP-MS analysis technique, aqueous samples are ionised at extreme temperatures in argon plasma. The ions are focused into a stream of material that is accelerated toward detectors that measure the masses of specific isotopes (Robinson, 1990). Standard ICP-MS techniques is capable of detecting elements in concentrations of a few parts per billion to parts per million, however, detection of a few to hundred parts per trillion is permitted as per recently developed guidelines. A sample need only to be ionised once, thus rapid, simultaneous or sequential determination of multiple elements in a single analytical session is permitted with ICP-MS analysis, though interference from plasma gases, background radiation from other elements, and interferences from larger excesses of single elements are primary demerits of the analytical technique (U.S.EPA, 1986).

IC was also used for water analysis. IC is used to measure the concentrations of common anionic constituents (U.S. EPA, 1983). The technique uses a series of columns filled with ion-exchange resins to separate the anions from solution and combine them with hydrogen to form acids (Harris, 1987, Patniak, 1997). A conductivity detector is used to measure electrical conductivities of the different acids, which are variably strong electrolytes from which anions concentrations can be determined.

Total carbon ($C_{total}$) and sulphur ($S_{total}$) contents were determined by a catalytic oxidation using a LECO elemental analyser at Council for Geoscience, sulphate sulphur ($S_{sulphate}$) content was determined by $NH_4$-oxalic, hot leach and sulphide sulphur ($S_{sulphide}$) was determined from the difference. According to Smith et al. (1974), methods for characterising acid-forming minerals were developed during the 1970's in areas eastern U.S. mined for coal. These techniques ultimately lead to standardised EPA protocol for characterization of mine soils and overburden (Sobek et al., 1978). In these analytical techniques the amount of sulphur present in the geologic materials is measured and attributed to being either an acid-forming minerals such as pyrite ($FeS_2$) or non-acid-forming mineral such as gypsum ($CaSO_4.2H_2O$). The relative amount of acid-forming minerals is then contrasted to the amount of neutralising minerals such as calcite ($CaCO_3$) to develop a prediction of probability of acid generation (Skousen et al., 2002).

#### 3.2.2.2 Batch Leaching Tests

Batch leaching methods have been used for several decades to estimate the potential release of contaminants from soils and other solid waste material in order to prevent human health and groundwater quality from contamination by metals. Several factors that affect the applicability of leaching protocols have been evaluated by Lowenbach (1978), Wilson and Young (1983), and Kimmel and Friedman (1986). These include the type of extraction fluid, the soil-to-liquid ratio, and the length of the test duration. Methods of batch leaching have been shown to be reproducible, easy to use, and less expensive than flow-through, continuous leaching protocols (Perket and Webster, 1981).

The U.S. Environmental Protection Agency (USEPA) has adopted several batch leaching protocols to evaluate the release of contaminants from wastes and these are the toxicity characteristic leaching protocol (TCLP), the synthetic precipitation leaching procedure (SPLP), and the extraction procedure toxicity (EP-TOX) (USEPA, 1973a; 1973b; 1986). Results of most batch leaching tests are general indicators of the potential release of metals from wastes and should be carefully evaluated before being used for regulatory or design purposes (Perket and Webster, 1981; Dragun et al., 1990).

To measure this, 20 g pulverized sample was weighed and transferred into a 1 L bottle. 400 ml of de-ionised water was added into a 1 L bottle and put on the en-to-end shaker and the slurry/mixture was stir and the sample was left to stand for 24 hours at which the initial pH of the fluid was measured. Electrical conductivity was also measured. The sample was filtered and split into triplicate. One replicate for cat-ion was acidified with 3M nitric acid, the second analysed for alkalinity and the third replicate was analysed for anions. For alkalinity, 35 ml of sample was titrated with 0.1M hydrochloric acid (HCl) to pH 4.5 end point. For acidity, 35 ml of sample was titrated with 0.1M HCl to pH 8.3 end point.

Batch leaching results are recorded in annexure 4.

# Chapter 4: Results and Discussion

## 4.1 Geochemical analysis of mine tailings

XRF results for major, minor and trace elements are presented in Annexure 1. Major and minor elements are presented in the form of oxides.

Quartz is dominant oxide in the Nestor Mine tailings (ranging from 66.7-91.25 wt. %; followed by $Fe_2O_3$ and $Al_2O_3$ (in range of 0.82-15.63 wt. %; 3.21-12.50 wt. % respectively); $TiO_2$ (0.18-10.18 wt. %) and CaO (0.005-3.2 wt. %; Table 5; Figure 7; and Figure 8). Also occurring in small amounts is $K_2O$ (0.51-2.27 wt. %), MgO (0.005-1.46 wt. %; Fig. 8), $P_2O_5$ (0.029-0.248), $Cr_2O_3$ (0.013-0.042 wt. %) and $Na_2O$ (0.005-0.05 wt. %).

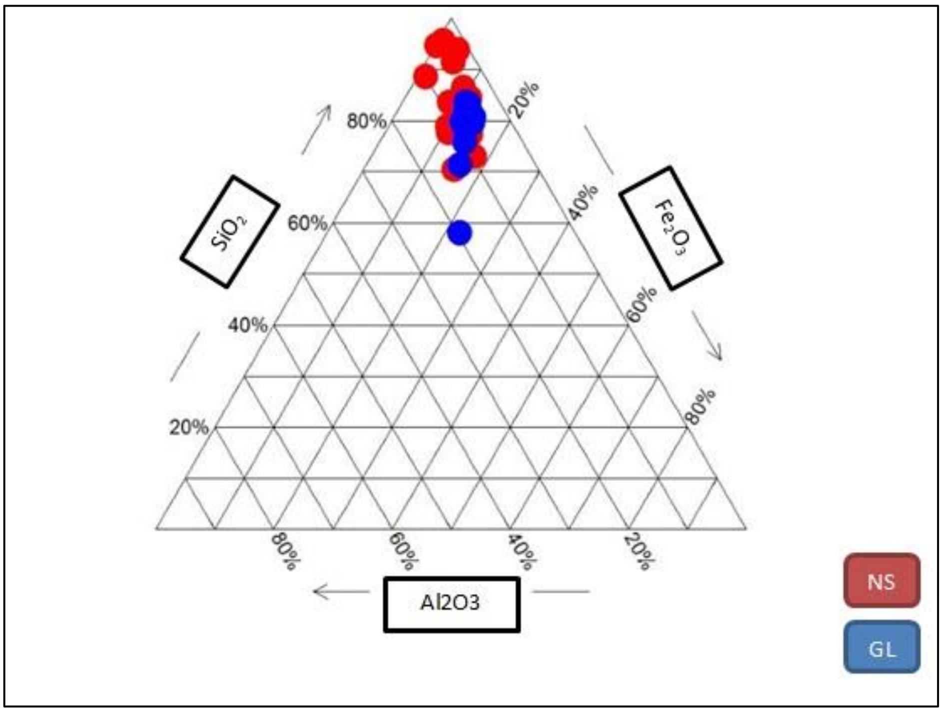

Figure 7 Distribution of dominant oxides in Nestor and Glynn's Lydenburg gold mine TSFs

There is higher concentration of quartz and $Fe_2O_3$ in Nestor Mine TSF samples compared to Glynn’s Lydenburg Mine TSF samples. This is because mineralization in the earlier took place in the quartzite of Black Reef Formation while in the Glynn’s Lydenburg the host rocks are dolomite of Malmani Subgroup. The Nestor gold tailings are represented by the abbreviation NS and red colour and blue colour represents Glynn’s Lydenburg gold tailings with abbreviation GL in both Figure 7 and 8 below.

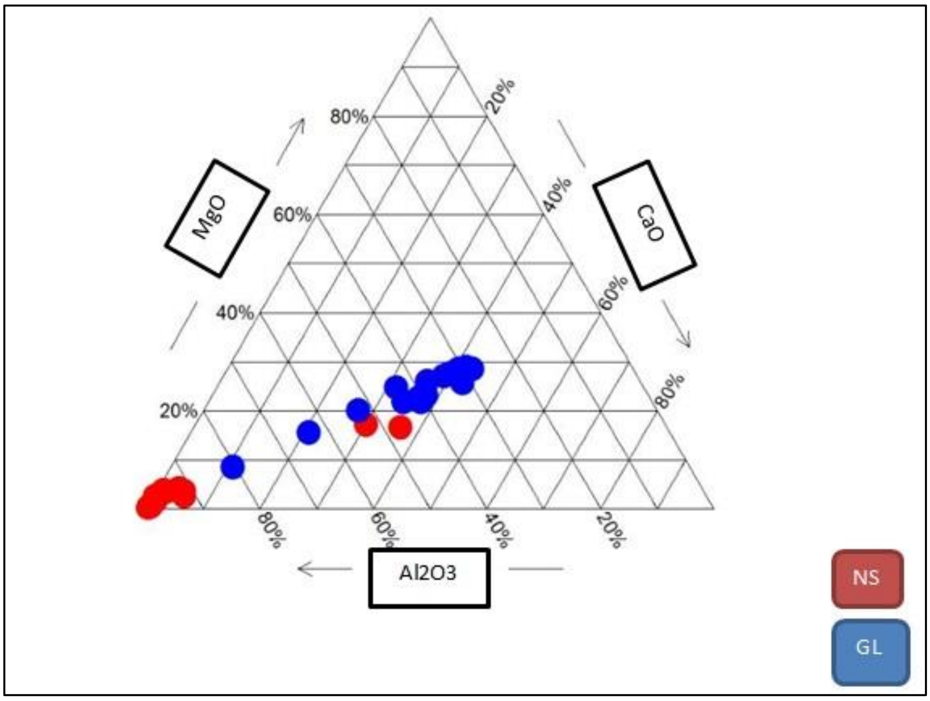

Figure 8 Distribution of dominant neutralizing oxides and acid-forming oxide in Nestor and Glynn's Lydenburg gold mine tailings

CaO and MgO are occurring in higher concentrations in the Glynn’s Lydenburg TSF samples compared to Nestor TSF samples (Fig. 8). This is because the Glynn’s Lydenburg Mine mineralization is on the Malmani Dolomite of Cheniespoort Group while Nestor Mine has mineralization on the Black Reef Quartzite Formation. The buffering capacity in Nestor TSF is less than in the Glynn’s Lydenburg TSF as supported by oxides of calcium and magnesium respectively.

Figure 9 show variation in metal distribution in three handheld-auger depth profile drilled in Nestor TSF. The samples from Nestor Mine TSF also contain significant amounts of As (137-1599 ppm), Cu (34-571 ppm), Cr (43-273 ppm), Pb (12-276 ppm), Ni (16-157 ppm), V (29-255 ppm), and Zn 7-485 ppm) (Fig. 9).

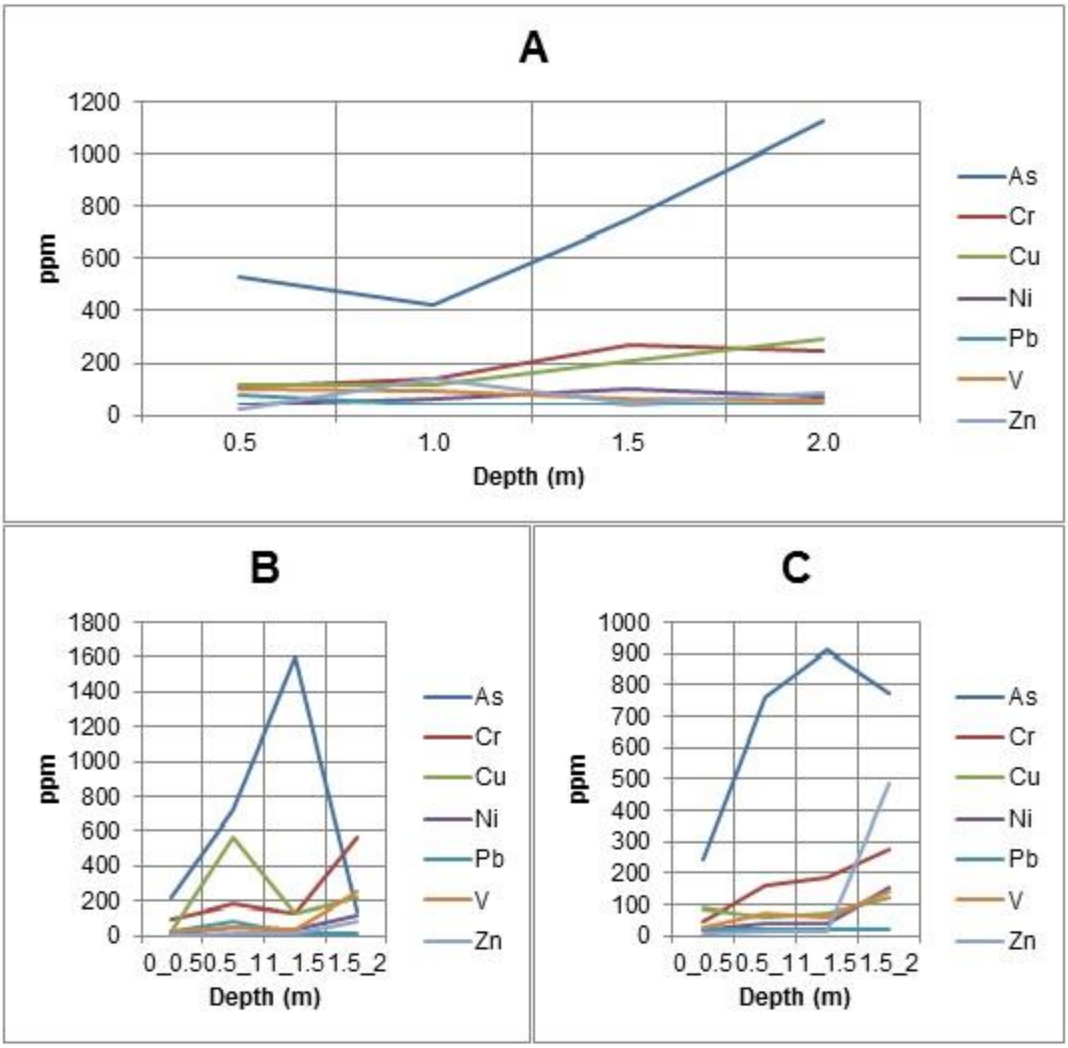

Figure 9 Nestor TSF depth profiles

Arsenic is occurring in high quantities and showed an increase with depth trend, ranging between 137-1599 ppm (Fig. 9). Cr and Cu also showed an increase with depth trend (86-566 ppm and 43-273 ppm respectively); while Ni, Pb, V and Zn showed a decrease or almost no change in concentrations with increasing depth. Elements As, Cr and Cu are very mobile and that's why they are increasing with depth in concentrations compared to Ni, Pb, V and Zn.

In the Glynn's Lydenburg Mine tailings (Annexure 1; Figure 7 and Figure 8) quartz ($SiO_2$) is also the most dominant oxide ranging between 47.95 and 65.89 wt. %, followed by $Al_2O_3$ (4.31 to 16.19 wt. %), $Fe_2O_3$ (8.48 to 11.70 wt. %), CaO (2.18 to 7.10 wt. %), MgO (2.74 to 4.7 wt. %). Occurring in small amounts is $K_2O$ (1.12-1.70

wt. %), MnO (0.089-0.175 wt. %), $P_2O_5$ (0.058-0.144 wt. %) and $Cr_2O_3$ (0.015-0.027 wt. %).

Arsenic (As), is also occurring in significant amounts (807-2502 ppm), followed by Cr (117-238 ppm), Cu (10-104 ppm), V (56-235 ppm), Ni (45-132 ppm), Pb (13-63 ppm) and Zn (90-240 ppm) (Figures 10; 11; 15). Figure 10 shows weathered tailings from Nestor TSF. These tailings are eroded towards Sabie River and they have considerable concentrations of metals, namely, As, Cr, Cu, Pb, Ni, V and Zn (Anexure 1; ON 001).

Figure 10 Weathered Nestor TSF

Figure 11 shows distribution of metals with depth profile of one of truck-mounted auger and two drilled handheld auger holes in Glynn's Lydenburg tailings storage facility. As shows an irregular pattern with increasing depth as it increased from 1045 ppm to 1390 between 0.5 and 1 m; increased drastically between 1 and 1.5 m (2065 ppm) which fell to 1390 ppm between 1.5 and 2 m depth. Cr shows a decrease with depth trend (139-127 ppm), Cu also showed a slight decrease with depth trend (26-15 ppm). Also showing a decrease in concentration with depth are Ni (75-47 ppm), Pb (63-39 ppm), and Zn (243-105 ppm). Vanadium showed a slight increase with depth (63-65 ppm). Quartz is dominant mineral and shows an almost constant trend throughout the tailings storage facilities samples from both Nestor and Glynn's Lydenburg Mines. That can be attributed to the physical property (hardness) of quartz as it is unlikely to be affected by chemical weathering (Fig. 7 and Fig. 8). The concentrations of aluminium oxide ($Al_2O_3$) and ferric oxide ($Fe_2O_3$) show an increase with depth trend. That can be attributed to the fact that these minerals are more reactive in the unsaturated zone of the tailings storage facilities. From figure 8, it can be noticed that Glynn's Lydenburg Mine tailings have high potential of neutralizing the acid as supported by oxides of magnesium and calcium compared to less dominant alumina. Trace elements such as As, Cr, Cu, Ni, Pb, V and Zn occur in significant amount within the tailings of Nestor and Glynn's Lydenburg Mine tailings storage facilities respectively as compared to the South African soil screening levels (Table 6 and 7).

The study established high concentration of arsenic (As) in tailings of Nestor Mine ranging from 137-1599 ppm and very high concentrations were also found within tailings of Glynn's Lydenburg Mine of 807-2502 ppm. This is likely to result in As poisoning through dust inhalation and food chain, especially in the vicinity of Nestor tailings storage facility which is highly weathered and exposed to erosion of tailings to the adjacent Sabie River (Fig. 10). Concentration of 100 mg/kg As in soil can reduce crop yield by 90% and lead to As poisoning resulting skin cancer and lung cancer (Harada, 1996), and possible effects of vascular disease and diabetes (Centeno and Finkelman, 2007).

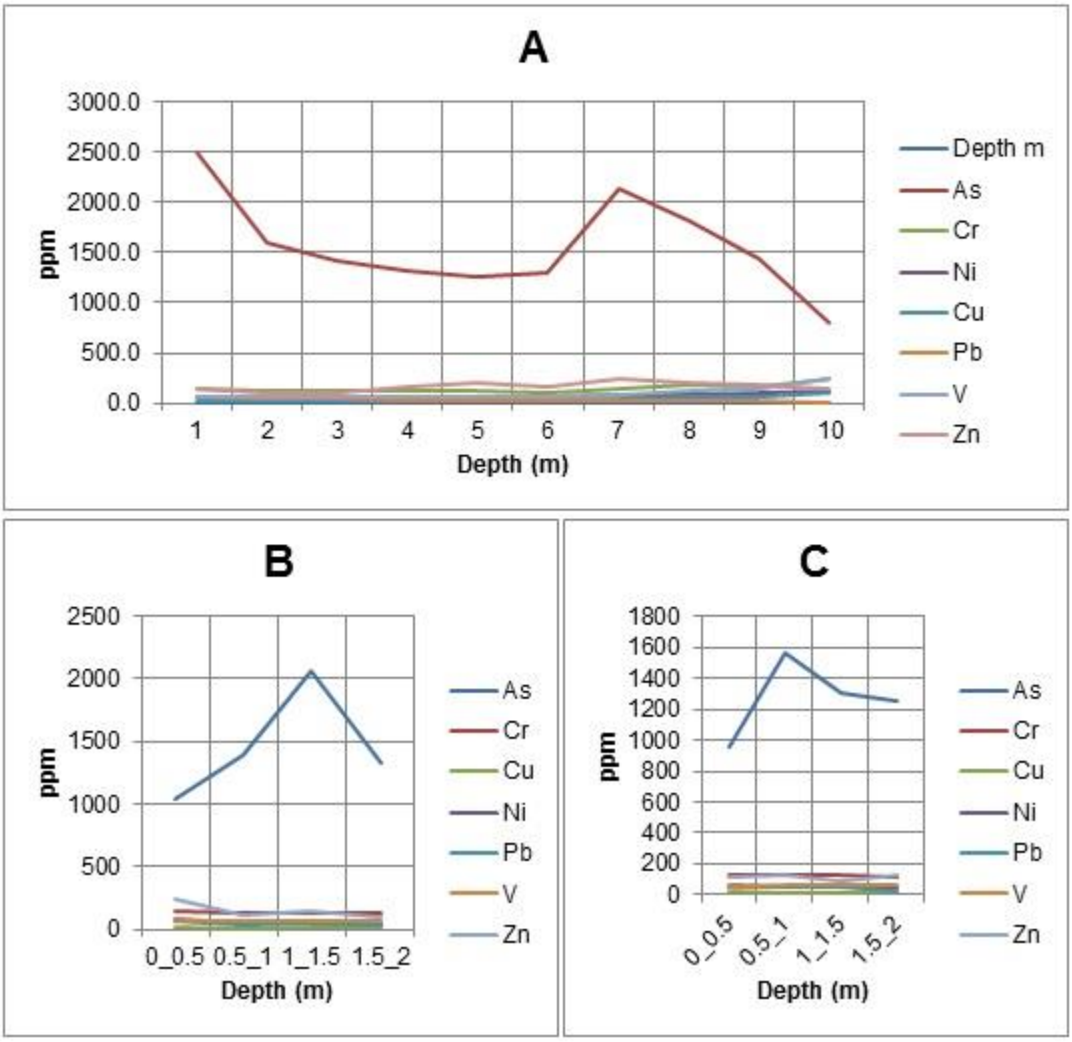

Figure 11 Glynn's Lydenburg depth TSF depth profiles

Cr, Ni, Cu Pb, and V maintained almost same regular trend with depth (Figure 11). There is slight or no change in concentrations of these metals with depth.

Zn concentration was up to 485 ppm in Nestor Mine Tailings Dumps and 240 ppm in Glynn's Lydenburg Mine Tailings Dumps. This can lead to contamination of Sabie River through weathering and erosion of tailings storage facilities, especially Nestor TSF which is highly exposed to such processes. Concentration of over 15 mg/L of Zn in water is considered toxic and can result into renal damage. High concentration of Zn salts in fish gills can lead to their death (USEPA, 2009).

Concentration of copper was up to 571 ppm in Nestor TSF and 104 ppm Glynn's Lydenburg TSF respectively. Copper offers crucial micronutrients to plants, animals and humans. Nevertheless, Cu concentration in water over 30 mg/l results in liver, kidney and blood cells damage (DWAF, 1996).

Chromium is a micronutrient which is essential for carbohydrate metabolism in animals. Cr VI is more toxic than Cr III, wherein Cr VI concentration of more than 0.5 g/ml is considered to have negative effect (Alloway and Ayres, 1997). Excessive ingestion of Cr VI is carcinogenic. Concentration of Cr in plants growing on mine spoil and various types of Cr waste are commonly in the range of 10-19 mg/kg (Alloway and Ayres, 1997). In the present study, the concentrations of Cr were up to 273 ppm in Nestor Mine Tailings Dumps and 238 ppm in Glynn's Lydenburg Mine Tailings Dumps. This can lead to dust ingestion to the community residing next to Nestor Mine and also result in food chain poisoning through water contamination.

Table 5 South African Soil Screening values for metals

| **Metal** | **Units** | **SSV1 All Land-Uses Protection of the Water Resource** | **SSV2 Informal Residential** | **SSV2 Standard Residential** | **SSV2 Commercial/ Industrial** | **Protection of Ecosystem Health** |
|---|---|---|---|---|---|---|
| Arsenic | mg/kg | 5.8 | 23 | 48 | 150 | 580 |
| Cadmium | mg/kg | 7.5 | 15 | 32 | 260 | 37 |
| Chromium | mg/kg | 6.5 | 6.5 | 13 | 40 | 260 |
| Cobalt | mg/kg | 300 | 300 | 630 | 5000 | 22000 |
| Copper | mg/kg | 16 | 1100 | 2300 | 19000 | 16 |
| Lead | mg/kg | 20 | 110 | 230 | 1900 | 100 |
| Manganese | mg/kg | 740 | 740 | 1500 | 12000 | 36000 |
| Mercury | mg/kg | 0.93 | 0.93 | 1.0 | 6.5 | 4.1 |
| Nickel | mg/kg | 91 | 91 | 1200 | 10000 | 1400 |
| Vanadium | mg/kg | 150 | 150 | 320 | 2600 | _ |
| Zinc | mg/kg | 240 | 9200 | 19000 | 150000 | 240 |

Table 6 South African soil screening values for anions

| **Anion** | **Soil Screening Level (mg/kg)** |
|---|---|
| Chlorides | 12000 |
| Fluorides | 30 |
| Nitrates-nitrite | 120 |
| Sulphates | 4000 |

Both the Nestor Mine and Glynn's Lydenberg Mine gold tailings showed significant concentrations of arsenic that are above intervention values (Table 6 and 7). There is high risk of arsenic poisoning posed by both tailings dumps to the environment (Figure 11). Also occurring in significant amount is Cr as it exceeds target value in most cases more especially on samples collected at more than one metre depth (unoxidized tailings). For Cu, most of the samples are around and above target level for soil contamination. Occurring in low levels are Zn and Pb.

### 4.2 Mineralogical analysis of mine tailings

The mineralogical composition based on X-ray diffraction expressed in weight percent (wt. %) of bulk samples is shown in Annexure 2. Both primary and secondary minerals were deduced from XRD mineralogical analysis. Jambor (1994) defined primary minerals for tailings as the ore and gangue minerals that were processed and deposited in an impoundment without any changes other than reduction in grain size by comminution. Secondary minerals are those that have been formed by processes that lead to precipitation, namely, evaporation, oxidation, reduction, dilution, mixing and neutralisation (Alpers et al., 1994). Sulphide minerals, hydroxy sulphate, hydroxide, metal oxide as well as efflorescent sulphate salt forms part of secondary minerals.

Figure 12 shows mineralogical composition of Nestor TSF samples. In the Nestor TSF, predominant minerals include primary minerals: quartz ($SiO_2$) ranging from 64-87 wt. %, followed by mica [$K (Mg, Fe)_3(AlSi_3O10)(OH)_2$] ranging from 4-23 wt. %, plagioclase ($NaAlSi3O_8$ – $CaAl_2Si_2O_8$) ranging from 1 to 5 wt. %, and k-felspar at 1 wt. % (Annexure 2). Kaolinite is the secondary clay mineral which was found mostly on grab samples and on the depth of 2 m on one of handheld auger drilled holes, jarosite {$KFe_3(SO_4)_2(OH)_6$} and gypsum ($CaSO_4.2H_2O$) are secondary minerals which are dominant on top layers of the tailings of Nestor Mine. Goethite is a secondary oxide mineral absent in grab samples from Nestor tailings and is most concentrated in handheld auger samples. Gibbsite is not present in all Nestor TSF samples except for the one recorded at unoxidized 2 m depth in one of handheld auger samples (Annexure 2; Figure 12D). This indicates that the rate of sulphide oxidation is high in this saturated zone.

Quartz is the most dominant primary mineral and shows a constant trend from both grab samples and handheld auger samples with depth. This shows that it is less reactive in oxidizing conditions. Minerals such as quartz have no potential to neutralize acid, and this is mainly due to their physical property (hardness) and it has a relative reactivity of 0.004, which is twice slower than the relative reactivity of kaolinite (Sverdrup, 1990; Kwong, 1993). Pyrite ($FeS_2$) is the major acid producing mineral and hematite at concentrations ranging from 1-8 and 1-6 wt. % respectively.

Mica is also common in high concentrations in both samples collected using handheld auger and grab samples. There is irregular trend in handheld auger drilled samples with some showing decrease with depth (Figure 12B; Annexure 2) which shows that these mineral species might have reacted with acid generated in the oxidation zone.

Oxidation of sulphides produces secondary minerals like jarosite. Evaporation of acidic, iron, and sulphate-rich water within mine waste material precipitates jarosite which stores acid generated by oxidation process. Acidity of water is also influenced by the dissolution of soluble and less soluble iron sulphate minerals, however, most of AMD from sulphide-bearing geological formations are from oxidation of sulphide minerals (Lapakko, 2002). Figure 12 shows concentrated secondary minerals on the Nestor tailings storage facility.

Calcite is absent in Nestor Mine tailings and dolomite was only found in two oxidized grab samples (Figure 12C; Annexure 2) indicating that these tailings are acidic. The acidic nature of Nestor mine tailings would provide adverse conditions for growth of plants and grass that can be maybe used for revegetation of the dump.

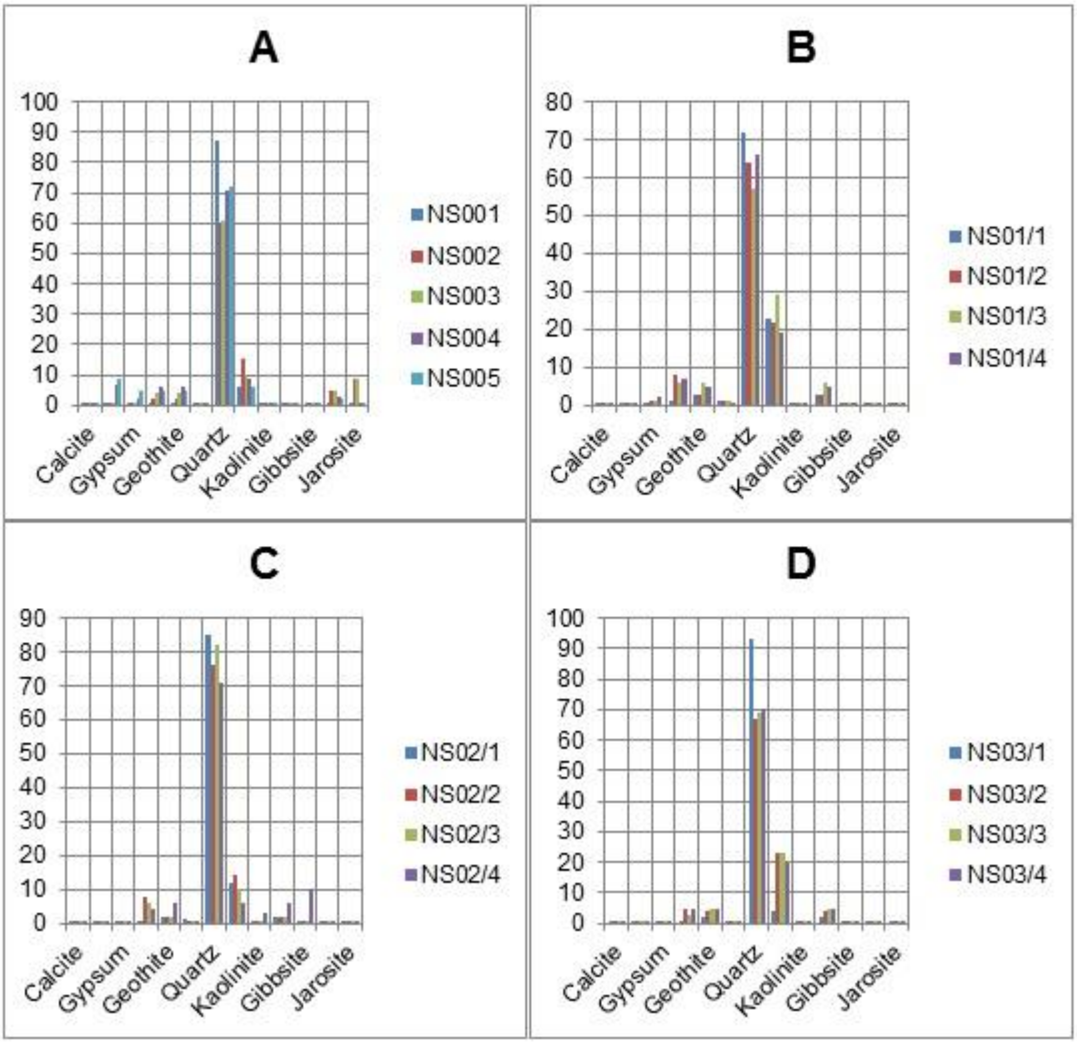

Figure 12 Mineralogical composition of Nestor TSF samples as wt. %

Tailings from Glynn's Lydenburg are comprised of quartz and dolomite [CaMg $(CO_3)$] as major mineral assemblages (Figure 13). Figure 13A shows truck-mounted auger profile of major oxides species drilled to the maximum depth of ten meters in Glynn's Lydenburg tailings dump. Quartz shows a constant trend with increasing depth. This shows that it is less reactive even under oxidizing conditions. $Al_2O_3$ and $Fe_2O_3$ show a slight constant trend with increasing depth and increases at depths. $Cr_2O_3$, $K_2O$, MnO and $TiO_2$ show a constant trend with depth.

Other primary minerals that are acid neutralizing include mica and plagioclase. Gypsum and goethite are also present as secondary minerals as neutralizing minerals, while the absence of jarosite in Glynn's Lydenburg Tailings dump could be attributed to less acidic conditions due to the presence of high concentrations of carbonates within the Malmani dolomite host rocks. Plagioclase was mainly found in truck-mounted auger samples and showed a constant trend of decreasing with depth (Figure 13C). Mica being common in all three drilled holes including handheld auger samples also showed a decrease with depth trend. This can be attributed to low aid generation at unoxidized zones of the tailings dump (3-10 m) compared to semi-oxidized top part (0-2 m). Gypsum show a decreasing trend with depth in both handheld and truck-mounted augers drilled holes (Figure 13). The highest concentrations occur between 1 and 2 m; this indicates that the concentration of sulphates secondary minerals in the Glynn’s Lydenburg decreases with decreasing rate of oxidation.

The absence of dolomite in borehole GL 02/1-4 (Figure 13B) can be attributed to oxidation that might be taking place within the top oxidized zone (0-2 m); however, the presence of calcite can add into neutralization potential to the acid that might be produced by primary mineral hematite. Gypsum is present in both truck-mounted auger samples and handheld auger samples showing a decrease with depth trend. This might be attributed to limited oxidation at depth as pyrite on top layers (0-1 m) of tailings reacted with both dolomite and calcite at top oxidized part to produce secondary mineral goethite. This can be also confirmed by the absence of primary acid neutralizing mineral of kaolinite within the Glynn’s Lydenburg tailings. Kaolinite was only found at unoxidized lower parts of the tailings dump between 8 and 10 meters depth (Figure 13A; Annexure 2) showing a rapid increase with depth.

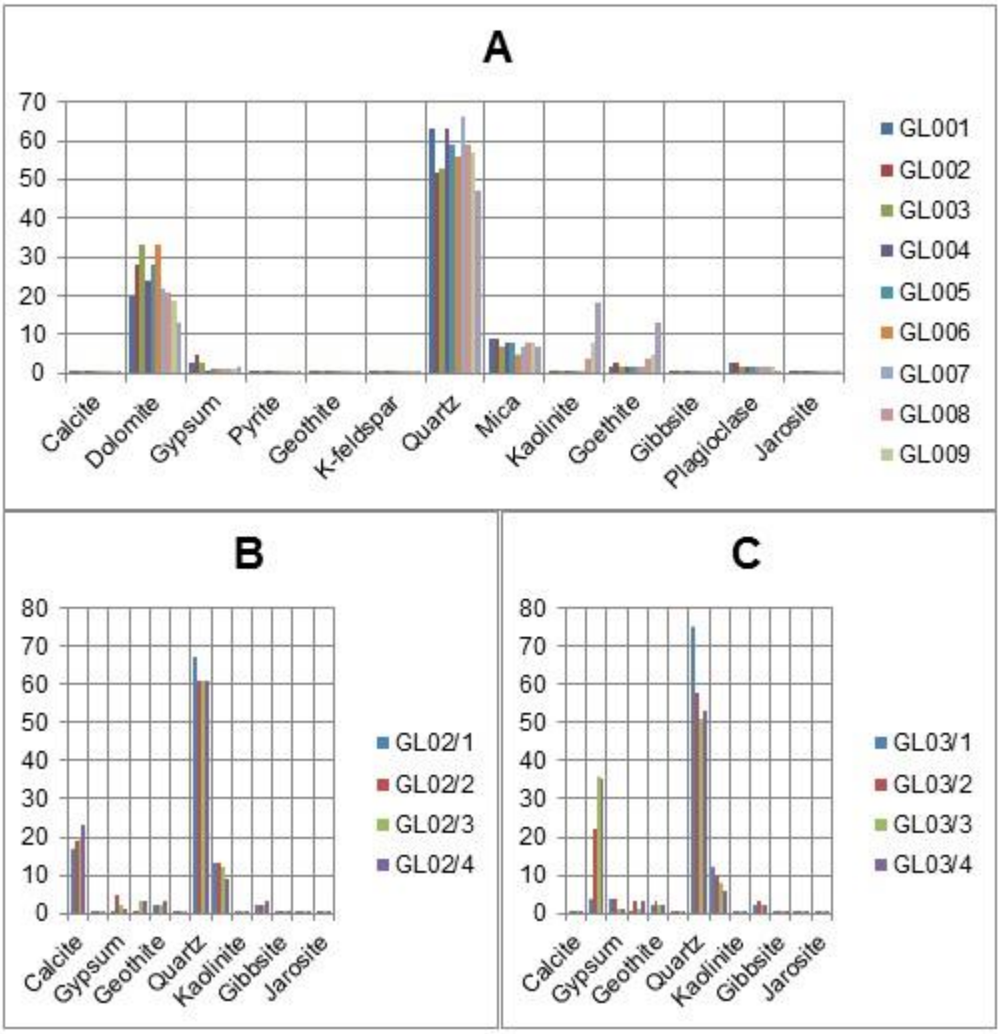

Figure 13 Mineralogical composition of Glynn's Lydenburg TSF as wt. %

Figure 14 shows hardpans in Nestor Mine tailings dump, mainly composed of primary acid-producing mineral pyrite and secondary acid-producing mineral jarosite (Annexure 2, Figure 12A). Goethite and gypsum are also present, indicating neutralizing conditions taking place within this oxidized zone. Mica, kaolininte and plagioclase are also common as buffering minerals (Figure 12A). The absence of jarosite in semi-oxidized zones (Figure 12) indicates that hardpans are limiting penetration of oxygen to unoxidized pyrite present in deeper zones of the tailings dump; hence preventing further acid mine drainage from occurring in saturated zones.

Figure 14 Secondary minerals in Nestor Mine tailings storage facility

Kaolinite and plagioclase primary acid buffering minerals are also absent in semi-oxidized zones (Figure 12) indicating that have reacted with the acid likely generated in the oxidized zones. Mica is a silicate mineral present in variable concentrations. Mica is capable of neutralizing acid generated and that can be confirmed by its slight decrease with depth (Figure 12).

### 4.3 Acid Base Accounting

Acid base accounting results are presented in Annexure 3 in terms of paste/initial pH, reactive S (%), AP (as kg/ton $CaCO_3$), and NP (as kg/ton $CaCO_3$). The calculated parameters, namely, net neutralizing potential (NNP as kg/ton $CaCO_3$) and net potential ratio (NPR) are also presented and they have been used as criteria the acid potential of samples. Graphically, these results clearly show the dominant trends in results as shown in figures. The criteria used to classify the acid-producing potential of the samples analysed are those used by Usher et al. (2003), and these should not be used in isolation, but in combination to categorise material from non-acid generating to acid generating with a slight grey area in between. The following criteria have been used:

- Paste pH; which is a measure of sample’s immediate acidity or alkalinity;

- Net neutralizing potential (NNP): (NP-AP)

Table 7 Classification criteria based on the net neutralizing potential (NNP)

| | |
|---|---|
| NNP>0 | Sample had acid-generating potential |
| NNP<0 | Sample had a potential to neutralize produced acid |
| -20>NNP<20 | If sample has NNP value within this range, its acid producing potential remains inconclusive and other criteria should also be considered in order to determine its acid generating status |

- Neutralizing potential ratio (NPR): Price et al. (1995) provided screening criteria based on the NPR generated during static ABA analyses (Table 9).

Table 8 Criteria for classification based on neutralization potential ratio (NPR)

| **Potential for AMD** | **Initial NPR Screening Criteria** | **Comments** |
|---|---|---|
| Likely | <1 | Likely AMD generating |
| Possibly | 1 to 2 | Possibly AMD producing if NP is insufficiently reactive or is depleted at a faster rate than sulphides |
| Low | 2 to 4 | Not potentially AMD producing unless significant preferential exposures of sulphides along fracture planes or extremely reactive sulphides in combination with insufficiently reactive NP |
| none | >4 | No further AMD testing required unless materials are to be used as source of alkalinity |

- Percent Sulphide-Sulphur and NPR

Soregaroli and Lawrence (1998) have shown that a sample is required to have a minimum content of 0.3% sulphide-sulphur in order to generate acid for an extended period of time. It had been observed that material with sulphide-sulphur below 0.3% may produce acid for a short period of time, but that acid would not be sustainable. This observation has been combined with NPR to create a set of criteria as shown in Table 10 below.

Table 9 Percent sulphide-sulphur and NPR

| **Sulphide-Sulphur Content and NPR** | **Acid Generating Status** |
|---|---|
| Samples with <0.3% sulphide-sulphur with NPR values greater than 4 | Low Probability of Acid Generation |
| Samples with <0.3% sulphide-sulphur with NPR values less than 4 | Inconclusive Probability of Acid Generation |
| Samples with >0.3% sulphide-sulphur with NPR values greater than 1 | Inconclusive Probability of Acid Generation |
| Samples with >0.3% sulphide-sulphur with NPR values less than 1 | High Probability of Acid Generation |

The institute for Groundwater studies did not provide Percent sulphide-sulphur, so this was calculated using the below calculations (Usher, 2003):

AP=Sulphur x 31.25 (Open System)

AP=Sulphur x 62.5 (Closed System)

An open dissolution system can be defined as a system where water (such as pore water or surface water) is in contact with a gas phase, allowing for interchange of $CO_2$ and $O_2$ in particular. A closed dissolution system is a system where no gas phase is present into which $CO_2$ can escape when calcite dissolves. Such situations may prevail below the water table or below the surface of tailings ponds.

If limestone is added to a stockpile in an attempt to neutralize AMD, $CO_2$ will be produced as part of the neutralization reaction. In an open system, any $CO_2$ produced will escape into the atmosphere. However, in a closed system this will not be possible and any $CO_2$ produced will react with water to form carbonic acid. A closed system represents, therefore, a “worst case scenario” in terms of number of moles of $CaCO_3$ required to neutralize AMD.

From Table 8, it can be noticed that all samples from Nestor Mine tailings have high acid-generating potential (up to 140.31 $CaCO_3$/ton; Annexure 3) and have a very low

NNP (up to -202.06 $CaCO_3$/ton) (Fig. 15). However, Glynn's Lydenberg Mine tailings showed high neutralization potential and are characterized by high NNP. Eroded tailings collected from Nestor Mine falls within uncertainty zone and this can be attributed to oxidation they have undergone since they were eroded from the main tailings storage facility.

Figure 15 below shows subdivision based on acid potential (AP), neutralisation potential (NP) (i.e. NNP) and paste pH of the tailings collected in Nestor and Glynn's Lydenburg Mine tailings storage facilities. The tailings are having both potential to generate acid and acid-neutralising depending on the mineralization of the source rocks. Based on this subdivision, samples from Nestor Mine tailings storage facility is characterized by high AP than NP with considerable amount of sulphur. Their AP ranges from 1.56-140.31 kg $CaCO_3$/ton while NP ranges from -57.75 to -0.3 kg $CaCO_3$/ton and their NNP ranges from as low as -202.06 to -0.3 $CaCO_3$ (annexure 3; Figure 15).

However, Glynn's Lydenburg Mine tailings storage facility which is associated with dolomite mineralization shows no potential to leach any acid drainage. Based on ABA results, the tailings samples have more NP than AP. Their AP ranges from 7.5 $CaCO_3$/ton to 56.56 $CaCO_3$/ton while NP ranges from 57 $CaCO_3$/ton to 207.88 $CaCO_3$/ton with NNP ranging from 33.9 $CaCO_3$/ton to 176.9 $CaCO_3$/ton (Annexure 3; Figure 15).

Eroded tailings from Nestor Mine falls within uncertain zone and this can be attributed to the oxidation they have undergone since they were eroded from the main tailings storage facility.

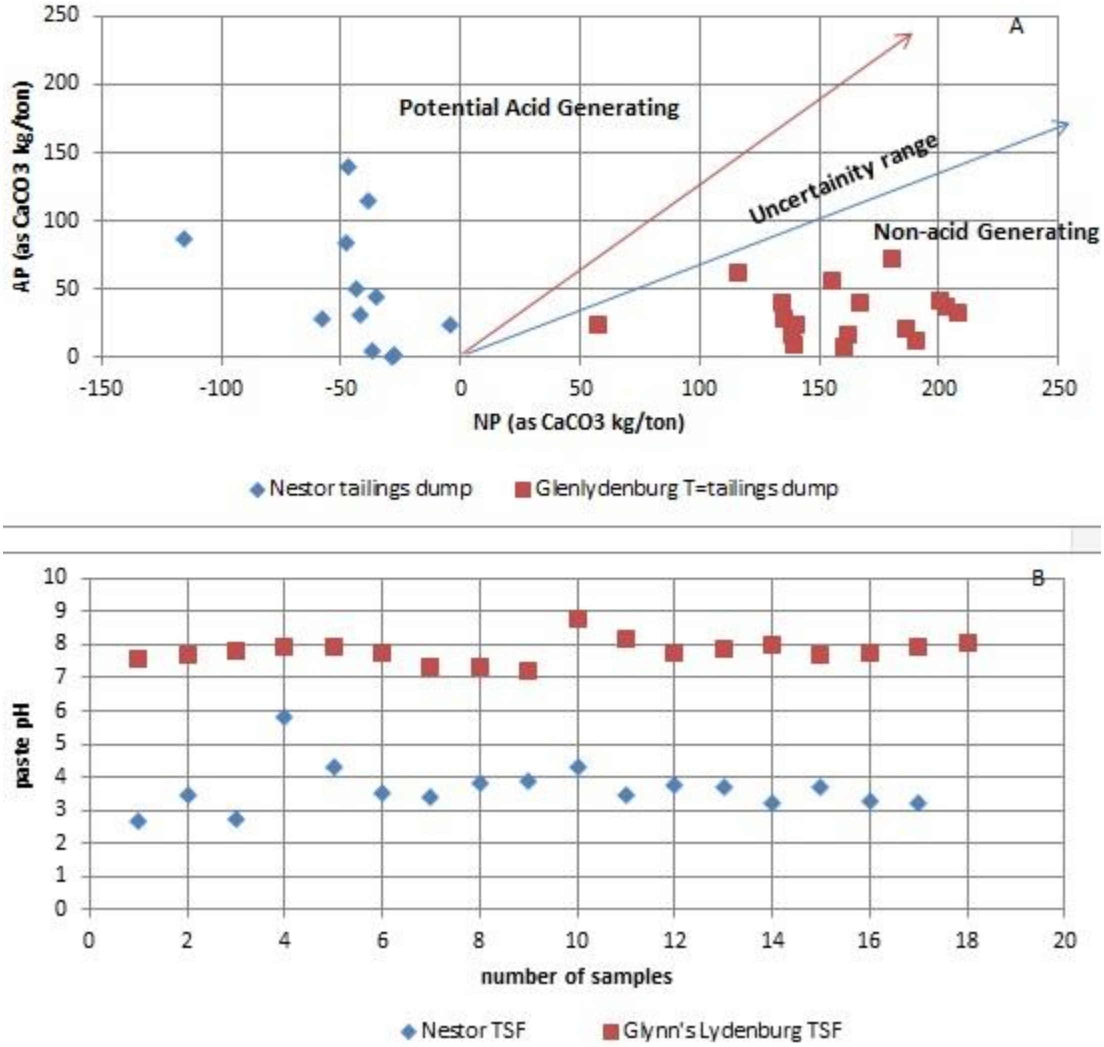

Figure 15 Classification based on (A) acid potential (AP), neutralization potential (NP) and (B) paste pH

Samples of Nestor Mine gold tailings are characterized of high EC (1599 mS/cm) with a very low paste pH range of 3.22 to 4.3 and this can be attributed to the fact that mineralization in this mine took place within the Black Reef Formation. Those samples taken from Malmani Dolomite mineralization in Glynn's Lydenberg Mine are having high paste pH (ranging between 7.21 and 8.17) and very high paste electrical conductivity up to 1911 mS/cm.

The results of AP/NP (NPR) are also confirmed by paste pH of the samples (Fig. 15). Nestor TSF samples are characterised by low paste pH (2.7 to 5), which is indicative of sulphides or sulfates that have reacted to form acid. On the other hand, Glynn's

Lydenburg TSF samples are characterized by high paste pH (7 to 8.8), which could be an indicative of high neutralizing minerals.

The neutralization potential ratio was (NPR) calculated on the basis of modified methods of Sobek (Jambor, 2003), where neutralization potential (NP) and acidity potential (AP) were calculated from $C_{inorg}$ and $S_{sulphide}$ expressed as $CaCO_3$/ton of waste material, respectively.

Gold tailings of Nestor Mine are characterized of very low NPR of less than one (NPR<1) with considerable percentage of sulphur and are having greater potential of acid production (Fig. 16; annexure 3). Glynn's Lydenberg Mine tailings are having a higher than four NPR (NPR>4) and most of them fall on the zone wherein no further testing is necessary (Figure 16; annexure 3).

From Annexure 3, it can be deduced that Nestor Mine tailings have high sulphide concentration (in a range of 0.29 and 4.49 wt. %) and negative NPR (ranging between -17.63 and 0), hence are potentially acid producing as they had sulphur per cent exceeding 0.03 wt. % described as acid producing by Soregoli and Lawrence (1998). On the other hand, Glynn's Lydenberg tailings have low sulphur concentration (ranging between 0.29 and 2.30 wt. %) with high NRP values of up to 21.4, hence low AMD generating capacity.

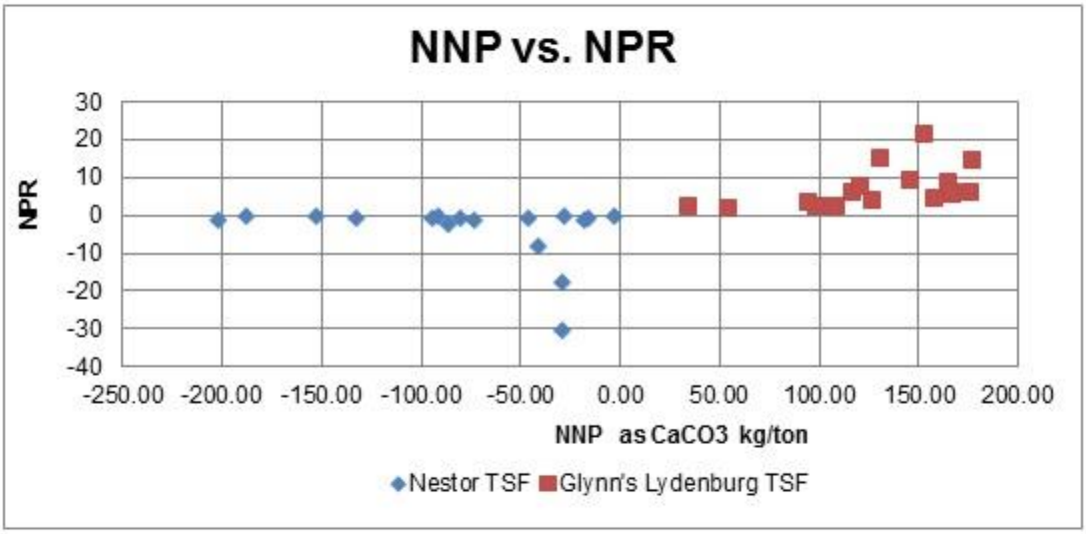

Figure 16 NPR vs net neutralizing potential of Nestor TSF and Glynn's Lydenburg TSF

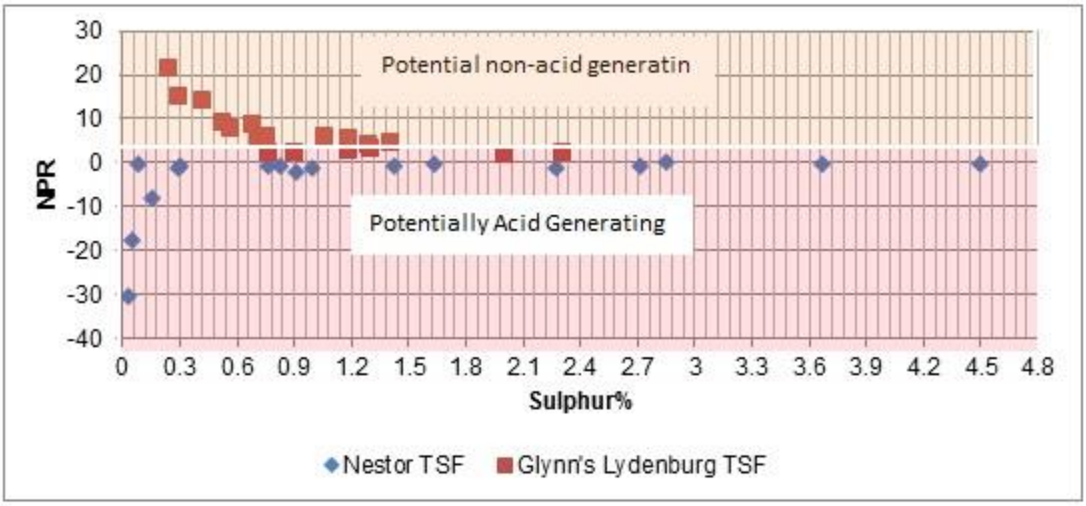

Figure 17 Sulphur percentage vs NPR in Nestor Mine TSF and Glynn's Lydenburg TSF

Nestor Mine tailings are characterized by a very low NPR (<1) (Figures 17 and 18). Based geochemical results, Nestor Mine tailings contains considerable amount of sulphur (in range of 0.29 to 4.49 wt. %; Table 10), consistent the mineralogical data, which indicated the presence of pyrite as primary acid producing mineral and jerosite as a secondary acid producing mineral.

Sulphur percentage in Glynn's Lydenburg Mine tailings is less compared to Nestor Mine tailings (Annexure 3 and Figures 16; 17). Based on ABA results, NPR>2 in Glynn's Lydenburg Mine tailings, hence less likely to generate acid. This is confirmed by paste pH which ranges from 7.58 to 8.8.

Based on geochemical results, samples from Nestor Mine tailings storage facility is characterized by high AP than NP with considerable amount of sulphur, and its net potential ratio is less than 1 (NPR<1) (Annexure 3, Figures 15 & 18). Its AP ranges from 1.56-140.31 kg $CaCO_3$/ton while NP ranges from -57.75 to -0.3 kg $CaCO_3$/ton. However, Glynn's Lydenburg Mine Tailings which is associated with dolomite mineralization do not leach any acidic drainage. Based on ABA results, the tailings have more NP than AP, and their NPR>2, hence less likely to generate acid. Their AP ranges from 7.5 $CaCO_3$/ton to 56.56 $CaCO_3$/ton while NP ranges from 7.5 to 207.88 $CaCO_3$/ton to 190 $CaCO_3$/ton (Figure 18).

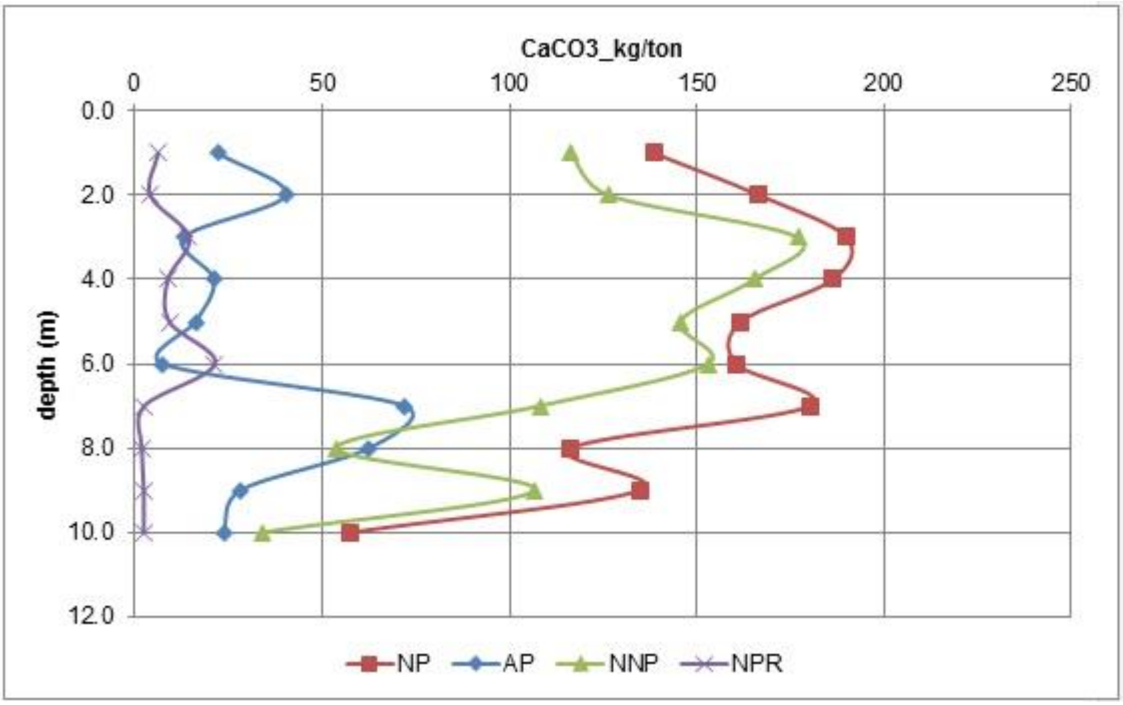

Figure 18 Depth profile for acid production, neutralization potential, net neutralizing potential, neutralizing potential ratio in Glynn's Lydenburg TSF (GL001-010)

All samples from Nestor gold tailings dam showed a potential of acid generation while Glynn's Lydenberg Mine tailings are within acid neutralizing range.

### 4.4 Batch Leaching

Waste rock, spent ore, or tailings materials that are exposed to the environment can potentially contribute to metal or other contaminants to the environment. Even under neutral conditions metals can still be leached from geologic materials, however, it is accelerated by materials that generate acid as a consequence of sulphide oxidation. Single stage batch leaching test was employed to determine the constituents in both Nestor and Glynn's Lydenburg TSFs are potentially mobile under the expected environmental conditions of Sabie.

Aluminium is occurring in high concentrations from Nestor TSF samples. The values range between 0.030 and 17.801 mg/L (Annexure 4) and exceed standards as per WHO, Dutch, South African, and U.S. (Table 11). Low concentrations of aluminium are found at Glynn's Lydenburg TSF samples (0.005).

High concentrations of copper were also recorded in Nestor TSF, ranging between 0.023-12.784 mg/L, exceeding South African, Dutch and U.S. Standards for drinking water (Table 11).

There are no guidelines for iron from WHO, Dutch and U.S. Standards for drinking water (Table 11). However, the concentration of iron in Nestor TSF is exceeding South African guidelines for drinking water as it ranges between 0.001-3.200 mg/L (Annexure 4).

Very low concentrations of manganese were recorded from Nestor TSF samples (0.030-0.510 mg/L) falling within the acceptable range for South African drinking water guidelines. Nevertheless, the Glynn's Lydenburg TSF samples were found to have high concentration of manganese (0.001-1.260 mg/L), exceeding WHO, Dutch and U.S. guidelines for drinking water and some samples also exceeded South African guidelines for drinking water (Table 4; Annexure 4).

Concentration of zinc in Nestor TSF is greater than in Glynn's Lydenburg TSF. The former's concentration ranges between 0.030-0.550 mg/L while the latter's concentrations are at 0.030 mg/L (Annexure 4).

Sulphate in Nestor TSF is occurring at low concentration except for borehole NS01 (31.54-528.800 mg/L; Annexure 4), and boreholes NS02 and NS03 were characterized of low concentration of sulphate, 8.500-83.880 mg/L and 5.420-36.510 mg/L respectively. High concentrations were recorded at Glynn's Lydenburg TSF, borehole GL02 have concentrations ranging between 12.670-633.980 mg/L while borehole GL3 have concentration between 194.260-868.800 mg/L (Annexure 4).

Based on data obtained from batch leaching analyses, the potential contaminants from Nestor TSF are Al, Cu and Fe; while potential contaminants from Glynn's Lydenburg TSF are Mn and SO4 (Annexure 4). The tailings from Nestor TSF are potentially acid generating as confirmed by paste pH (from initial of 5.43 to final off 3.36) with higher electrical conductivity (from 8.93 µS/cm initial to 939 µS/cm). The samples also showed zero (0) alkalinity and are highly acidic (from 7.86 mg/L $CaCO_3$/L to 77.50 mg/L $CaCO_3$/L acidity). However, samples from Glynn's Lydenburg TSF showed low on no potential for acid generation. This is confirmed by paste pH which went from 5.43 to 8.08, highly alkaline from alkalinity test and zero acidity (Annexure 4). The paste EC is very high in Glynn's Lydenburg tailings samples (8.93 initial to the high value of 1166.00 µS/cm).

### 4.5 The quality of seepage water and adjacent Sabie river water

Pollution has become a key cause of degradation in water quality, and therefore, the main constraint to biodiversity. The effects of pollution on aquatic ecosystems have allowed the World Health Organisation (WHO) and many governments such as South Africa, Dutch and United States to define standard values or criteria for the protection of aquatic life. These guidelines are summarised in Table 11.

Table 10 Water quality standards and guidelines

| **Metal species** | **WHO criteria[$1] (µg/l)** | **Dutch criteria[$2] (µg/l)** | **South Africa criteria[$3] (µg/l)** | **U.S. criteria[$9] (µg/l)** |
|---|---|---|---|---|
| Al | 200 | 200 | 100[$4] | 100 |
| Cu | 1000 | 50 | 4.6[$5] | 100 |
| Fe | - | - | 200-1000[$6] | - |
| Mn | 100 | 50 | 1300[$7] | 50 |
| Ni | - | 9 | 25-50[$6] | - |
| Zn | 500 | 200 | 36[$8] | 300 |

$1: from WHO (1987); Musibono (1992); Hespanol and Prost (1994); $2: from Enserik et al. (1991), Musibino (1992); $3: from DWAF (1996b)- Acute Effect value (AEV); $4: acid soluble aluminium concentrations; pH <6 in aquatic ecosystem; $5: dissolved copper concentration for medium water hardness (60-119 mg $CaCO_3$/l) in aquatic ecosystem; $6: from Kempster et al. (1980); $7: dissolved manganese concentration; $8: dissolved zinc concentration; $9: from Department of Environmental Affairs (1980).

Figure 19 shows reddish-orange seepage accumulated on the paddocks of Nestor Mine TFS. Compared to Acute Effect Values summarised for Al, Cu, Fe, Mn, Ni and Zn in Table 11, the water leachate from gold tailings storage facility of Nestor Mine and surface water from the adjacent Sabie River exceed the South African criteria. The Acute Effect Values (AEV) is a criterion used to identify those cases requiring urgent management attention because the aquatic environment is threated, even if the situation persists only for a brief period (DWAF, 1996b).

Figure 19 Seepage from Nestor Mine tailings storage facility

Water chemistry of the seepage samples collected from Nestor Mine paddocks and under flowing water from Sabie River Bridge is presented on Tables 12 and 13.

Table 11 Onsite analysis of Nestor Mine tailings leachate and water from Sabie River

| **Sample ID** | **pH** | **EC (mS/m)** | **TDS (mg/l)** | **DO (mg/l)** | **Salinity** | **Temperature(°C)** |
|---|---|---|---|---|---|---|
| ON 001 | 2.2 | 4.01 | 4 | 6.61 | 2.1 | 27.2 |
| ON 002 | 3.5 | 11.01 | 10.94 | 7.03 | 0.5 | 19.7 |

Table 12 Analytical data for Nestor Mine tailings leachate and water from Sabie River

| **Sample ID** | **Al (mg/l)** | **As (mg/l)** | **Cu (mg/l)** | **Fe (mg/l)** | **Mn (mg/l)** | **Ni (mg/l)** | **Pb (mg/l)** | **Zn (mg/l)** | **Cl (mg/l)** | **SO4 (mg/l)** |
|---|---|---|---|---|---|---|---|---|---|---|
| | **0-0.15*** | **0-0.1*** | **0-1*** | **0-0.1*** | **0-0.05*** | | **0-10*** | **0-3*** | | **0-200*** |
| ON 001 | 65.07 | 9.58 | 2.88 | 1078.64 | 6.61 | 0.87 | 0.02 | 1.61 | 2.7 | 1968.11 |
| ON 002 | 126.35 | 0.02 | 0.1 | 3.65 | 8.66 | 0.34 | 0.007 | 0.78 | 3.4 | 748.5 |

*****Department of Water Affairs Limit for Human Consumption, (DWAF, 1996)

Onsite and laboratory analyses of water parameters, such as pH, Electrical Conductivity (EC), temperature, Dissolved Oxygen (DO), TDS, salinity and elemental concentrations have been conducted to identify pollution sources and water quality status of the adjacent Sabie River and results are displayed on Table 14. Leachates were collected from the paddocks of the Nestor tailings storage facility (ON 001). Water samples were also collected under the bridge of the adjacent Sabie River (ON 002) which located approximately 200 m from the Nestor Mine TSF. The analytical data is compared with the limit for human consumption, as per Department of Water Affairs (DWAF) guideline.

The leachate from Nestor Mine TSF was characterized of very low pH of 2.2 to a pH of 3.5 recorded in water from Sabie River, high electrical conductivity (EC) in range between 4.01 to 11.01 mS/cm respectively (Table 12).

The dominant cation is Ca, but the concentrations of Mg and K are also significant (Fig. 20). Sulphate is the principal anion (Fig. 22), and the Cl concentration is almost negligible with elevated concentrations of metals Fe, Mn, Co, Al, Cu, and Zn exceeding levels for human consumption as per Department of Water Affairs (DWAF) national standards.

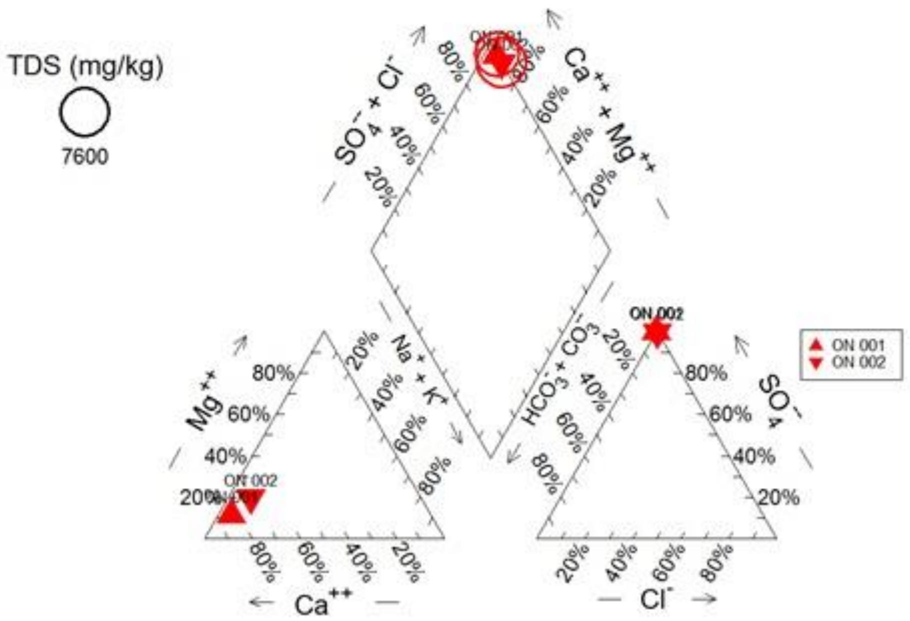

Figure 20 Chemical constituents distribution in Nestor Mine Seepage (ON 001) and Sabie River water (ON002)

High concentrations of manganese are toxic and may lead to disturbances in various metabolic pathways, in particular disturbance of central nervous system caused by inhabitation of the formation of dopamine (Pulles et al., 1996). Manganese concentrations were found to be high from the leachate from Nestor Mine Tailings Dam as well as the adjacent Sabie River ranging up to 6605 and 8663 mg/l respectively.

According to Galvin (1996), the mean Zn concentration in surface water is lower than 10 mg/l. However, in the case of Sabie River, there is a potential of Zn contamination as Zn concentration was at 0.78 mg/l and the leachate from Nestor Mine TSF was also found to be having 1.61 mg/l Zn concentration.

Dallas and Day (1993), indicated that sulphates are not toxic at moderate concentrations and where the rivers a poorly buffered, $SO_4$ levels can increase significantly, causing sharp drops in pH. The concentration of $SO_4$ from Nestor Mine tailings was found to be 1968.1 mg/l with 748.5 being recorded from Klein-Sabie River. This implies that the sediments eroded from Nestor Mine Tailings are adding into sulphates concentration into the adjacent Sabie River.

Al, Fe, Mn, and SO4 concentrations are exceeding standards as per DWAF (1996) and they pose contamination threat to the adjacent Sabie River.

# Chapter 5: Conclusions AND Recommendations

## 5.1 Conclusions

Gold mineralization in the Sabie area occurs within the Malmani Dolomite as well as Black Reef Formation, and this played an important role in the geochemistry of the associated tailings. Bulk geochemical and mineralogical analysed showed a clear variation in chemistry of samples from Nestor and Glynn's Lydenberg Mine tailings storage facilities, and this also conforms to the likely leachate from the samples as determined by static geochemical techniques. These gold tailings storage facilities are characterized by both acid generation and acid neutralizing potential and this can be attributed to variations in the mineralogy of source rocks. The potential for acid generation and neutralization is highly influenced by mineralized host rocks. Exploitation of gold was done from Malmani dolomite mineralized rocks in Glynn's Lydenberg and exploitation from Nestor Mine was from Black Reef quartzite mineralized host rocks. Tailings eroded from Nestor Mine tailings storage facility were also found to be characterized of high content of metals, namely, As, Cu, Ni, Pb, V, and Zn with $SiO_2$, $Fe_2O_3$ and $TiO_2$ oxides also occurring in high concentrations. These tailings were observed eroded into the Klein-Sabie River where AMD precipitate (yellow boy) was also observed, indicating further oxidation downstream. Field observations, onsite analyses of water samples and laboratory results revealed that Nestor Mine tailings are discharging acid with considerable amounts of Al, As, Cu, Fe, Mn, Zn and $SO_4$ and very low pH of 2.2 from leachate from tailings as well as 3.5 pH recorded from the adjacent Klein-Sabie River exceeding the limit as per South African water quality standards. Nestor Mine tailings have NPR<2, hence more likely to generate acid; and their AP range 1.56 to 140.31 $CaCO_3$/ton and NP range from -57.75 to -0.3 $CaCO_3$/ton. It can be concluded from these results that Nestor Mine Tailings are acid producing. Glynn's Lydenburg Mine tailings dump which is associated with dolomite mineralization, however, was not leaching acid. Based on ABA results, these tailings have more NP (ranging between 57.6 and 207.88 $CaCO_3$/ton) than AP (ranging between 7.5 and 72.1 $CaCO_3$/ton); and their NPR>2, hence unlikely to produce acid. This is confirmed by paste pH which ranges between 7.35 and 8.17. Tailings from Glynn's Lydenburg Mine are not acid producing based on these results.

Based on mineralogical studies, plagioclase, mica and kaolinite are potential buffer minerals, whereas jarosite is the potential acid producer. Nestor Mine tailings contain significant concentration of sulphur ranging from 0.29 to 4.59 wt. % mostly as sulphate, namely, gypsum and jarosite, dominantly on oxidized zone and hardpans. Pyrite is also occurring as primary acid producing mineral within throughout the tailings dump indicating advanced oxidation as supported by secondary mineral goethite present at semi-oxidized zones. The presence of gypsum and goethite at semi-oxidized zone (0.5-2 m) indicate advanced oxidation state of the tailings. Dolomite is the major mineral found in Glynn's Lydenburg tailings dump with mica and plagioclase also occurring as primary acid neutralizing mineral assemblage. The absence of dolomite in borehole GL 02/1-4 (Fig. 13B) can be attributed to oxidation that might be taking place within the top oxidized zone (0-2 m); however, the presence of calcite can add into neutralization potential to the acid that might be produced by primary mineral hematite. Gypsum is present in both truck-mounted auger samples and handheld auger samples showing a decrease with depth trend. This might be attributed to limited oxidation at depth as pyrite on top layers (0-1 m) of tailings reacted with both dolomite and calcite at top oxidized part to produce secondary mineral goethite. Thus the presence of heavy metals and their easy dispersal and acid mine drainage is hazard to the environment.

## 5.2 Recommendations

- Static geochemical characterizations can be used as cost-effective tools for risk-assessment at both active and derelict mine sites;
- There is a need to conduct kinetic test to ascertain the rate of reaction, to determine the quality of leachate with time.
- Rehabilitation of Nestor TSF to prevent further weathering and erosion of tailings into the adjacent Sabie River; phytoremediation or covers and seals rehabilitation methods are recommended in this case.
- In addition, there is an urgent need to carry out a proper management and/or rehabilitation plan to minimize environmental impacts/contaminants that could result into contamination of the Sabie River, impacting Kruger National Park and cross border problems.

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## Appendices

## Annexure 1 Analytical results for XRF data for major, minor and trace elements

| Sample | SiO2 | Fe2O3 | Al2O3 | TiO2 | MnO | MgO | CaO | Na2O | K2O | P2O5 | Cr2O3 | As | Cr | Cu | Ni | Pb | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NS001 | 88.49 | 0.82 | 3.21 | 4.96 | 0.013 | 0.13 | 0.04 | 0.005 | 0.97 | 0.029 | 0.008 | 255 | 86 | 34 | 18 | 12 | 52 | 7.1 |
| NS002 | 66.7 | 9.27 | 9.91 | 1.06 | 0.024 | 0.44 | 0.4 | 0.005 | 3.22 | 0.076 | 0.017 | 498 | 129 | 65 | 49 | 26 | 132 | 21 |
| NS003 | 68.22 | 1.08 | 7.67 | 10.18 | 0.048 | 0.36 | 0.30 | 0.005 | 2.40 | 0.129 | 0.016 | 522 | 113 | 163 | 42 | 27 | 108 | 64 |
| NS004 | 76.39 | 0.21 | 3.98 | 8.92 | 0.090 | 1.30 | 2.27 | 0.005 | 1.17 | 0.036 | 0.013 | 397 | 94 | 139 | 41 | 276 | 31 | 115 |
| NS005 | 75.68 | 7.69 | 4.13 | 0.18 | 0.091 | 1.46 | 3.2 | 0.005 | 1.20 | 0.039 | 0.013 | 310 | 96 | 189 | 15 | 172 | 28 | 105 |
| NS01/1 | 77.70 | 7.42 | 7.82 | 0.93 | 0.025 | 0.23 | 0.04 | 0.03 | 2.34 | 0.081 | 0.022 | 530 | 112 | 113 | 37 | 75 | 98 | 22 |
| NS01/2 | 69.38 | 8.85 | 9.77 | 0.73 | 0.032 | 0.28 | 0.57 | 0.03 | 2.73 | 0.120 | 0.027 | 423 | 136 | 120 | 64 | 41 | 94 | 136 |
| NS01/3 | 69.52 | 12.53 | 8.80 | 0.35 | 0.058 | 0.33 | 0.14 | 0.02 | 2.79 | 0.081 | 0.042 | 753 | 273 | 205 | 102 | 38 | 64 | 47 |
| NS01/4 | 65.03 | 15.63 | 8.54 | 0.28 | 0.053 | 0.35 | 0.45 | 0.04 | 2.52 | 0.089 | 0.040 | 1125 | 249 | 290 | 69 | 36 | 56 | 89 |
| NS02/1 | 88.29 | 4.49 | 3.73 | 0.38 | 0.011 | 0.05 | 0.02 | 0.03 | 1.09 | 0.120 | 0.015 | 221 | 92 | 29 | 16 | 28 | 29 | 1.5 |
| NS02/2 | 74.32 | 10.89 | 6.19 | 0.31 | 0.013 | 0.12 | 0.03 | 0.03 | 1.56 | 0.132 | 0.030 | 721 | 188 | 571 | 48 | 80 | 47 | 19 |
| NS02/3 | 78.37 | 10.10 | 4.31 | 0.22 | 0.005 | 0.08 | 0.03 | 0.005 | 1.22 | 0.248 | 0.024 | 1599 | 132 | 132 | 37 | 18 | 36 | 8.8 |
| NS02/4 | 61.77 | 13.44 | 12.50 | 0.68 | 0.031 | 0.03 | 0.02 | 0.05 | 0.51 | 0.096 | 0.078 | 137 | 566 | 220 | 116 | 16 | 255 | 87 |
| NS03/1 | 91.25 | 4.12 | 1.98 | 0.37 | 0.006 | 0.005 | 0.005 | 0.04 | 0.51 | 0.040 | 0.010 | 242 | 43 | 90 | 18 | 18 | 29 | 7 |
| NS03/2 | 73.16 | 10.75 | 8.37 | 0.50 | 0.023 | 0.23 | 0.005 | 0.01 | 2.49 | 0.081 | 0.030 | 761 | 163 | 60 | 38 | 22 | 69 | 14 |
| NS03/3 | 71.40 | 13.48 | 7.44 | 0.39 | 0.037 | 0.20 | 0.02 | 0.04 | 2.21 | 0.107 | 0.032 | 912 | 186 | 73 | 41 | 23 | 58 | 16 |
| NS03/4 | 68.61 | 9.21 | 9.77 | 0.62 | 0.019 | 0.06 | 0.03 | 0.005 | 0.77 | 0.205 | 0.040 | 771 | 273 | 120 | 157 | 18 | 140 | 485 |
| GL001 | 65.89 | 11.39 | 5.46 | 0.21 | 0.132 | 2.74 | 4.28 | 0.005 | 1.70 | 0.061 | 0.019 | 2502 | 134 | 21 | 61 | 55 | 69 | 136 |
| GL002 | 63.59 | 10.62 | 4.60 | 0.17 | 0.110 | 3.75 | 6.28 | 0.005 | 1.41 | 0.058 | 0.016 | 1593 | 117 | 15 | 49 | 44 | 63 | 101 |

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GL003 | 60.63 | 9.93 | 4.65 | 0.18 | 0.150 | 4.67 | 7.10 | 0.005 | 1.46 | 0.060 | 0.017 | 1412 | 128 | 22 | 50 | 43 | 63 | 104 |
| GL004 | 64.03 | 9.04 | 4.34 | 0.17 | 0.172 | 4.28 | 6.23 | 0.005 | 1.35 | 0.056 | 0.015 | 1327 | 124 | 28 | 58 | 29 | 65 | 160 |
| GL005 | 66.37 | 8.48 | 4.58 | 0.18 | 0.218 | 3.80 | 5.46 | 0.005 | 1.40 | 0.059 | 0.016 | 1264 | 118 | 18 | 68 | 26 | 72 | 198 |
| GL006 | 66.21 | 8.91 | 4.31 | 0.17 | 0.161 | 4.07 | 5.86 | 0.005 | 1.26 | 0.057 | 0.015 | 1294 | 110 | 28 | 56 | 26 | 64 | 173 |
| GL007 | 64.16 | 10.99 | 5.33 | 0.26 | 0.266 | 3.69 | 5.18 | 0.005 | 1.33 | 0.069 | 0.019 | 2129 | 151 | 42 | 77 | 26 | 90 | 240 |
| GL008 | 62.07 | 11.70 | 8.05 | 0.55 | 0.379 | 3.08 | 4.17 | 0.005 | 1.33 | 0.082 | 0.023 | 1824 | 179 | 54 | 86 | 19 | 117 | 209 |
| GL009 | 59.03 | 13.09 | 10.64 | 0.92 | 0.409 | 2.62 | 3.49 | 0.005 | 1.26 | 0.096 | 0.024 | 1431 | 168 | 66 | 95 | 18 | 148 | 178 |
| GL010 | 47.95 | 18.59 | 16.19 | 2.02 | 0.487 | 1.71 | 2.18 | 0.005 | 1.12 | 0.144 | 0.027 | 807 | 238 | 104 | 132 | 13 | 235 | 142 |
| GL02/1 | 61.97 | 9.87 | 6.45 | 0.26 | 0.174 | 3.65 | 4.68 | 0.03 | 1.98 | 0.073 | 0.026 | 1045 | 139 | 26 | 75 | 63 | 63 | 243 |
| GL02/2 | 60.72 | 9.70 | 6.53 | 0.23 | 0.089 | 3.50 | 5.99 | 0.10 | 1.87 | 0.065 | 0.025 | 1 390 | 138 | 10 | 57 | 40 | 62 | 122 |
| GL02/3 | 60.42 | 10.29 | 5.89 | 0.20 | 0.106 | 3.60 | 5.63 | 0.03 | 1.67 | 0.065 | 0.025 | 2065 | 138 | 13 | 60 | 50 | 65 | 139 |
| GL02/4 | 64.40 | 9.28 | 5.68 | 0.20 | 0.137 | 4.50 | 6.46 | 0.005 | 1.60 | 0.067 | 0.022 | 1326 | 127 | 15 | 47 | 39 | 66 | 105 |
| GL03/1 | 60.71 | 9.00 | 6.36 | 0.25 | 0.176 | 3.55 | 5.73 | 0.04 | 1.78 | 0.068 | 0.024 | 961 | 130 | 27 | 70 | 54 | 56 | 114 |
| GL03/2 | 62.68 | 10.72 | 5.72 | 0.17 | 0.107 | 3.36 | 5.50 | 0.02 | 1.67 | 0.069 | 0.022 | 1557 | 133 | 13 | 51 | 48 | 65 | 126 |
| GL03/3 | 62.52 | 9.09 | 4.86 | 0.17 | 0.120 | 4.20 | 6.05 | 0.005 | 1.35 | 0.065 | 0.020 | 1303 | 129 | 16 | 45 | 49 | 58 | 90 |
| GL03/4 | 60.52 | 9.75 | 5.07 | 0.17 | 0.175 | 4.71 | 6.76 | 0.005 | 1.25 | 0.070 | 0.021 | 1 250 | 120 | 30 | 50 | 30 | 60 | 124 |

***NS: Nestor Mine tailings***

***GL: Glynn's Lydenburg Mine Tailings***

**Annexure 2 Mineralogical results for XRD analysis**

| Sample | Calcite | Dolomite | Gypsum | Pyrite | Hematite | K-feldspar | Quartz | Mica | Chlorite | Goethite | Gibbsite | Plagioclase | Jarosite |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NS001 | 0.01 | 0.1 | 1 | 1 | 1 | 0.1 | 87 | 6 | 1 | 0.1 | 0.01 | 1 | 1 |
| NS002 | 0.01 | 0.01 | 1 | 2 | 2 | 0.01 | 60 | 15 | 0.01 | 0.01 | 0.01 | 5 | 9 |
| NS003 | 0.01 | 0.01 | 1 | 4 | 4 | 0.01 | 61 | 10 | 1 | 0.01 | 0.01 | 5 | 9 |
| NS004 | 0.01 | 7 | 2 | 6 | 6 | 0.01 | 71 | 9 | 1 | 0.01 | 0.01 | 3 | 1 |
| NS005 | 0.01 | 9 | 5 | 5 | 5 | 0.01 | 72 | 6 | 1 | 0.01 | 0.01 | 2 | 0.01 |
| NS01/1 | 0.01 | 0.01 | 0.01 | 1 | 3 | 1 | 72 | 23 | 0.01 | 3 | 0.01 | 0.01 | 0.01 |
| NS01/2 | 0.01 | 0.01 | 1 | 8 | 3 | 1 | 64 | 22 | 0.01 | 3 | 0.01 | 0.01 | 0.01 |
| NS01/3 | 0.01 | 0.01 | 1 | 6 | 6 | 1 | 57 | 29 | 0.01 | 6 | 0.01 | 0.01 | 0.01 |
| NS01/4 | 0.01 | 0.01 | 2 | 7 | 5 | 0.01 | 66 | 19 | 0.01 | 5 | 0.01 | 0.01 | 0.01 |
| NS02/1 | 0.01 | 0.01 | 0.01 | 0.01 | 2 | 1 | 85 | 12 | 0.01 | 2 | 0.01 | 0.01 | 0.01 |
| NS02/2 | 0.01 | 0.01 | 0.01 | 8 | 2 | 0.01 | 76 | 14 | 0.01 | 2 | 0.01 | 0.01 | 0.01 |
| NS02/3 | 0.01 | 0.01 | 0.01 | 6 | 2 | 0.01 | 82 | 10 | 0.01 | 2 | 0.01 | 0.01 | 0.01 |
| NS02/4 | 0.01 | 0.01 | 0.01 | 4 | 6 | 0.01 | 71 | 6 | 3 | 6 | 10 | 0.01 | 0.01 |
| NS03/1 | 0.01 | 0.01 | 0.01 | 1 | 2 | 0.01 | 93 | 4 | 0.01 | 2 | 0.01 | 0.01 | 0.01 |
| NS03/2 | 0.01 | 0.01 | 0.01 | 5 | 4 | 1 | 67 | 23 | 0.01 | 4 | 0.01 | 0.01 | 0.01 |
| NS03/3 | 0.01 | 0.01 | 0.01 | 3 | 5 | 0.01 | 69 | 23 | 0.01 | 5 | 0.01 | 0.01 | 0.01 |
| NS03/4 | 0.01 | 0.01 | 0.01 | 5 | 5 | 1 | 70 | 20 | 0.01 | 5 | 0.01 | 0.01 | 0.01 |
| GL001 | 0.01 | 20 | 3 | 0.01 | 0.01 | 0.01 | 63 | 9 | 0.01 | 2 | 0.01 | 3 | 0.01 |
| GL002 | 0.01 | 28 | 5 | 0.01 | 0.01 | 0.01 | 52 | 9 | 0.01 | 3 | 0.01 | 3 | 0.01 |
| GL003 | 0.01 | 33 | 3 | 0.01 | 0.01 | 0.01 | 53 | 7 | 0.01 | 2 | 0.01 | 2 | 0.01 |
| GL004 | 0.01 | 24 | 0.01 | 0.01 | 0.01 | 0.01 | 63 | 8 | 0.01 | 2 | 0.01 | 2 | 0.01 |
| GL005 | 0.01 | 28 | 1 | 0.01 | 0.01 | 0.01 | 59 | 8 | 0.01 | 2 | 0.01 | 2 | 0.01 |
| GL006 | 0.01 | 33 | 1 | 0.01 | 0.01 | 0.01 | 56 | 5 | 0.01 | 2 | 0.01 | 2 | 0.01 |
| GL007 | 0.01 | 22 | 1 | 0.01 | 0.01 | 0.01 | 66 | 7 | 0.01 | 2 | 0.01 | 2 | 0.01 |
| GL008 | 0.01 | 21 | 1 | 0.01 | 0.01 | 0.01 | 59 | 8 | 4 | 4 | 0.01 | 2 | 0.01 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GL009 | 0.01 | 19 | 1 | 0.01 | 0.01 | 0.01 | 57 | 8 | 8 | 5 | 0.01 | 2 | 0.01 |
| GL010 | 0.01 | 13 | 2 | 0.01 | 0.01 | 0.01 | 47 | 7 | 18 | 13 | 0.01 | 0.01 | 0.01 |
| GL02/1 | 17 | 0.01 | 0.01 | 0.01 | 2 | 0.01 | 67 | 13 | 0.01 | 2 | 0.01 | 0.01 | 0.01 |
| GL02/2 | 19 | 0.01 | 5 | 0.01 | 2 | 0.01 | 61 | 13 | 0.01 | 2 | 0.01 | 0.01 | 0.01 |
| GL02/3 | 20 | 0.01 | 2 | 3 | 2 | 0.01 | 61 | 12 | 0.01 | 2 | 0.01 | 0.01 | 0.01 |
| GL02/4 | 23 | 0.01 | 1 | 3 | 3 | 0.01 | 61 | 9 | 0.01 | 3 | 0.01 | 0.01 | 0.01 |
| GL03/1 | 0.01 | 4 | 4 | 0.01 | 2 | 0.01 | 75 | 12 | 0.01 | 2 | 0.01 | 0.01 | 0.01 |
| GL03/2 | 0.01 | 22 | 4 | 3 | 3 | 0.01 | 58 | 10 | 0.01 | 3 | 0.01 | 0.01 | 0.01 |
| GL03/3 | 0.01 | 36 | 1 | 1 | 2 | 0.01 | 51 | 8 | 0.01 | 2 | 0.01 | 0.01 | 0.01 |
| GL03/4 | 0.01 | 35 | 1 | 3 | 2 | 0.01 | 53 | 6 | 0.01 | 2 | 0.01 | 0.01 | 0.01 |

**Annexure 3 Acid Base Accounting results**

| Sample | Paste pH | Paste EC | Total S% | NP | AP | NNP | NPR |
|---|---|---|---|---|---|---|---|
| NS001 | 2.7 | 3230 | 0.3 | -6.3 | 9.5 | -15.8 | -0.7 |
| NS002 | 3.45 | 1620 | 0.29 | -9.5 | 9 | -18.5 | -1.1 |
| NS003 | 2.77 | 1279 | 0.83 | -20.3 | 26 | -46.3 | -0.8 |
| NS004 | 5.83 | 4250 | 2.85 | -2.5 | 89.1 | -91.6 | 0 |
| NS005 | 4.3 | 830 | 0.08 | -0.3 | 2.6 | -2.9 | -0.1 |
| NS01/1 | 3.55 | 1599 | 0.15 | -36.88 | 4.67 | -41.55 | -7.88 |
| NS01/2 | 3.42 | 308 | 2.71 | -47.75 | 84.69 | -132.44 | -0.56 |
| NS01/3 | 3.86 | 836 | 1.42 | -35.63 | 44.38 | -80 | -0.81 |
| NS01/4 | 3.87 | 1577 | 2.27 | -115.5 | 86.56 | -202.06 | -1.33 |
| NS02/1 | 4.3 | 117 | 0.03 | -28.38 | 0.93 | -29.31 | -30.42 |
| NS02/2 | 3.48 | 569 | 4.49 | -47.3 | 140.31 | -187.61 | -0.34 |
| NS02/3 | 3.79 | 1370 | 3.67 | -38.38 | 114.69 | -153.07 | -0.33 |
| NS02/4 | 3.72 | 349 | 0.91 | -57.75 | 28.44 | -86.19 | -2.03 |
| NS03/1 | 3.23 | 445 | 0.05 | -27.5 | 1.56 | -29.06 | -17.63 |
| NS03/2 | 3.74 | 103.1 | 1.63 | -4.25 | 23.75 | -28 | -0.18 |
| NS03/3 | 3.29 | 564 | 0.76 | -43.88 | 50.94 | -94.82 | -0.86 |
| NS03/4 | 3.22 | 505 | 0.99 | -42.38 | 30.94 | -73.32 | -1.37 |
| GL001 | 7.58 | 1958 | 0.71 | 138.5 | 22.2 | 116.3 | 6.24 |
| GL002 | 7.7 | 1726 | 1.28 | 166.7 | 40.2 | 126.5 | 4.15 |
| GL003 | 7.82 | 1691 | 0.42 | 190 | 13.1 | 176.9 | 14.5 |
| GL004 | 7.93 | 1579 | 0.67 | 186.3 | 21.1 | 165.2 | 8.83 |
| GL005 | 7.94 | 1489 | 0.52 | 161.8 | 16.3 | 145.5 | 9.23 |
| GL006 | 7.73 | 1795 | 0.24 | 160.5 | 7.5 | 153 | 21.4 |
| GL007 | 7.35 | 1669 | 2.3 | 180.1 | 72.1 | 108 | 2.5 |
| GL008 | 7.34 | 1842 | 1.99 | 116.4 | 62.5 | 53.9 | 1.86 |
| GL009 | 7.21 | 2040 | 0.9 | 134.8 | 28.2 | 106.6 | 2.43 |
| GL010 | 8.8 | 396 | 0.76 | 57.6 | 23.7 | 33.9 | 2.43 |
| GL02/1 | 8.17 | 171.4 | 0.29 | 139.75 | 9.06 | 130.69 | 15.42 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| GL02/2 | 7.76 | 1819 | 0.56 | 138.25 | 17.5 | 120.75 | 7.9 |
| GL02/3 | 7.89 | 1911 | 1.18 | 154.88 | 56.56 | 98.32 | 2.74 |
| GL02/4 | 7.98 | 144.6 | 1.18 | 203.13 | 36.88 | 166.25 | 5.51 |
| GL03/1 | 7.67 | 1637 | 0.75 | 140.25 | 23.44 | 166.81 | 5.98 |
| GL03/2 | 7.74 | 1769 | 1.3 | 134.5 | 40.63 | 93.87 | 3.31 |
| GL03/3 | 7.93 | 1504 | 1.4 | 200.13 | 42.18 | 157.94 | 4.74 |
| GL03/4 | 8.07 | 1267 | 1.06 | 207.88 | 33.13 | 175.75 | 6.27 |

**Annexure 4 Batch Leaching Results**

| **Sample ID** | **pH (Init)** | **EC (Init) µS/cm** | **pH (Fin)** | **EC (Fin) µS/cm** | **Alkalinity mg/L CaCO3** | **Acidity mg/L CaCO3** | **As µg/L** | **Al µg/L** | **Ca µg/L** | **Cu µg/L** | **Fe µg/L** | **Mg µg/L** | **Mn µg/L** | **Zn µg/L** | **SO4 mg/L** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NS01/1 | 5.43 | 8.93 | 3.36 | 261 | 0 | 41.18 | 2 | 463.2811 | 1573.63 | 22.841 | 193.44 | 107.13 | 30.11 | 30 | 31.54 |
| NS01/2 | 5.43 | 8.93 | 4.42 | 939 | 0 | 77.5 | 2 | 17801.31 | 123459.8 | 151.8319 | 2720.16 | 210.76 | 508.90 | 512.39 | 528.80 |
| NS01/3 | 5.43 | 8.93 | 4.42 | 388 | 0 | 56.77 | 18.8501 | 6412.251 | 43588.71 | 761.1656 | 88.12 | 72.64 | 54.9633 | 254.4439 | 107.09 |
| NS01/4 | 5.43 | 8.93 | 4.24 | 822 | 0 | 69.21 | 8.0366 | 7284.43 | 111194.4 | 1908.097 | 340.61 | 180.68 | 156.41 | 547.98 | 405.86 |
| NS02/1 | 5.43 | 8.93 | 3.9 | 63.9 | 0 | 11.15 | 2 | 69.1858 | 532.965 | 10.435 | 1894.47 | 26.43 | 7.5028 | 30 | 8.50 |
| NS02/2 | 5.43 | 8.93 | 4.28 | 164.7 | 0 | 81.22 | 6.79 | 8677.02 | 189.65 | 12784.6 | 1894.47 | 44.11 | 56.04 | 186.65 | 73.68 |
| NS02/3 | 5.43 | 8.93 | 3.99 | 106.8 | 0 | 37.61 | 78.59 | 2822.945 | 86.10 | 853.67 | 1376.74 | 56.98 | 14.04 | 30 | 30.80 |
| NS02/4 | 5.43 | 8.93 | 4.31 | 187.9 | 0 | 95.51 | 2 | 10405.18 | 798.61 | 216.65 | 877.172 | 70.27 | 66.97 | 473.1646 | 83.88 |
| NS03/1 | 5.43 | 8.93 | 4.04 | 46.7 | 0 | 7.864 | 2 | 30.926 | 20 | 7.9659 | 10 | 10 | 16.97 | 30 | 5.42 |
| NS03/2 | 5.43 | 8.93 | 3.51 | 214 | 0 | 50.9 | 2 | 2416.48 | 189.65 | 219.94 | 3201.85 | 49.23 | 20.34 | 106.5888 | 36.51 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NS03/3 | 5.43 | 8.93 | 3.51 | 193.5 | 0 | 27.88 | 2 | 987.90 | 86.10 | 136.48 | 2787.12 | 34.54 | 26.63 | 100.3129 | 31.55 |
| NS03/4 | 5.43 | 8.93 | 3.57 | 192 | 0 | 44.18 | 8.874 | 2002.88 | 284.99 | 419.41 | 10 | 113.23 | 46.04 | 30 | 33.25 |
| GL02/1 | 5.43 | 8.93 | 8.08 | 78.2 | 44.33 | 0 | 2 | 5 | 10714.61 | 8.9682 | 10 | 3948.58 | 1 | 30 | 12.67 |
| GL02/2 | 5.43 | 8.93 | 7.79 | 1166 | 22.88 | 0 | 2 | 5 | 228856.1 | 2 | 10 | 3766.59 | 1 | 30 | 633.98 |
| GL02/3 | 5.43 | 8.93 | 7.73 | 912 | 38.61 | 0 | 2 | 5 | 196546.9 | 2 | 10 | 8641.35 | 1258.08 | 30 | 568.34 |
| GL02/4 | 5.43 | 8.93 | 7.9 | 870 | 33.75 | 0 | 6.821 | 5 | 155963.6 | 2 | 10 | 5014.08 | 1389.82 | 30 | 479.97 |
| GL03/1 | 5.43 | 8.93 | 7.74 | 1230 | 23.16 | 0 | 2 | 5 | 264097.6 | 2 | 10 | 4599.72 | 15.54 | 30 | 813.40 |
| GL03/2 | 5.43 | 8.93 | 7.4 | 1320 | 13.58 | 0 | 2 | 5 | 294050.5 | 2 | 10 | 7851.00 | 374.06 | 30 | 868.80 |
| GL03/3 | 5.43 | 8.93 | 7.57 | 902 | 33.32 | 0 | 2 | 5 | 188623 | 2 | 10 | 7003.50 | 1857.41 | 30 | 530.18 |
| GL03/4 | 5.43 | 8.93 | 7.63 | 518 | 24.02 | 0 | 2 | 5 | 73994.63 | 2 | 10 | 6514.10 | 809.41 | 30 | 194.26 |