



# HYDROGEOCHEMICAL DETERMINATION OF THE SALT LOAD FROM COPPER MINE WASTE IN THE BUSHVELD IGNEOUS COMPLEX

BY

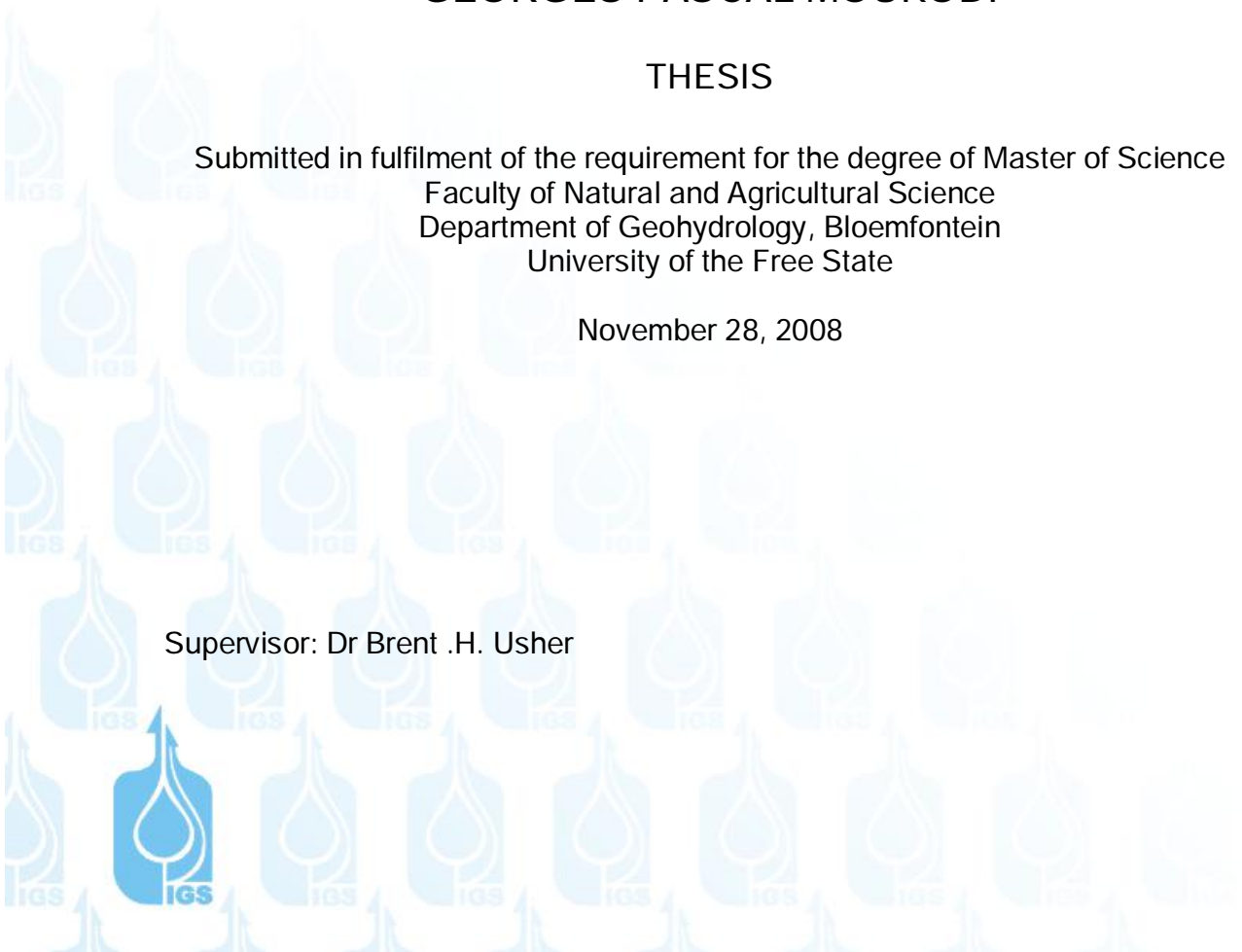
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THESIS

Submitted in fulfilment of the requirement for the degree of Master of Science  
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## Declaration

I, Georges Pascal Moukodi, declare that this dissertation hereby submitted by me for the Magister Scientiae degree in the Faculty of Natural and Agricultural Sciences, Department of Geohydrology at the University of the Free State is my own independent work and has not previously been submitted by me at another university/faculty. I furthermore cede copyright of the dissertation/thesis in favour of the University of the Free State. All sources cited are indicated in References section.

G.P. MOUKODI

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*“The stone that the builders tossed aside is now the most important stone of all. (...).”*

Matthew 21:42

To my beloved late mother,  
I wish you were here to see who I have become on this day, but I  
know you are watching over me from Heaven. You are the Lady and  
inspiration of my life. I live for you. I love you forever.

Tribute to my supervisor  
*"The heart never forgets what the eye has seen".*  
My eyes have seen a Great man: my heart shall never forget you.  
Remain blessed always.

### List of acronyms used for this thesis

DME: Department of Minerals and Energy of South Africa

SAMI: South Africa Minerals Industry

GDP: Gross Domestic Product

IMF: International Monetary Fund

PMC: Palabora Mining Company

Ma: Mega annum (Million years).

WRC: Water Research Commission of South Africa

DWAF: Department of Water Affairs and forestry of South Africa

ICSG: International Copper Study Group

LHD: Load Hauls Dump

NAG: Net Acid Generation

NNP: Net Neutralizing Potential

AP: Acid-generating Potential

TDS: Total Dissolved Solids

pH: Hydrogen Potential

NPR: Neutralizing Potential Ratio

ABA: Acid- Base Accounting

AMD: Acid Mine Drainage

NP: Neutralisation Potential

XRD: X-ray Diffraction

XRF: X-ray Fluorescence

SRK: Steffen, Robertson and Kirsten

RMB: Red Mud Bauxite

CS: Copper Sulphide dam

HT/Hi-Ti: High Titanium content tailings

WR: Waste Rock

LT/Lo-Ti: Low Titanium content tailings

SL: Slag

GPS: Global Positioning System

US EPA: United States Environment Protection Agency

QAMS: Quality Assurance Management Staff

ABACUS: Acid Base Accounting Cumulative Screening Tool

ABATES: Acid-Base Accounting Tools Earth Systems

NAPP: Net Acid Producing Potential

APP: Acid Producing Potential

ANC: Acid Neutralising Capacity

RWD: Return Water Dam

RWT: Return Water Tailings

## LIST OF CONTENTS

1	INTRODUCTION .....	1
1.1	Background information .....	1
1.2	South African mining in context .....	2
1.3	Scope of the investigation.....	4
2	OVERVIEW OF THE MINE.....	6
2.1	Geology.....	7
2.2	Surface hydrology and climate .....	9
2.3	Geohydrology .....	11
2.4	Production/activities .....	12
2.5	Waste deposits.....	14
2.6	In-depth activities .....	16
3	METHODOLOGY.....	18
3.1	Acid-Base accounting (ABA).....	21
3.1.1	Paste and Rinse pH.....	21
3.1.2	Sulphur species and Acid Potentials .....	22
3.1.3	Neutralization Potentials (NP).....	22
3.1.4	Net Neutralizing Potentials (NNP).....	23
3.1.5	Neutralization Potential Ratio (NPR).....	24
3.2	Mineralogy.....	25
3.3	Grain-Size Analysis and Particle-Surface Area .....	26
4	ACID ROCK DRAINAGE / ACID MINE DRAINAGE .....	28
4.1	Stages in the development of Acid Mine Drainage .....	28
4.2	Basic Chemistry of AMD/ARD Generation.....	29
4.3	AMD neutralization .....	30
4.4	Chemistry of the Copper Sulphide Acid/Alkaline Drainage.....	32
a)	Neutralization reaction of Chalcocite ( $\text{Cu}_2\text{S}$ ) .....	34
b)	Neutralization reaction of Covellite ( $\text{CuS}$ ) .....	35
4.5	AMD treatment .....	36
4.6	Considerations, advantages and short-comings of Acid-Base Accounting .....	37
4.6.1	Advantages.....	37
4.6.2	Short-comings.....	37
5	WASTE SAMPLING.....	39
5.1	Test Pits (rock samples).....	42
5.2	Augered holes .....	43
5.3	Representativeness and adequateness of the samples .....	44
5.4	Mine site conceptualization .....	46
6	RESULTS AND DISCUSSION .....	48
6.1	The Acid Base Accounting (ABA) results.....	48
6.1.1	Waste samples .....	48
6.1.1.1	Methodology .....	48
6.1.1.2	Analysis per facility .....	58



6.1.1.3	The Waste Rock dump.....	60
6.1.1.4	The Copper Tailings dump.....	75
6.1.1.5	The Magnetite Tailings (HT, LT) dams.....	89
6.2	X-Ray Diffraction/Fluorescence, investigation of rock samples (summary for all facilities).....	107
6.2.1	Introduction.....	107
6.2.1.1	Method of investigation.....	107
6.3	Groundwater monitoring.....	111
6.3.1	Waste Rock Monitoring 2000-2008.....	116
6.3.2	Monitoring the Copper Sulphide tailings 2000-2008.....	127
6.3.3	The Magnetite tailings, (2000-2008).....	133
6.4	Salinity generated within the mining area, (surface water) .....	135
6.5	Salinity generated within the mining area, (groundwater) .....	139
6.6	Salinity generated beyond the mining area .....	146
6.7	Radioactivity.....	148
7	GEOCHEMICAL MODELLING USING PHREEQC.....	150
8	SALT LOADS ESTIMATIONS.....	156
9	CONCLUSIONS .....	160
	SUMMARY.....	163
	RESUME .....	165
10	REFERENCES.....	167
	APPENDIX.....	176

## LIST OF FIGURES

Figure 1-1: Map of copper ore deposits in South Africa, Lesotho and Swaziland (DME, 2006), (area on interest in blue square) .....	2
Figure 1-2: Graph of employment in South Africa mining industry (DME, 2007).....	3
Figure 2-1: Aerial overview of Palabora Mining Company, (google.com).....	6
Figure 2-2: 3D map of the study area, (values in m.a.m.s.l.).....	7
Figure 2-3: A simplified geology section through the Loolekop pipe, (Wilson and Anhaeusser, 1998).....	8
Figure 2-4: Average rainfall at PMC from 1997 to 2008, (PMC archives, 2008). .....	9
Figure 2-5: Surface channel inside the mine.....	10
Figure 2-6: Catchment map of the Limpopo province, Phalaborwa indicated by the arrow, (Le Roy, 2005). .....	11
Figure 2-7: Map of the PMC and the limits of the waste facilities. (Google Earth™, 2008). .....	15
Figure 2-8: One LHD transporting rocks at PMC. This utility vehicle helps the mine extract 30,000 tons of ore per day, (www.palabora.com). .....	16
Figure 3-1: Sampling on Hi-Ti at PMC using an Auger driller.....	18
Figure 3-2: Surface sampling at PMC; note the white deposits.....	20
Figure 3-3: Plot showing different categories of acid-generation potential based on NPR (Usher <i>et al</i> , 2003). .....	25
Figure 3-4: Procedure for grain size analyses and particle-size distribution.....	27

Figure 4-1: Stages in pH-evolution because of different buffering minerals (after Morin, 1983)....	29
Figure 4-2: Stability diagram of copper, (McNeil and Little, 1992).....	33
Figure 5-1: Sampling positions for different waste facilities, with the limits of the facilities.....	40
Figure 5-2: Groundwater sampling positions for different wastes and the limits of the facilities....	41
Figure 5-3: Rock sampling at PMC in 2007.....	42
Figure 5-4: Tailings sampling with an auger at PMC.....	43
Figure 5-5: Generalized conceptual model of sources, pathways, mitigation and receptors at PMC.....	47
Figure 6-1: Initial pH of the waste facilities.....	49
Figure 6-2: Oxidised pH of the waste facilities.....	49
Figure 6-3: Groundwater monitoring data pH from 2007.....	50
Figure 6-4: AP for the waste facilities.....	51
Figure 6-5: NP diagram of the waste facilities.....	52
Figure 6-6: NNP diagram of the waste facilities.....	52
Figure 6-7: Initial and Oxidized pH vs. Closed NNP.....	55
Figure 6-8: Acid-generating probability of the material, (AMIRA, 2002).....	56
Figure 6-9: AP vs. NP for all waste.....	57
Figure 6-10: AP vs. NP from different types of waste.....	58
Figure 6-11: Waste rock sampling positions.....	60
Figure 6-12: NNP vs. pH in Waste Rock.....	61
Figure 6-13: %S vs. NPR for Waste Rock.....	62
Figure 6-14: AP vs. NP.....	62
Figure 6-15: Variation in waste rock samples obtained in sequential holes.....	63
Figure 6-16: Heavy metals in WR samples (kg/tonne) with respect to pH.....	65
Figure 6-17: Base components in WR soil samples.....	66
Figure 6-18: Other elements from WR.....	67
Figure 6-19: Graph of major elements liberated from WR.....	67
Figure 6-20: General conceptual model of the Waste Rock.....	71
Figure 6-21: Hydrogeological conceptual model of the Waste Rock.....	72
Figure 6-22: Hydrochemical conceptual model of the Waste Rock and its activities.....	73
Figure 6-23: Waste sampling locations on CS.....	75
Figure 6-24: NNP vs. pH for CS.....	76
Figure 6-25: NPR diagram of CS.....	77
Figure 6-26: Acid-generating probability of CS material.....	77
Figure 6-27: Base metals in CS tailings.....	78
Figure 6-28: Heavy metals in CS waste dump.....	79
Figure 6-29: A view of the CS tailings dam.....	80
Figure 6-30: Total amount potentially released per element per kg per ton of waste for CS.....	80
Figure 6-31: General conceptual model of the Copper Tailings.....	86
Figure 6-32: Hydrogeological model of the Copper Tailings.....	87
Figure 6-33: Hydrochemical conceptual model of the Copper Tailings.....	88
Figure 6-34: Sampling points at HT (PMC 2007).....	90
Figure 6-35: AP vs. NP of HT dam.....	91
Figure 6-36: pH vs. NNP diagram for HT.....	92
Figure 6-37: NPR vs. Sulphide diagram for HT.....	92
Figure 6-38: Elements released after oxidation in HT waste samples.....	93
Figure 6-39: Heavy metals in HT (notice Strontium).....	93
Figure 6-40: Oxidized vs. water-liberated elements for HT.....	94
Figure 6-41: Sampling at HT. Notice the colour of the waste.....	96
Figure 6-42: Sampling points on LT.....	98
Figure 6-43: NPR diagram of LT.....	99
Figure 6-44: Final vs. initial pH diagram for LT.....	99
Figure 6-45: NPR diagram of LT.....	100
Figure 6-46: Elements in LT waste after oxidation.....	100
Figure 6-47: Metals in LT waste material.....	101
Figure 6-48: Elements released after further oxidation for LT waste material.....	101

Figure 6-49: General conceptual model of the Magnetite Tailings.....	105
Figure 6-50: Conceptual model for the Magnetite Tailings. ....	106
Figure 6-51: Average sieve analysis results for fine-grained material.....	109
Figure 6-52: Simplified geology of South Africa, (Wilson and Anhaeusser, 1998).....	112
Figure 6-53: TDS in monitored boreholes until the end of the year 2000. ....	113
Figure 6-54: TDS in monitored boreholes for 2001-2008. ....	114
Figure 6-55: % NaCl in TDS in all monitoring boreholes. ....	115
Figure 6-56: Durov diagram for all boreholes, (average values). ....	116
Figure 6-57: Sulphate concentrations of boreholes around WR. ....	117
Figure 6-58: Stiff diagram of WR.....	118
Figure 6-59: Bicarbonate concentration at WR-related boreholes. Note the average value.....	119
Figure 6-60: pH values for WR-related boreholes, (2000-2008). ....	120
Figure 6-61: Stiff diagrams from the borehole near the waste rock dump.....	121
Figure 6-62: Positions of some Boreholes with their corresponding TDS values. ....	122
Figure 6-63: EC vs. SO <sub>4</sub> of the three boreholes.....	123
Figure 6-64: Stiff Diagram of borehole PGSM-B12, PGSM-B16, and PGSM-B21 (average values). .....	124
Figure 6-65: Piper diagram of the three different groundwater. ....	125
Figure 6-66: pH of the selected boreholes. ....	126
Figure 6-67: CS-related boreholes. ....	127
Figure 6-68: Durov Diagram of CS and WR related groundwater (2000-2008). ....	128
Figure 6-69: Stiff Diagram of some CS-related groundwater (2000-2008). ....	129
Figure 6-70: Total alkalinity graph for CS-related boreholes. ....	130
Figure 6-71: Groundwater facies of CS (average values). ....	131
Figure 6-72: Bicarbonate concentration at CS-related boreholes. Note the average value.....	132
Figure 6-73: pH values of CS-related boreholes, (2000-2008). ....	132
Figure 6-74: Sampling boreholes at the magnetite tailings.....	133
Figure 6-75: TDS values for Magnetite tailings-related boreholes. ....	134
Figure 6-76: Durov diagram in HT and LT-related boreholes.....	135
Figure 6-77: Positions of RWD and RWT on the Return Water Dam. ....	137
Figure 6-78: Return water from the Copper Tailings dam: EC is of the range of 7000 µS/cm.....	138
Figure 6-79: Stiff Diagrams of RWT and RWD. ....	138
Figure 6-80: EC, sulphate concentrations and pH of the return water. (Standard values in red lines). ....	139
Figure 6-81: Selected boreholes for sampling. ....	141
Figure 6-82: Durov diagram of PPM-B10 and PPM-B10-N.....	141
Figure 6-83: Durov diagram of PPM-B25 and PPM-B25-N.....	142
Figure 6-84: Average values of samples PPM-B25 and PPM-B-25-N. ....	143
Figure 6-85: Average values of PPM-B29s. ....	143
Figure 6-86: Monitoring of PPM-B29s from 1996 to 2008.....	144
Figure 6-87: Durov diagram of boreholes PPM-B30 and PPM-B30a-N. ....	145
Figure 6-88: Chemical analysis of boreholes PPM-B30 and PPM-B30a-N. ....	146
Figure 6-89: Position of SEL001, at the Selati River. ....	147
Figure 6-90: Analysis of Selati River water. ....	148
Figure 7-1: Calcite and Dolomite saturation with respect to pH.....	150
Figure 7-2: Saturation of gypsum as a function of sulphate concentration. ....	151
Figure 7-3: Saturation Indices of minerals vs. pH (1). ....	152
Figure 7-4: Saturation indices of minerals vs. pH (2). ....	154
Figure 8-1: Expected water quality profile at the Copper Tailings with return water used as input (very high waste: water ratios), (Usher and Moukodi, 2008). ....	157
Figure 8-2: Expected water quality profile at the Copper Tailings with rain water used as input (very high waste: water ratios), (Usher and Moukodi, 2008). ....	158
Figure 8-3: Dissolved ion profile from the waste rock over time (reactive case), (Usher and Moukodi, 2008).....	159

## LIST OF TABLES

Table 2-1: Copper production and usage by country, (ICSG, 2007).....	13
Table 3-1: Summary of the work performed on each waste facility. ....	19
Table 3-2: Net Acid Generating test pH, (Lappako & Lawrence, 1993). ....	22
Table 3-3: Guidelines for screening criteria based on ABA (Price et al, 1997b). ....	24
Table 4-1: Buffering pH of some common minerals as reported in several publications. ....	31
Table 4-2: Sulphide minerals in terms of likely acid generation (Skousen <i>et al.</i> , 1998). ....	35
Table 5-1: Waste samples per waste facilities.....	39
Table 6-1: Areas and volumes of different waste types (PMC, 2007). ....	59
Table 6-2: Summary of acid vs. base potentials in the Waste Rock dump (kg/ton). ....	63
Table 6-3: Water liberated elements from the waste rock (kg/t). ....	64
Table 6-4: Oxidized liberated elements from the waste rock samples (kg/t). ....	64
Table 6-5: Physical parameters of the Waste Rock.....	69
Table 6-6: XRF results obtained from WR samples. ....	70
Table 6-7: Mineral occurrences in WR as obtained by XRD. ....	70
Table 6-8: XRF results obtained from CS waste samples.....	82
Table 6-9: Mineral occurrences in CS obtained by XRD. ....	82
Table 6-10: Overall XRF results of Copper Tailings only. ....	83
Table 6-11: NAPP results using the ABATES software. ....	84
Table 6-12: Physical parameters of the Copper Sulphide dam.....	85
Table 6-13: XRF results obtained from HT waste samples.....	95
Table 6-14: Mineral occurrences in HT , obtained by XRD.....	95
Table 6-15: Physical parameters of the Lo-Ti waste facility.....	97
Table 6-16: XRF results obtained from LT waste samples. ....	103
Table 6-17: Mineral occurrences in LT obtained by XRD.....	103
Table 6-18: Physical parameters of the Lo-Ti waste dump.....	104
Table 6-19: Summary of mineral oxides on the waste facilities.....	107
Table 6-20: Summary of mineralogy on the waste facilities.....	108
Table 6-21: Estimated grain surface areas (m <sup>2</sup> /kg) for major waste types. ....	110
Table 6-22: Tonnages of different waste types on site (PMC, 2007). ....	136
Table 6-24: Aquifer parameters of the new boreholes. ....	140
Table 6-25: Inhalation of Uranium (ATSDR, 1999). ....	149
Table 8-1: Elements released (tons) per facility using the ABA.....	156
Table 8-2: Expected loads from each facility (t/year), (Usher and Moukodi, 2008).....	159

# 1 INTRODUCTION

## 1.1 Background information

South Africa is a country blessed with an abundance of minerals. For more than a century, South Africa's mineral industry - largely supported by gold, diamond, coal and platinum group metals production - has made an important contribution to the national economy. It has provided the impetus for the development of an extensive and efficient physical infrastructure, and has contributed greatly to the establishment of the country's secondary industries (Department of Minerals and Energy (DME), 2006). South Africa is a leading world supplier of a range of minerals and mineral products with consistently high quality. In 2005, about 55 different minerals were produced from 1113 mines and quarries - of these, 45 produced gold, 26 produced platinum-group minerals, 64 produced coal and 202 produced diamonds, all as primary commodities, with an increase of 120 mines from 2004 (SAMI, 2006).

In South Africa, there are few copper mines in comparison with coal, platinum and gold mines. Copper mines are generally located at the extremities of the country, due to the scattered occurrence of copper deposits in South Africa (Figure 1-1). The main copper mines in South Africa are located in the Northern Cape Province, although most of these have closed down. In the Limpopo Province, the Palabora Mining Company operates the biggest South African copper mine so far in terms of output (DME, 2008).



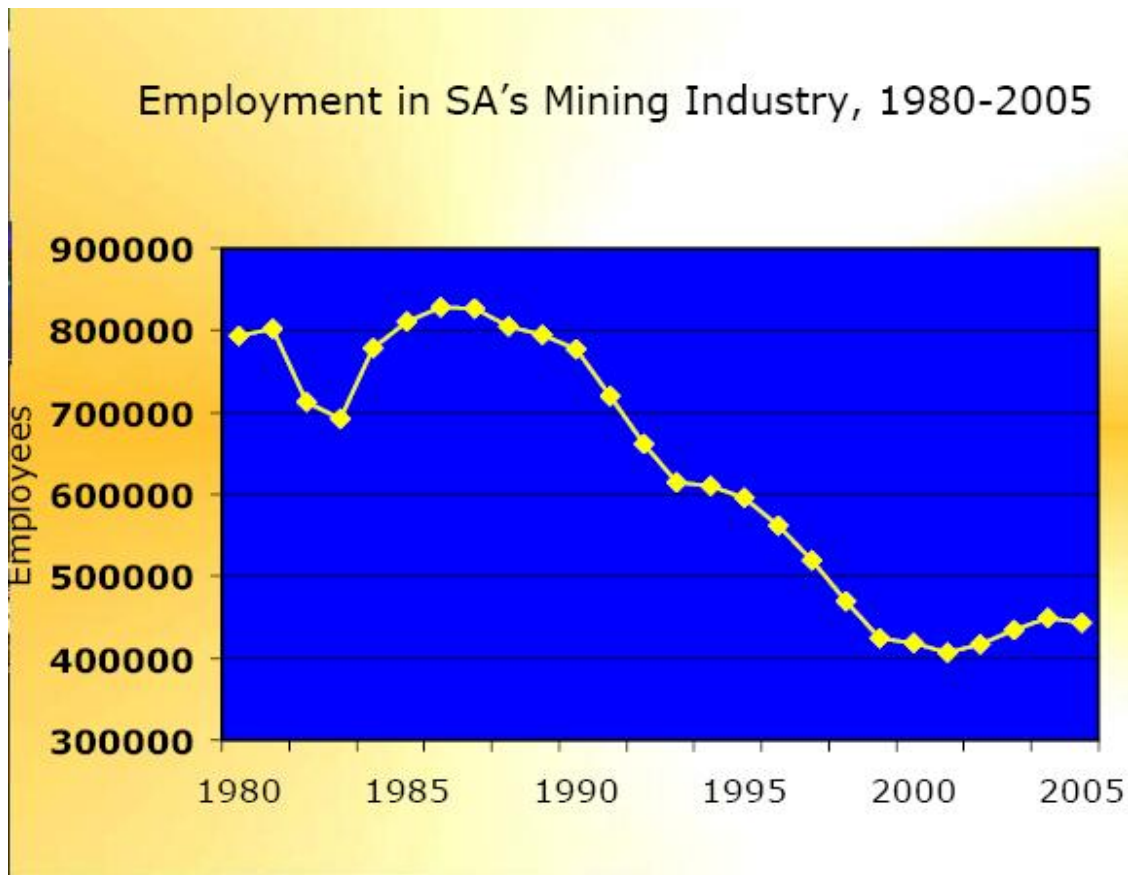


Figure 1-2: Graph of employment in South Africa mining industry (DME, 2007).

Although employment in South African mines has declined over the last two decades, (Figure 1-2) mining alone has still contributed directly to close to 6% of the country's economy by the year 2005 (SAMI, 2006).

However, mining is inevitably associated with environmental problems, as tons of waste of all sorts are dumped on land close to the mining areas on a daily basis. This results not only in land surface disturbance, but also in underground and especially groundwater pollution. Moreover, after mining, these dumps are abandoned on site without any treatment or concern. The long-term effects on the environment range from reversible to irreversible; sometimes depending on the pollutants encountered. Since South Africa is a water-scarce country, a significant impact on the environment has been forecast as long ago as 1983 (Funke, 1983).

### 1.3 Scope of the investigation

Upon mining, the Palabora Mining Company (PMC) faces a huge challenge with millions of tons of waste rock and tailings dams stored on its sites. With the large volume of waste stored on site, the research would provide data that could predict the long term geochemical behaviour of each waste material, so as to optimise the management of the waste repositories, and therefore to predict long term mitigation requirements and environmental impacts. This has always been of great concern for the mine as characterising the waste is used to assist PMC's Integrated Water and Waste Management Plans, (IWWMP).

The following are the specific aims of this investigation:

- Ø To determine the composition of the mineral waste deposits.
- Ø To determine the acid or alkaline producing potential of each of the tailings and waste rock dumps: samples will be analyzed for their acid potential and base potential. The hazard potentials relative to environmental significance will be obtained from this step.
- Ø Mine site conceptualisation of each waste deposit.
- Ø To determine the potential long-term sulphate and metal release from each material type: A combination of mineral saturation indices and annual groundwater chemistries would be interpreted in this step.
- Ø To identify the sources and causes of the high sulphate released and its effect on the environment.

The results from these analyses are interpreted to the best knowledge, assumptions and limitations of the specific prediction techniques. It is important to note that all the experimental techniques and results are validated to actual field conditions as far as possible. It is also important to note that the results from this assessment do not carry a general signification in terms of copper mine waste, as an assessment of the same type on other copper mines might yield different results; and thus this study should be seen more as a broadening of the insights of the copper mining impacts than a comparative perspective. The waste



released from each mine is specific to the ore body mined. A covellite ore body would yield different waste material compared to a chalcopyrite ore body. Though they both are sulphides of copper, the presence of iron in the former and not in the latter plays the determining role in the quality of the waste.

## 2 OVERVIEW OF THE MINE

The Palabora Mining Company (PMC) is located in the north-eastern part of the Limpopo Province in South Africa, 6 km southeast of the town of Phalaborwa, which itself is located 550km northeast of Johannesburg, and adjacent to the Kruger National Park, (Wilson and Anhaeusser, 1998). It operates the country's largest copper mine (DME, 2006). The company was incorporated in South Africa in August 1956. It is South Africa's only producer of refined copper, and is part of the Rio Tinto world groups of mines.



Figure 2-1: Aerial overview of Palabora Mining Company, (google.com)

## 2.1 Geology

The Phalaborwa Complex is unique in that it is the only economically viable carbonatite-hosted copper deposit in the world. The Complex represents the remains of an alkaline volcano that was active 2047 Ma (Wilson and Anhaeusser, 1998). The unique ore body outcropping at a small saddleback hill, later known as Loolekop, contains a unique variety of minerals - copper, phosphates, magnetite, uranium, zirconium, nickel, gold, silver, platinum, and palladium (Figure 2-3). Two other volcanic nearby pipes contain vermiculite and phosphate ([www.palabora.com](http://www.palabora.com)).

The Complex was intruded on several stages. Initially, ultramafic magma welled up from depth along fissures, tearing off segments of the surrounding wall rocks and carrying them upwards. A long non-violent period of metasomatic activity followed, and irregular, near-vertical pegmatoids were placed at three centres in the pipe. Intrusions of foshkorite and carbonatite followed, which host the copper, magnetite, uranium, zirconium, rare earths and precious metals. Much of the copper mineralisation is hosted in late-stage fracture zones. After the formation of these, a swarm of east-west-striking dolerite dykes intruded the Complex (Figure 2-3) (Wilson and Anhaeusser, 1998).

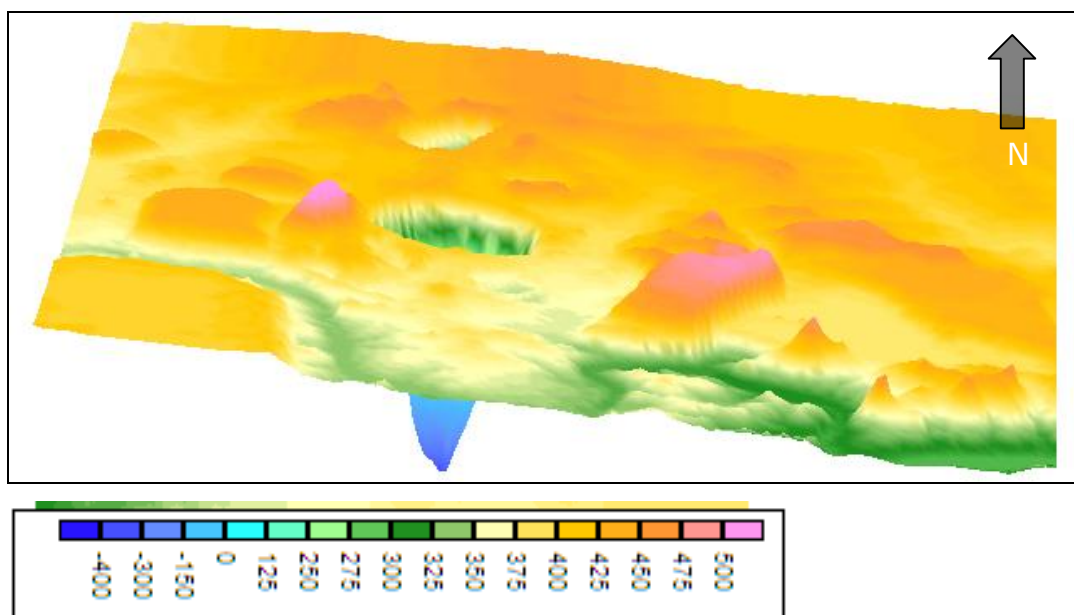


Figure 2-2: 3D map of the study area, (values in m.a.m.s.l.).

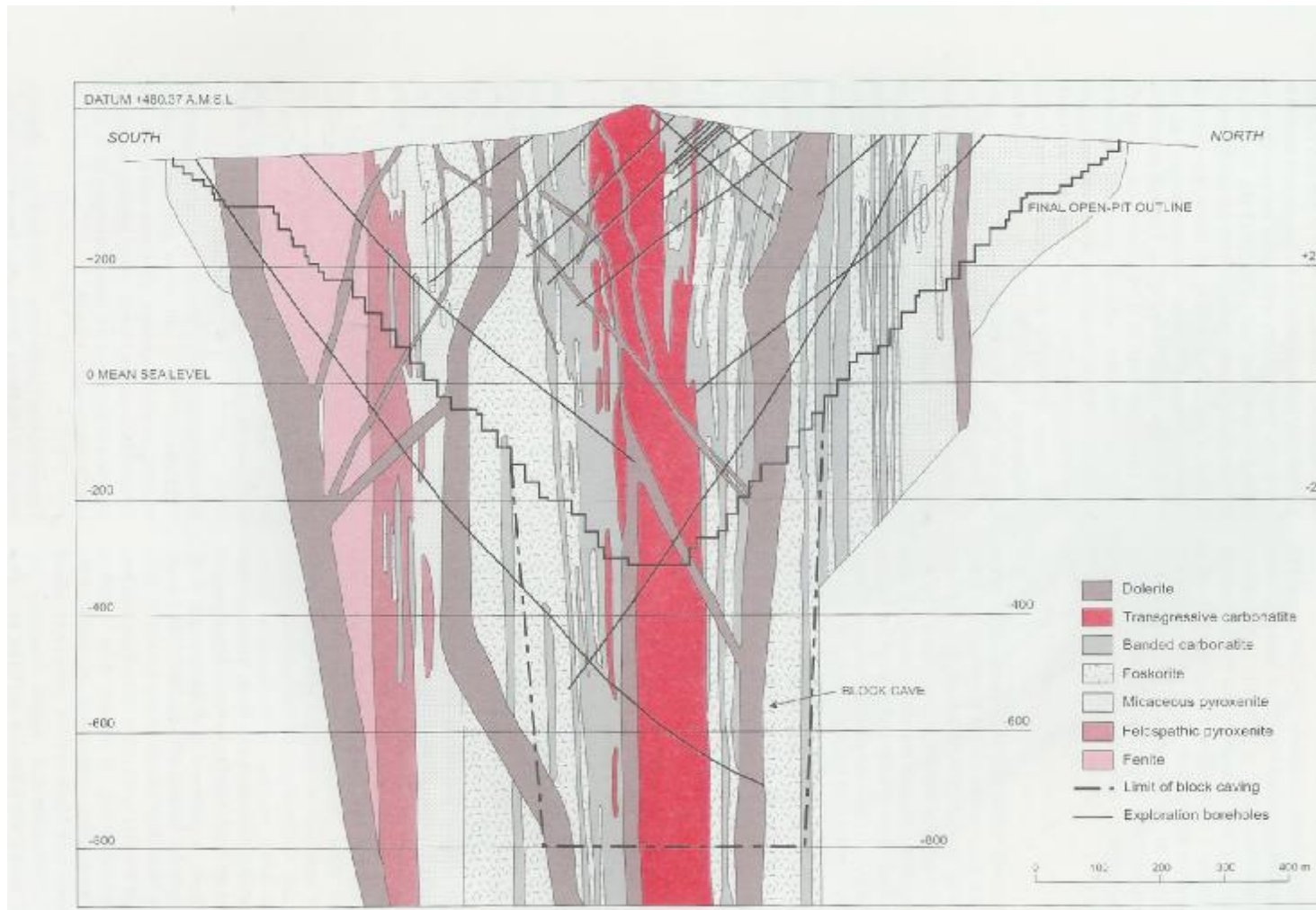


Figure 2-3: A simplified geology section through the Loolekop pipe, (Wilson and Anhaeusser, 1998).

## 2.2 Surface hydrology and climate

The Palabora Mining Company lies in the Region 19 Lowveld, ranges between the Great Escarpment in the west and the Lebombo Range in the east. The climate is warm to hot, and the biome is savannah. The greater part of the Lowveld lies at an elevation between 300 and 600 mamsl., and receives between 500 to 600 mm of rain during the summer (Figure 2-4) (Vegter, 2003). Average daily maximum temperatures are of the order of 30°C in January and around 25°C in July (Schulze, 1994).

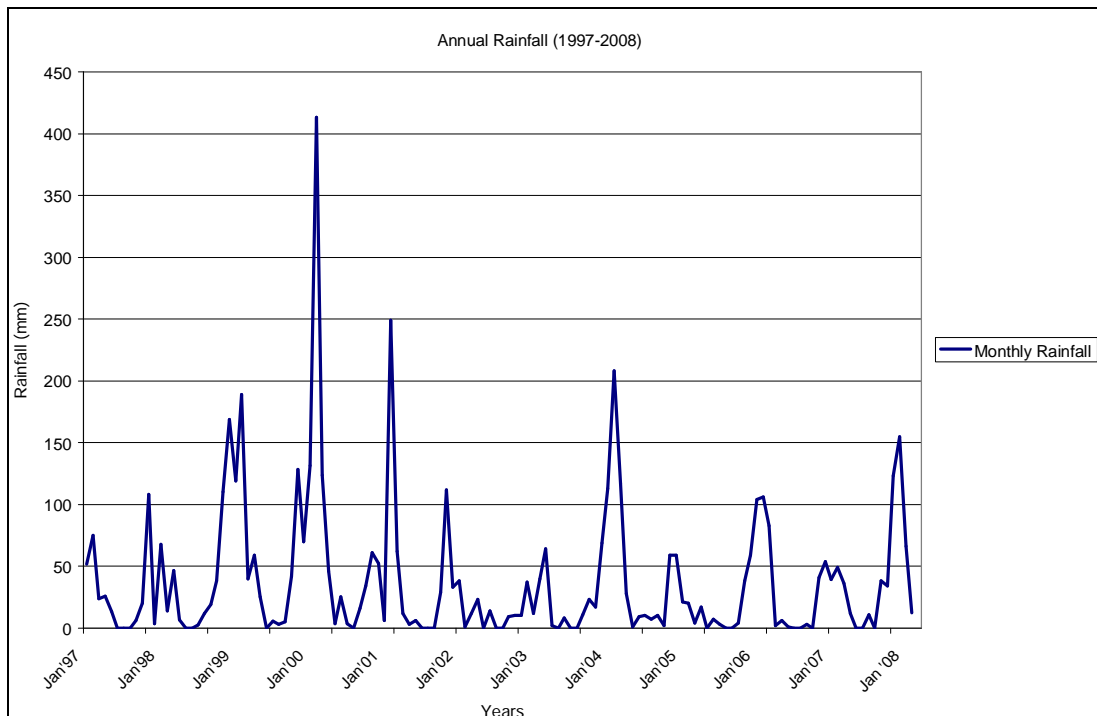


Figure 2-4: Average rainfall at PMC from 1997 to 2008, (PMC archives, 2008).

Surface run-off is mainly by means of the Lower Olifants River and its tributaries, the Klaserie, Selati, and Lower Blyde River (Vegter, 2003), although small streams are formed within the mine (Figure 2-5). The area of investigation is generally sloping south-southeast. Water drainage is to the south-southeast into the Olifants River. This is very important in the understanding of the flow path of

the leachate as all the waste facilities are found upstream the Selati and oliphants Rivers, (Figure 2-7 and Figure 5-1). It is equally important to have a knowledge of the rainfall as it (the rainfall) is the main source of water ingress in most of the waste facilities. A good estimation of the recharge from the rainfall is invaluable in the modelling of the leachate to the groundwater.



Figure 2-5: Surface channel inside the mine.



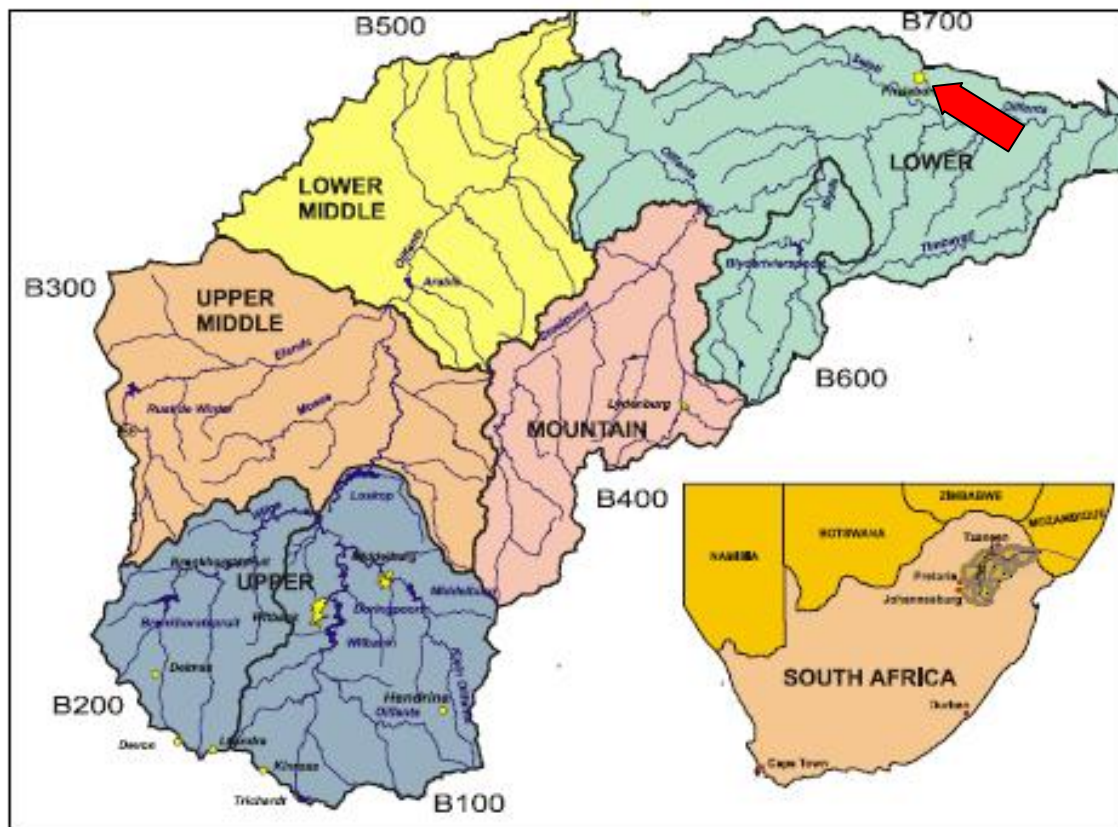


Figure 2-6: Catchment map of the Limpopo province, Phalaborwa indicated by the arrow, (Le Roy, 2005).

## 2.3 Geohydrology

The current body of knowledge about groundwater in the region is mostly contained in the following sources :

- A set of national groundwater maps (WRC, 1995) and
- Information and data at the Department of Water Affairs and Forestry (Vegter, 2003).

Groundwater is the sole water source for more than a quarter of a million people in this region; in the Kruger National Park, human consumption and game watering are provided partly from groundwater (Vegter, 2003). Groundwater in the area generally occurs in weathered or fractured granite, gneiss, pegmatite and dolerite (De Villiers, 1967). Weathering seldom extends deeper than 36

metres, ((boreholes logs from Jasper Muller Associates, 1995), section 6.3). Rocks are less weathered on higher ground and in the foothills of the escarpment than in the valleys. Ninety-nine per cent of boreholes State-drilled in the region in 2003 yielded water from depths of less than 45 metres (Vegter, 2003). The abundance of springs along the escarpment in the west (De Villiers, 1967; Kok, 1976; Kent and Groeneveld, 1964 and Visser and Verwoerd, 1960) indicates that groundwater is recharged and produces base flow. During droughts, which may last for seasons, weakening and drying up of boreholes may be expected in the higher-lying areas of shallow weathering and fracturing. According to the saturated interstice map (WRC, 1995), groundwater is principally stored in fractured rocks. The volume is therefore limited, except for localised areas of deep weathering and where water-bearing alluvial deposits are present. The groundwater yield potential is classified as sufficient on the basis that the boreholes on record produce between 0.5 and 2 l/s (Aqua Earth Consulting, 2008).

## 2.4 Production/activities

Palabora Mining Company Limited extracts and beneficiates copper and vermiculite from its mines in the Limpopo Province. It is South Africa's only producer of refined copper. The mining of the company's copper ore-body commenced in 1956. During the 1960s, 1970s and 1980s, the company's open-pit copper mine and associated processing plants produced over 2.7 million tones of copper. During the early 1990s, the company embarked on a series of feasibility studies on underground mining. In 1996, it announced that it would proceed with the development of an underground block caving mine with a production rate of 30 000 tons per day. This was achieved for the first time in May 2005, giving Palabora's block cave one of the fastest ramp-ups to full production in the world, ([www.palabora.com](http://www.palabora.com)). The primary product of the company is copper, together with by-products, which include magnetite, nickel sulphate, anode

slimes, sulphuric acid and vermiculite. The Industrial Minerals division produces and markets vermiculite.

Table 2-1: Copper production and usage by country, (ICSG, 2007).

Copper Production and Usage for selected Countries, 2006			
Thousand metric tonnes			
Source: ICSG			
	Mine	Refined	Refined
	Production	Production	Usage
Argentina	160	16	30
Australia	859	429	143
Brazil	143	220	339
Bulgaria	99	66	46
Canada	607	500	301
Chile	5,361	2,811	111
China	844	3,047	3,674
Colombia	2	10	10
India	29	647	440
Indonesia	816	218	220
Iran	217	201	130
Japan	0	1,532	1,282
Kazakhstan	434	428	71
Korea, North	12	15	15
Korea, South	0	575	812
Laos	61	61	
Mexico	338	318	302
Peru	1,049	508	53
Philippines	18	181	50
Poland	497	556	267
Romania	15	28	28
Russian Fed.	675	943	678
South Africa	90	100	90
Spain	7	256	319
Sweden	87	229	184
Turkey	46	106	320
United States	1,220	1,250	2,130
Uzbekistan	80	115	45
Zambia	509	461	27
Zimbabwe	3	7	10

The copper operations comprise an underground mine, a concentrator, a copper smelter with anode casting facilities, and an associated acid plant, an electrolytic refinery tank house, a casting plant, and by-product recovery plants.



The vermiculite operation comprises an open-pit mining operation and recovery plant.

## 2.5 Waste deposits

On site, nine waste disposal facilities are present, together with the giant hole known as the "copper pit". These include:

- Ø The Main copper tailings dam (CS);
- Ø The High Titanium content (Hi-Ti) magnetite dam (HT);
- Ø The Low-Titanium content magnetite (Lo-Ti) dam (LT);
- Ø The Magnetite infill dam
- Ø The Waste Rock Dump (WR);
- Ø The Spills pond;
- Ø The Vermiculite waste rock dumps (VR);
- Ø The Slag dumps (SL);
- Ø The Vermiculite Tailings (VT);

Since the mine started operating in the 1950's, it is estimated that all the waste facilities, excluding the Waste Rock dump, represent a volume of  $3.12 \times 10^8 \text{ m}^3$  (PMC, 2007), with the Main Copper Tailings alone estimated at  $2.17 \times 10^8 \text{ m}^3$  or 70% of the total volume.

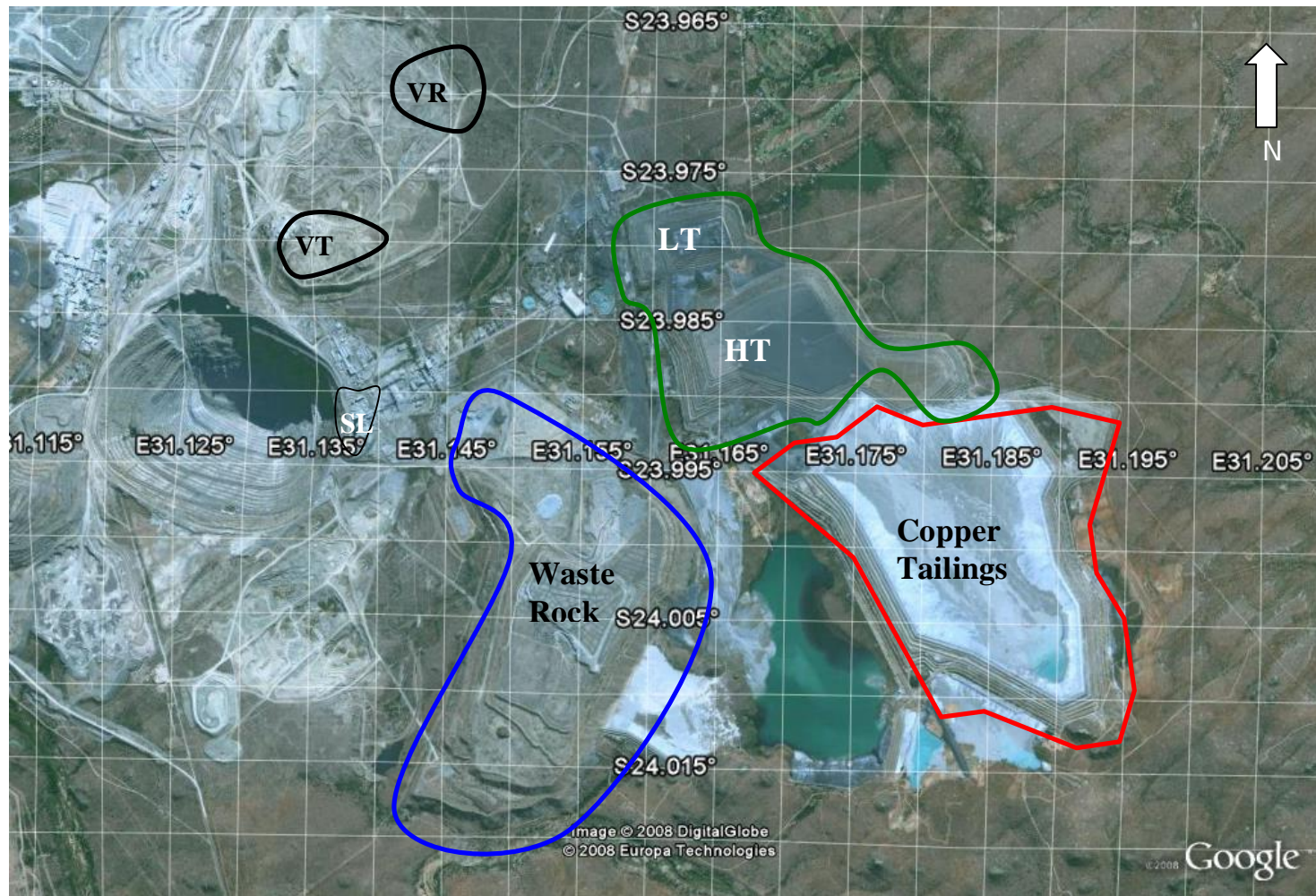


Figure 2-7: Map of the PMC and the limits of the waste facilities. (Google Earth™, 2008).

## 2.6 In-depth activities

The production footprint is geographically small, measuring 650m long by 200m wide. It consists of 20 production crosscuts and 320 draw points, through which the mine breaks and loads 30,000 tons of ore per day (Figure 2-8). Ore is reduced to less than 220mm, and fed onto a high-capacity conveyor system up to the shaft complex for hoisting to surface.



Figure 2-8: One LHD transporting rocks at PMC. This utility vehicle helps the mine extract 30,000 tons of ore per day, ([www.palabora.com](http://www.palabora.com)).

A shaft sinker was contracted to install the main service shaft and a 1,280m deep production shaft, while RUC Mining Contracting has been carrying out the underground development. This includes driving around 36km of tunnels and the underground crusher stations, ore handling infrastructure and the undercut level for the first block cave, situated 500m below the final pit bottom. The crushing stations are fitted with four ThyssenKrupp 900t/h double-toggle jaw crushers that feed a 1.32km conveyor linking to the production shaft. Primary crushers are

used for the initial phase after the ore is conveyed to stockpiles. These stockpiles feed two separate circuits. The conventional circuit takes the coarse ore through secondary and tertiary crushing.

Fine ore is fed into a circuit of rod and ball mills. Water is added during milling. An autogenously milling circuit is used to process coarse ore. Ore from both circuits is pumped into flotation cells, which produce concentrate containing about 36% copper (Infomine, 2007). The waste material is thus conveyed onto specific deposits or tailings dams.

### 3 METHODOLOGY

Between 1993 and 2003, several hydrogeological and hydrochemical programmes were conducted at the Palabora Mining Company (PMC) to monitor the quality of the water on both the surface and groundwater level. Furthermore, the mine monitors the quality of the groundwater on a quarterly basis.



Figure 3-1: Sampling on Hi-Ti at PMC using an Auger driller.

For this dissertation, the main area of interest lies in the possibility of drainage from the waste facilities, and the impacts on receptors, (i.e. human, animal, bio-vegetation). To achieve this, an assessment of the solid waste samples was performed, as well as an in-depth analysis of the groundwater samples. This later step involves interpreting the annual monitoring results of the borehole waters, reason out the causes of high concentrations and the water quality drivers, as well as the mineral saturation in the groundwater.



In terms of solid samples, the following Table 3-1 outlines the work on each of the waste types :

Table 3-1: Summary of the work performed on each waste facility.

Waste facilities	Scope of work performed
Main copper Tailings Waste Rock Magnetite Tailings (Hi-Ti and Lo-Ti)	<ul style="list-style-type: none"> <li>- Quantitative estimation of the waste material present.</li> <li>- estimation of water/oxidised elements released using Acid Base Accounting (ABA) techniques.</li> <li>- qualitative estimation of the waste material.</li> <li>- particle size distribution and mineralogy studies of the waste material.</li> <li>- sites' interactions with the groundwater.</li> </ul>
Vermiculite Tailings Slag dump Vermiculite waste rock dump	<ul style="list-style-type: none"> <li>- estimation of water/oxidised elements released using Acid Base Accounting (ABA) techniques.</li> <li>- Quantitative estimation of the waste material present.</li> </ul>

Waste samples were collected using an Auger driller (Figure 3-1) for samples at deep as four (4) meters, a spade and a hand auger for surface soils were white (presumably salts) deposits where noticed, (Figure 3-2). These samples were

then bagged in appropriate plastic bags, and were first tested for radioactivity before being taken to the University of the Free State for further analysis.



Figure 3-2: Surface sampling at PMC; note the white deposits.

The groundwater samples were analysed and interpreted based on the monitoring results obtained from the mine, and those data were collated.

The laboratory methods used in the analysis of the samples include:

- Acid-Base Accounting
- Mineralogy determination
- Particle-size distribution

### 3.1 Acid-Base accounting (ABA)

This is a first-order classification procedure, whereby the acid-neutralising potential, and acid-generating potential of rock samples are determined, and the difference (net neutralising potential) calculated (Usher *et al.*, 2003). The net neutralising potential and/or the ratio of neutralising potential to acid-generating potential, is compared with a predetermined set of values in order to divide samples into categories that either require or do not require further potential acid generation test work. ABA indicates only the overall balance of acidification potential (AP) and neutralisation potential (NP) (Schafer Laboratory, 1997). It does not in any case provide information on the speed with which acid generation or neutralisation will proceed. These methods are known as Static Methods (Mills, 1998; Ziemkiewicz and Meek, 1994). ABA only limits itself to predicting the outcome of acidic, near-neutral or alkaline drainage primarily based on the mineral balance (Morin and Hutt, 1997).

In order to expand the basic ABA procedures, other sub-methods have been identified. These include:

#### 3.1.1 Paste and Rinse pH

In this method, the pH of a mixture of distilled water and pulverised sample is measured. The result indicates whether the sample was acidic, near-neutral or alkaline at the time of measurement, (Sobek *et al.*, 1978). The initial pH of samples recommended is determined with a ratio of 1 g: 10 g deionised water. After addition of the water, the sample is stirred for 30 minutes and left overnight, (Usher *et al.*, 2003).

If distilled water is used in the measurement of paste or rinse pH, its pH is typically around 5.3, (Morin and Hutt, 1997). Consequently, any pH measurement less than 5.0 indicates the sample contained net acidity at the time of analysis, values between 5.0 and 10.0 can be considered near neutral, while pH values above 10.0 are unusually alkaline, (Morin and Hutt, 1997).



### 3.1.2 Sulphur species and Acid Potentials

ABA identifies the capacity of a sample to generate acidity based on various sulphur analyses. The most common analysis is for total sulphur (Total Sulphur as %S, or as %S total). The resulting value is then converted to a Total Acid Potential by:

$$\text{Total Acid Potential (TAP)} = (\%S \text{ total}) \times 31.25 \dots \text{Equation 3-1}$$

where TAP is provided in any of the three equivalent units: kg CaCO<sub>3</sub> equivalent/metric tonne (t) of sample, t CaCO<sub>3</sub> equivalent/1000 t of sample, or parts per thousands (ppt) CaCO<sub>3</sub> equivalent, (Morin and Hutt, 1997).

To provide a direct measure of the net amount of acid produced by a sample, a procedure known as the net acid generation (NAG) test was also used, developed by Miller *et al.*, 1994 and 1997). 250 ml of 30% H<sub>2</sub>O<sub>2</sub> would be added to about 1.0 g of pulverised sample in what is called a “closed system”. The following guideline, despite being rough was adopted:

Table 3-2: Net Acid Generating test pH, (Lappako & Lawrence, 1993).

Final pH in NAG test	Acid Generating Potential
>5.5	Non-acid generating
3.5 to 5.5	Low risk acid generating
<3.5	High risk acid generating

### 3.1.3 Neutralization Potentials (NP)

This is the capacity of a rock or tailings dam to neutralize acidity. In reality, rocks and tailings have a certain capacity to neutralize acidity under the site-specific environmental conditions, mineralogy, and rates of mineral reactions, (Morin and Hutt, 1997).

In this method, a sample is exposed to an excess hydrochloric acid (HCl), often around pH 1-2, and then heated to near boiling until all visible reactions cease, (Sobek *et al*, 1978).

In a similar experiment, sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), (0.06N) is added to pulverized samples. The pH of the slurry must be below 2.5 after 24 hours, before back titration to a pH of 7 is done with soda (NaOH), (0.06N). If the pH is >2.5, more H<sub>2</sub>SO<sub>4</sub> is added and the sample left for another 24 hours for reactions to complete, (Usher *et al*, 2003). The bulk neutralizing potential obtained from acid titration is often a good indicator of neutralizing capacity above 10 kg/t CaCO<sub>3</sub>, (Morin and Hutt, 2000).

#### 3.1.4 Net Neutralizing Potentials (NNP)

Laboratories and environmental geochemists are often sceptical about the use of this method, because of the uncertainties often involved. The reason for this is that research and experience have shown that there is a range from -20 to 20 kg/t CaCO<sub>3</sub>, where the system or sample can either become acidic or remain neutral, (Usher *et al.*, 2003). However, when used in conjunction with the other criteria, this uncertainty can be resolved (Usher *et al.*, 2003).

Thus, the NNP is given by:

NNP = Neutralising Potential (kg/t CaCO<sub>3</sub>) - Acid-Generating Potential (AP) (kg/t CaCO<sub>3</sub>).

- If  $NNP = NP - AP < 0$ , the sample has the potential to generate acid.
- If  $NNP = NP - AP > 0$ , the sample has the potential to neutralise acid.
- More specifically, any sample with  $NNP < 20$  is potentially acid generating, while those with  $NNP > -10$  might not generate acid (Usher *et al.*, 2003).

### 3.1.5 Neutralization Potential Ratio (NPR)

Below is an additional tool for AMD prediction and estimation.

Table 3-3: Guidelines for screening criteria based on ABA (Price et al, 1997b).

Potential for ARD	Initial NPR screening criteria	Comments
Likely	<1:1	Likely AMD generating
Possibly	1:1 - 2:1	Possibly AMD generating if NP is insufficiently reactive or is depleted at a faster rate than sulphides
Low	2:1 - 4:1	Not potentially AMD generating unless significant preferential exposure of sulphides along fracture planes, or extremely reactive sulphides in combination with insufficiently reactive NP
None	>4:1	No further AMD testing required unless materials are to be used as a source of alkalinity

The criteria above can also be plotted to give a visual indication of the likelihood of acid generation, as shown in Figure 3-3 below:

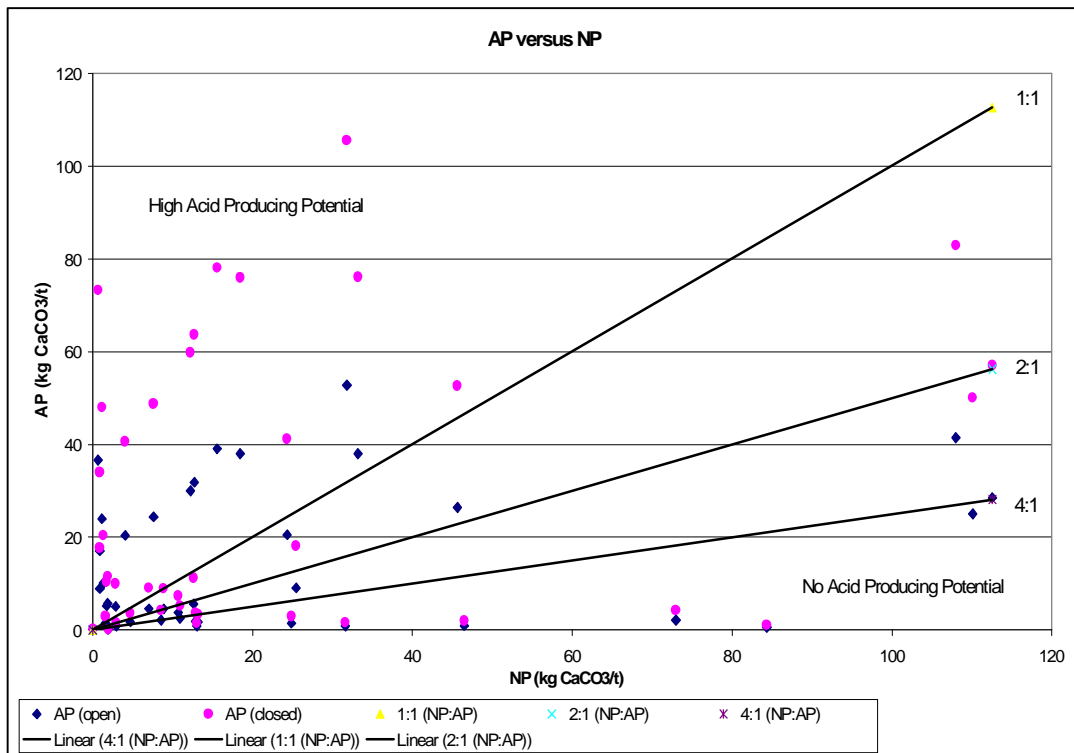


Figure 3-3: Plot showing different categories of acid-generation potential based on NPR (Usher *et al*, 2003).

### 3.2 Mineralogy

Because mine drainage chemistry is created by mineral reactions, the delineation of the mineralogy within a mine site component or rock unit is vital. Mineralogy examinations of samples ideally reveal the types, shapes, sizes, composition, spatial relationship and abundance of minerals; to achieve this, two methods were used:

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials.

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombardment with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of

metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology, among others.

These two methods were used in the analysis of the waste samples. While the first method yielded an estimate of the oxide minerals occurring per 100 g of solid phase sample, the second provided information on the particular minerals, as well as their relative abundance.

### 3.3 Grain-Size Analysis and Particle-Surface Area

This information is as important as the other methods, for several reasons:

- Ø Firstly, various size intervals can react at different rates.
- Ø Secondly, individual grain sizes can be submitted for independent static testing to detect any bias in mineral distribution with size.
- Ø Thirdly, physical parameters such as hydraulic conductivity and moisture retention are related to grain-size distribution.

The results can be used to calculate grain/particle surface areas based on the geometric shapes of the grains.

The surface area can be calculated for a sample with the assumption that the surface area of each particle is proportional to the cubic diameter in case of a sphere, or width in case of a cube (Morin and Hutt, 1997). The sum of this information is used to build a data-based conceptual model on each waste type.

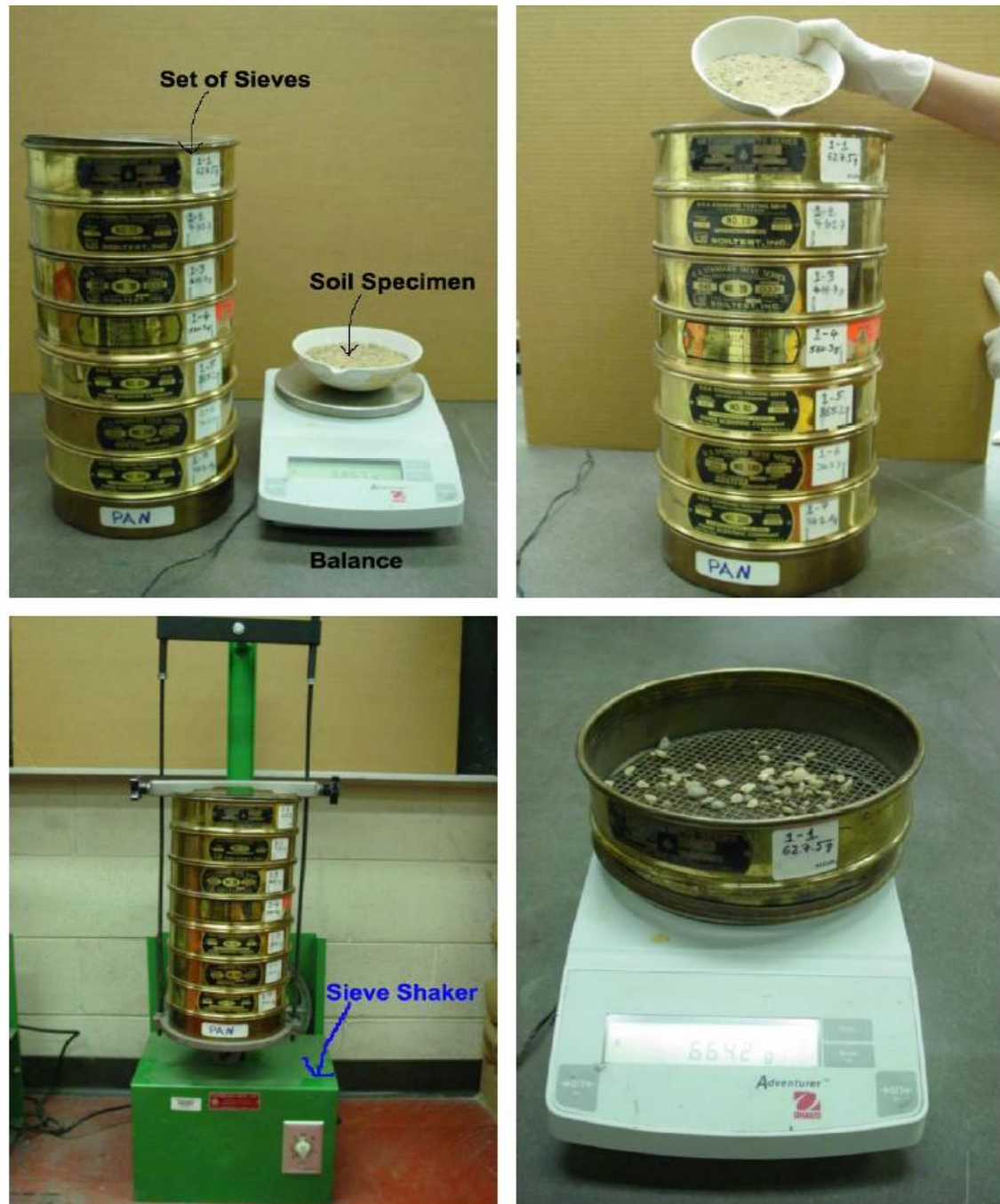


Figure 3-4: Procedure for grain size analyses and particle-size distribution.

## 4 ACID ROCK DRAINAGE / ACID MINE DRAINAGE

Millions of tons of waste stored at the Palabora Mining Company, the spills and leachate when water that comes into contact with these waste material are expected to have an impact on the groundwater and possibly surface water qualities in the entire area. Historically, no testing or no environmental geochemistry has been done to confirm of the impact from spills and leaching from the waste at Palabora Mining Company, (PMC, 2007); therefore, a thorough assessment of the waste is of great importance.

The following section outlines the occurrence and possible treatment methods of acidic mine drainage as it is an environmental concern.

### 4.1 Stages in the development of Acid Mine Drainage

When a rock is disturbed, it undergoes physical and chemical changes in response to its new environment: weathering. Exposure and weathering of unstable forms of base metal-bearing minerals can liberate heavy metals such as lead, zinc, iron, and aluminium, copper. The unstable minerals break apart, dissolve and/or alter to form other minerals in response to the new conditions.

Acid mine drainage (AMD) is produced when sulphur-bearing minerals, such as pyrite, come into contact with oxygen and water during mining. The relative amount of oxygen, water and the sulphides that are allowed to chemically interact dictate the rate and volume of AMD production, in other words, the potential of sulphide rocks to generate acid is strongly related to other types of material, often calcareous, present in the rock (Usher *et al.*, 2003). If the rate of acid generation remains high enough to remove all the neutralisation potential in the rock, low pH would be observed, and conversely, if the rate of acid buffering remains high enough, neutral to alkaline pH would be observed.

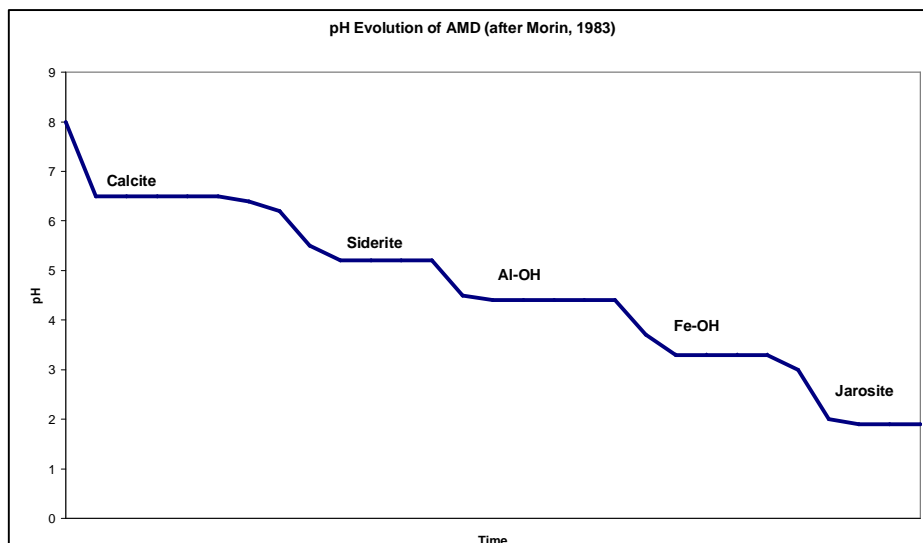
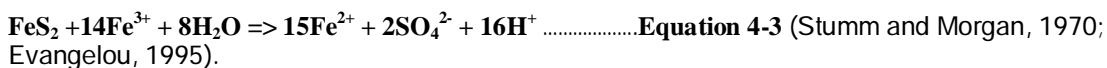
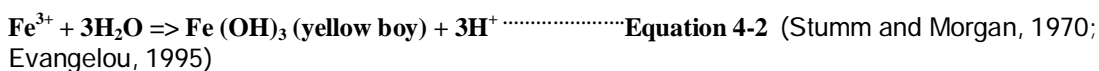
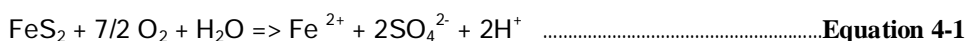


Figure 4-1: Stages in pH-evolution because of different buffering minerals (after Morin, 1983).

## 4.2 Basic Chemistry of AMD/ARD Generation

Acid rock drainage is produced by the exposure of sulphides to atmospheric oxygen and water. Sulphide minerals, predominantly pyrite ( $\text{FeS}_2$ ) undergo bacterially-catalysed, generating acidity and increasing iron ( $\text{Fe}$ ) and sulphate ( $\text{SO}_4^{2-}$ ) in recipient water bodies. The following reactions are a series of pyrite reactions under oxidising conditions to generate acid.

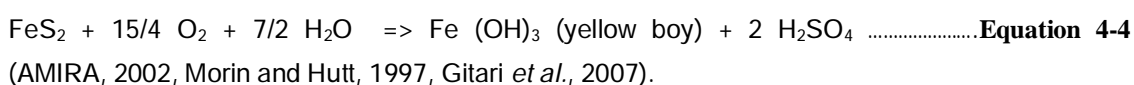


The most common pyrite-oxidising bacterium is *Acidithiobacillus ferrooxidans*, which is of great importance due to the extensive acid and metal pollution generated when this species releases metals from acid mine waters (Singer and Stumm, 1970). *Acidithiobacillus ferrooxidans* is an acidophilic chemolithotropic organism that is omnipresent in the geologic environment, containing pyrite



(Nordstrom, 1982), and it was found to accelerate pyrite oxidation by a factor of  $10^6$  compared to when it is not present (Singer and Stumm, 1970). Once pyrite oxidation and thus acid production have begun, conditions are favourable for bacteria to further acceleration of the rate. At pH values of about 6 and above, bacterial activity is thought to be of lesser importance to biotic reaction rates, (Rios *et al.*, 2007).

Whatever be the case, the bottom line is: Sulphides + water + oxygen (+ bacteria) give acidity + sulphates, and after extensive studies, the following reaction has been adopted as the overall reaction of acid rock drainage by pyrite:



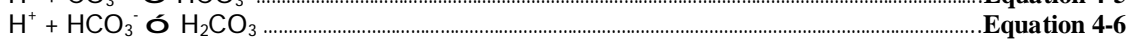
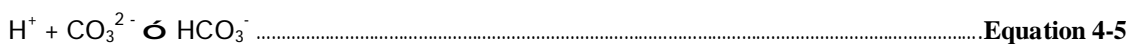
Limiting the supply of any one of those variable will help decrease the severity of ARD. This can be done as a natural process, whereby carbonates within the rocks react with the acidity produced, or artificially, but the latter would be very costly.

### 4.3 AMD neutralization

As stated above, it is possible to counter the effects of acid drainage both naturally within the rock material, or artificially.

In nature, carbonated minerals are the main drivers behind AMD neutralisation, with calcium carbonate ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) the main carbonated minerals responsible for the neutralisation.

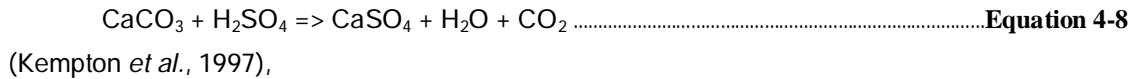
In general, human intervention portrays acid mine drainage as the depletion of the buffering ability of water by neutralising carbonate and bicarbonate ions to form carbonic acid ( $\text{H}_2\text{CO}_3$ ) (Drever, 1997).



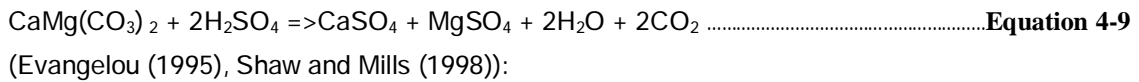
In nature, there are several other factors that could determine the neutralisation of AMD, in addition to carbonate and silicate minerals, these include pH, the partial pressure of carbon dioxide ( $\text{Pco}_2$ ), equilibrium conditions, temperature and the presence of "foreign" (those not deriving from the carbonates) ions.

Comparison of rates shows that sulphides react fastest, followed by carbonates and silicates (Sherlock *et al.*, 1995).

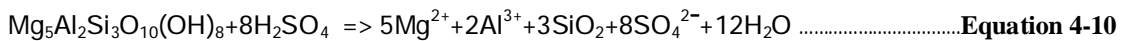
Overall, the neutralisation reaction of sulphuric acid by calcium carbonate is presented as:



while that of dolomite is presented as:



Although slower to react, aluminosilicates such as chlorite can also contribute to the acid neutralisation capacity (ANC) of the sample (Paktunc, 1999b), as



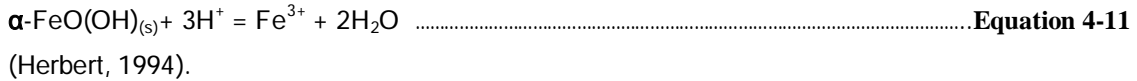
The following table has appeared in several publications regarding AMD (SRK (1991), Hodgson and Krantz (1998), and van Niekerk (1997)):

Table 4-1: Buffering pH of some common minerals as reported in several publications.

Mineral	Composition	Buffer pH
Calcite	$\text{CaCO}_3$	5.5-6.9
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	5.3-6.8
Siderite	$\text{FeCO}_3$	5.1-6.0
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	3.7-4.3
Gibbsite	$\text{Al}(\text{OH})_3$	3.7-4.3
Ferric hydroxide	$\text{Fe}(\text{OH})_3$	3.3-3.7
Goethite	$\alpha\text{-FeO}(\text{OH})$	2.1-2.2

This Table 4-1 is somewhat misleading, as it suggests that minerals such as kaolinite and siderite are effective buffers in the overall process, (Usher *et al.*, 2003), which is not the case. They participate in the buffering without playing the major role because of their slow to intermediate reaction rates. However, the

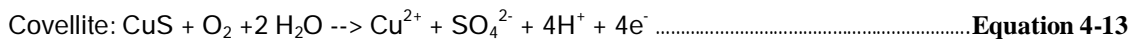
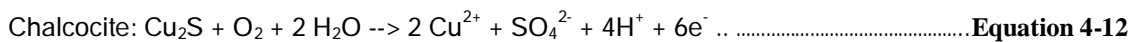
equilibrium precipitation/dissolution of Fe oxides, such as goethite can effectively buffer pH according to the following reaction:



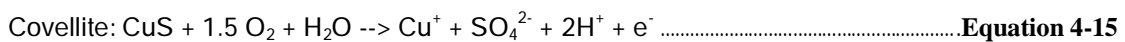
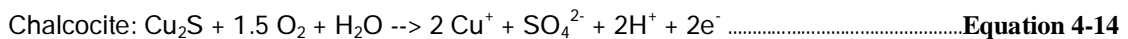
#### 4.4 Chemistry of the Copper Sulphide Acid/Alkaline Drainage

This section highlights the chemical reactions, the potential hazards and neutralisation of the copper sulphide processed.

The Palabora Mining Company (PMC) extracts mostly copper, with the major ore mineral being copper sulphide,  $\text{Cu}_2\text{S}$  (Chalcocite) and  $\text{CuS}$  (Covellite). When sulphide minerals are exposed to air and water, they oxidise. The sulphide is normally oxidised to sulphate. Sulphides themselves do not produce acids, but they do liberate soluble metals and sulphate. Examples are:



Depending on the conditions (oxidation or reduction), the moles of acidity can vary.



Under oxidising conditions, ( $E_h$  is positive) and the environment is in contact with the atmosphere, copper stabilises as copper (II), (Figure 4-2).

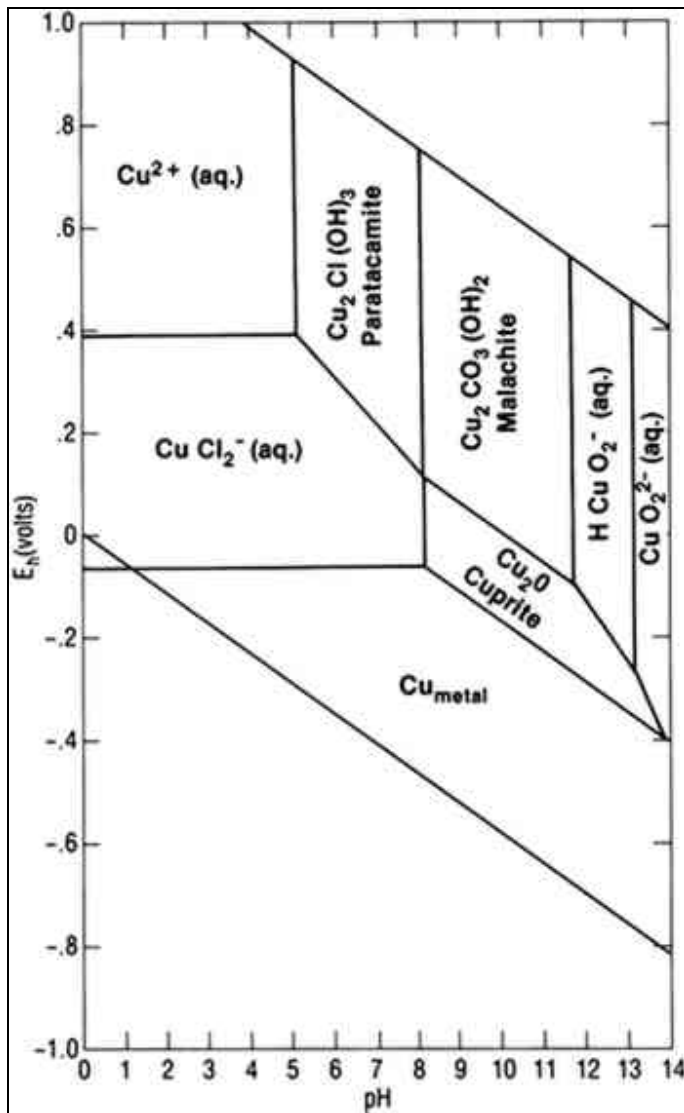
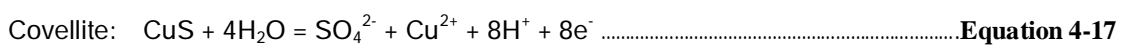
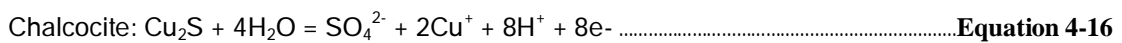


Figure 4-2: Stability diagram of copper, (McNeil and Little, 1992).

In the presence of water alone, more acidity is released. Examples are:



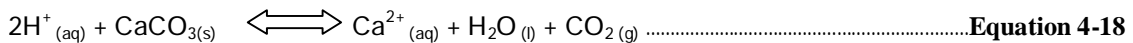
In other words, this means that, for every mole of chalcocite or covellite, eight (8) moles of acidity is released for Equation 4-16 and 4-17, or 2 moles of acidity for Equation 4-14 and/or Equation 4-15. Moreover, Equation 4-16 and 4-17 are

unlikely, because of the absence of oxygen in the equation, whereas the tailings are exposed to atmospheric conditions without any cover.

Surprisingly at Palabora, no sign of salient acid drainage was observed, as the analyses below show an increase in alkalinity as the years go by. This “auto-acid-neutralisation” is possible if neutralising minerals are present in the system; in such a case, some acidity would be consumed and some metal may be precipitated as secondary minerals. In the presence of excess amounts of neutralising minerals, acid mine drainage and/or alkaline mine drainage will not appear, even if kinetic rates are high (Morin and Hutt, 1997).

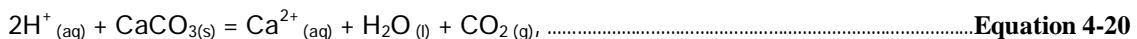
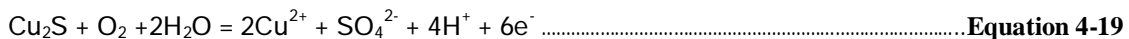
Copper ions liberated by the breakdown of sulphides are carried downwards and precipitates as oxides and carbonates as the acidity are neutralized by the reaction with silicates and/or carbonates.

Example:



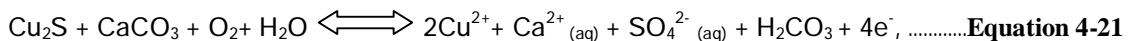
#### a) Neutralization reaction of Chalcocite (Cu<sub>2</sub>S)

Like pyrite (FeS<sub>2</sub>), we assume here that the “neutralizer” is calcium carbonate as shown in Equation 4-19, hence from equations 4-19 + Equation 4-20 and upon addition of copper carbonate,



where CO<sub>2</sub> is released into the atmosphere

Net reaction:

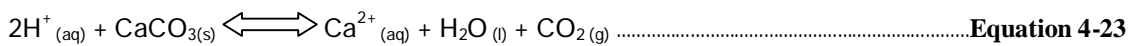
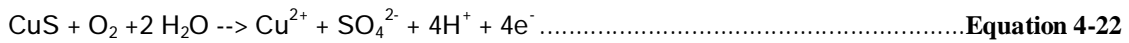


where H<sub>2</sub>CO<sub>3</sub> is carbon dioxide dissolved in water.

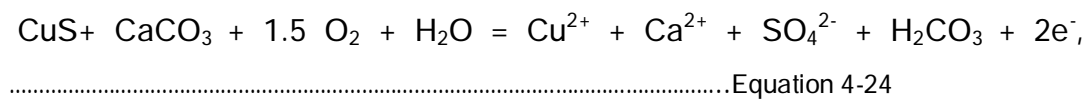
Thus, acidity produced from one (1) mole of Cu<sub>2</sub>S (32g sulphur) is neutralized by one (1) mole of CaCO<sub>3</sub> (100g) or 1g sulphur: 3.125g CaCO<sub>3</sub>.

b) Neutralization reaction of Covellite (CuS)

From Equation 4-19 and upon additional reaction with Equation 4-20, Covellite is neutralized as:



Net reaction



where  $\text{H}_2\text{CO}_3$  is carbon dioxide dissolved in water.

Like Chalcocite, the acidity released from 1 mole of CuS (32g sulphur) is neutralized by one (1) mole of  $\text{CaCO}_3$  (100g) or 1g sulphur: 3.125g of  $\text{CaCO}_3$ .

From the net reactions, copper and sulphate react in the aqueous medium to produce copper sulphate ( $\text{CuSO}_4_{(\text{aq})}$ ), salt is released, contributing to the increase in the salinity of the water. Moreover, sulphate ions have been the major anions found in the analyses, which can be attributed to the above reactions, among others

Table 4-2: Sulphide minerals in terms of likely acid generation (Skousen *et al.*, 1998).

Sulphide minerals	
Acid forming	Non-acid forming
Pyrite $\text{FeS}_2$	Galena $\text{PbS}$
Marcasite $\text{FeS}_2$	Sphalerite $\text{ZnS}$
Arsenopyrite $\text{FeAsS}$	Chalcocite $\text{Cu}_2\text{S}$
Pyrrhotite $\text{FeS}$	Covellite $\text{CuS}$
Chalcopyrite $\text{CuFeS}_2$	

## 4.5 AMD treatment

All these reactions have one peculiarity; the release of sulphate, which reacts with the excess calcium to form gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and dissolve in water.

Due to the seriousness of the problem, extensive research has led to suggesting other means of AMD neutralisation and treatments. The management of mine pollution demands a range of active and passive remediation technologies to minimise its impact on ground- and surface waters, which can require significant expenses. While the first treatment (active) requires the use of chemical treatment technologies to buffer acidity, the second (passive) allows naturally occurring chemical and biological processes to function in a controlled system outside of the receiving polluted effluent (Rios *et al.*, 2007). Studies are thus focused on the use of waste to fight waste. Lately, fly ash as ameliorative for the neutralisation of acid mine drainage has been tested in small-scale experiments. Fly ash is one of the main residues from the combustion of coal. It contains coal. significant amounts of silica (silicon dioxide,  $\text{SiO}_2$ ) (both amorphous and crystalline) and lime (calcium oxide,  $\text{CaO}$ ).

Warren and Dudas (1986) used column leaching experiments with weak sulphuric acid as an effluent to simulate fly ash weathering, the study showed two buffering actions at pH 12, with the hydrolysis and dissolution of  $\text{Ca}(\text{OH})_2$ , and another between pH 8.5-10, with the partial dissolution of the silicates, (Petrik *et al.*, 2005).

Similarly, Pérez-López *et al.*, (2006) were able to buffer a non-saturated column filled with pyritic-rich sludge and fly ash drained leachate experimentally from a pH of close to 2, to a pH of 10, with low sulphate concentration, and lack of iron and other metals in solution.

In a separate experiment, Paradis *et al.* (2007) succeeded in stabilising an acidic leachate from a pH of 3.5, using red mud bauxite (RMB) and brine water to a pH of 8. the composition of the RMB was 12.63% $\text{SiO}_2$ , 20.65% $\text{Al}_2\text{O}_3$ , and 35.26%  $\text{Fe}_2\text{O}_3$ .

These techniques of “waste recycling” can significantly contribute to solving some AMD issues.

#### 4.6 Considerations, advantages and short-comings of Acid-Base Accounting

Acid-Base Accounting is often a first or second step in determining mine drainage chemistry. It is the balance between the acid production and the acid consumption properties of a mine waste material. It has been used very widely, but it is important to point out that although it can be used very fruitfully, particularly in classifying samples into potentials for acid generation, there are several factors to consider.

##### 4.6.1 Advantages

The principal advantages of ABA are the following:

- Ø Cost effectiveness: in effect, the tests are of relatively low cost.
- Ø Promptness: results are very rapid.
- Ø Coherence: field observations correlate most often with results.
- Ø Provides an assessment for the potential of biochemical oxidation.

##### 4.6.2 Short-comings

The limitations of ABA are thus the following (most of these limitations also apply to several other methods):

- Ø It only provides a possibility of occurrence.
- Ø Reaction rates are ignored. (ABA generally tests the fast reacting species; slow reacting neutralizing species will usually not prevent acidification).
- Ø 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.
- Ø For samples with high sulphur contents, the amount of sample required by the test procedure might be too large leading to incomplete oxidation of the available sulphur due to inhibition of reaction by reaction products and low pH.

Despite all these limitations ABA is a very important tool of acid mine drainage prediction. When used in conjunction with mineralogy tests, the results could be very close-to-reality.

## 5 WASTE SAMPLING

Different kinds of materials were collected during the latest sampling run in 2007. These involve rock samples, solid phase samples from tailings dams and near run-off water bodies. However, during the last decade, groundwater samples have also been collected in a bid to assess the impact of leaching from tailings dams and intra-mine run-off.

The following samples were collected as part of this investigation.

Table 5-1: Waste samples per waste facilities.

Facility	Samples
Copper Tailings	94
Waste Rock	70
Hi-Ti	60
Lo-Ti	13
Slag	6
Vermiculite Tailings	10
Vermiculite Waste Rock	12
Spills	15
Total	280

Samples from the Copper Tailings, Hi-Ti and Lo-Ti were collected using an auger drilling machine. Samples from the Waste Rock and other facilities were collected with an excavator. Solid rock samples were packed appropriately. Solid sand waste samples were initially tested on-site for pH and EC before being packed. All samples were submitted for radioactivity testing in the mine, before being submitted for analysis at the University of the Free State.

The sampling rationale and approach were based on the following considerations:

- Ø Spatial representativity. The bigger the facility, the higher the number of samples collected for that facility.
- Ø In Waste Rock, multiple samples per hole were collected from different levels.
- Ø In Copper and Magnetite Tailings, auger holes provided depth-determined samples to determine variation with elevation and/or depth.
- Ø Samples were collected from the slopes of the tailings.

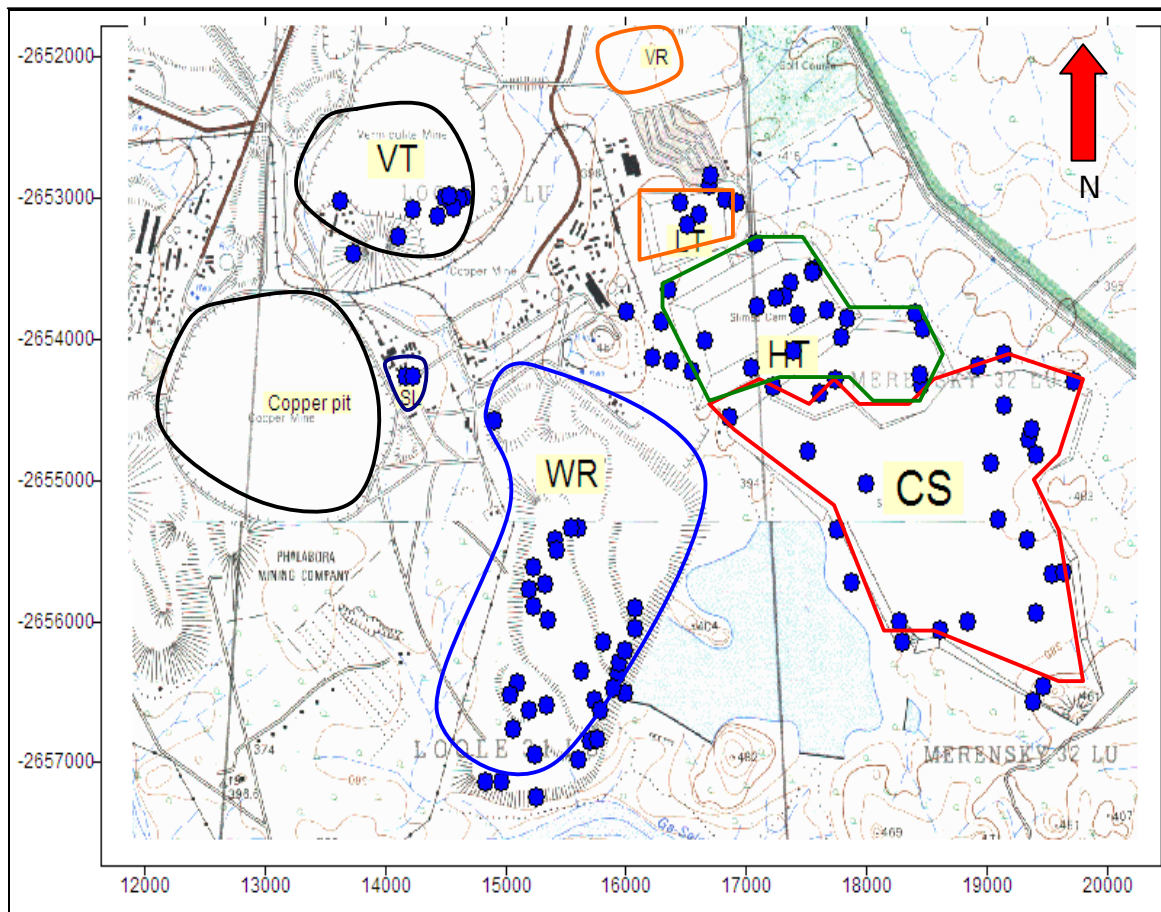


Figure 5-1: Sampling positions for different waste facilities, with the limits of the facilities.

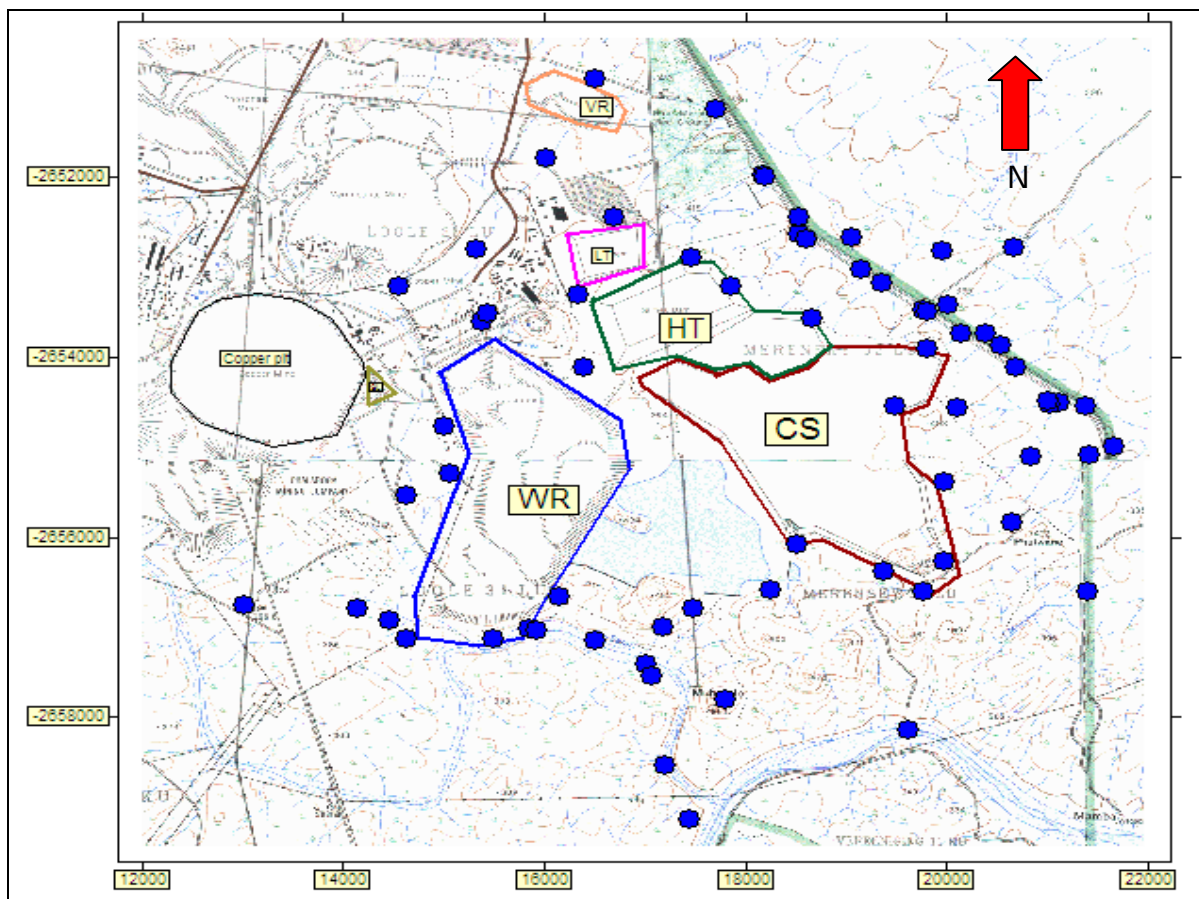


Figure 5-2: Groundwater sampling positions for different wastes and the limits of the facilities.

## 5.1 Test Pits (rock samples)

An excavator was used to dig the inspection pits to depths in excess of 3m. The aim was to evaluate the condition of the waste at different localities at first hand, and correlate this information with the field observations.



Figure 5-3: Rock sampling at PMC in 2007.

Data collected from each pit include:

- Ø Paste-pH values of the waste rock with depth. In most instances, samples were taken just below the topsoil, then at around 1m depth and at the bottom of the pit, as well as at any horizon where a variation in the waste rock was visible.
- Ø Samples were collected to represent each different feature. These were placed in airtight plastic bags and stored for later testing and analysis.
- Ø A visual inspection of the exposed sides was made to identify any striking features.

- Ø The depth to the topsoil was measured or averaged where a variation existed over the extent of the pit.
- Ø The localities of the pits were obtained with a Global Positioning System (GPS), and the relative age of the waste rock with respect to mining was noted.

## 5.2 Augered holes

An auger driller was used to drill the tailings and from ground level to depths in excess of 4m, where possible. The aim was to evaluate the condition of the waste as it is spilled, which is the difference in chemistry of the tailings and soils with respect to depth, and thus try to appraise the chemistry of the leachate and its effects by the time it reaches the groundwater.



Figure 5-4: Tailings sampling with an auger at PMC.

Data collected in each hole included:

- Ø Paste-pH values of the tailings and soil with depth. Each sample was measured for pH and EC as it was collected, after which samples representing each feature were placed in airtight plastic bags and stored, for later testing and analysis.
- Ø Visual inspection of the material was done to note any striking features, like change in colour of the surface of the tailings or the soil, e.g. a salt deposit after evaporation looked whitish on a black magnetite tailings.

- Ø Where augering was not possible, like on incompetent surfaces due to the weight of the drilling machine, samples were collected using a spade and a hand-auger, mainly at surface level or at a maximum depth of 50cm due to water at depths of one (1) meter.
- Ø Coordinates of the holes were recorded with a GPS so that further sampling could be performed on the same spots should any result look anomalous with respect to the other samples taken at the same area.

### 5.3 Representativeness and adequateness of the samples

Obtaining representative samples is a vital component of any drainage prediction methodology, since the remaining methods rely on adequate sampling and interpretation of results requires adequate and representative samples. As an analogy the 1 g sample representing 500 tons of material used in ABA can be compared with the testing of 1 apple for a 300 ha orchard (Tarantino and Shaffer, 1998).

Determining the number of samples to be taken and the representativeness of the sample set are critical considerations.

Empirical methods are useful for a preliminary guide; they are however, based on data from different environments to those encountered locally. It is therefore suggested that sampling programs be conducted in a stepwise fashion and that the representativeness of the sample set be determined. Once a more complete database is available for South African mines, analysis of the data should be able to provide a more generic areal guideline for sample numbers, (Usher *et al*, 2003).

There are several statistical methods to determine the adequacy of sampling. Several of these methods are very intricate and cumbersome in application, and their use would be impractical to enforce.

Several parameters pertaining to ABA have normal or lognormal distribution in the field. Examples of these are initial pH (normal in undisturbed strata) and acid potential (log normal). If a population exhibits a normal distribution, the following

equation can be used to evaluate the number of samples (n) required (Walpole, 1982):

where Z = the two tailed value of the standardized normal deviate associated with

$$n = (Z_{\alpha/2} S / e)^2$$

the desired level of confidence.

$\sigma$  = the preliminary estimate of the standard deviation.

e = the acceptable error (half the acceptable confidence interval).

An example would be for 80% confidence levels (considered at this stage to be the minimum acceptable level), Z=1.26 and the error value (e) would be 10% of the determined mean for the sample set, (Usher *et al*, 2003).

The error estimate associated with the (preliminary) sample set for each confidence level is largely determined by the number of samples in the set and

$$Z_{\alpha/2} (S / \sqrt{n})$$

the observed standard deviation (Walpole, 1982).

Use was made of the equation above to ascertain the adequacy of the samples obtained. Since the ABA data is the most quantitative, despite the other limitations, the acid potential and neutralisation potential were selected for this purpose. The program DQ-Pro application (Keith *et al*, 2000) was used. It was developed by the U.S. EPA Quality Assurance Management Staff (QAMS) to help decision makers define the specific questions that a data collection effort is intended to answer. The Enviro-Calc sub routine was used to analyse the data. This is designed to determine the number of samples needed to estimate an average analyte concentration in site-specific media within a pre-specified absolute or relative error with a specified confidence. This calculator assumes that measurements of analyte concentration will be normally distributed and that a random sampling plan will be used to collect samples.

For the purpose of this dissertation, an 80% confidence level is considered adequate, and the standard deviation in the sample set was used to determine variability.



Although the data is not normally strongly distributed, this assumption would provide a fair assessment of the samples. Thus, without log transforming the data, the following can be reported for the entire assessment:

- Ø For AP: 292 samples must be analysed using a method capable of generating data with no more than four units of standard deviation in order to calculate the average concentration from the 292 samples within a tolerable error of less than 10% of the mean, with 80% confidence.
- Ø For NP: 190 samples must be analyzed using a method capable of generating data with no more than 214 units of standard deviation in order to have the average concentration calculated from these 190 samples fall within the tolerable error of less than 10% of the mean with 80% confidence.

Overall, the number of samples therefore approaches a representative number, but not necessarily for each type of waste

## 5.4 Mine site conceptualization

A conceptual model is a necessary first step in the process of the successful prediction of water quality at a mine site. This concept is a qualitative description of the physical characteristics, hydrology and hydrochemistry of the site, and the effects of these on natural receptors. Information about the sources and mitigation measures will be obtained from the mine plan. A generalised mine site that illustrates the elements in the conceptualisation is depicted in

Figure 5-5.

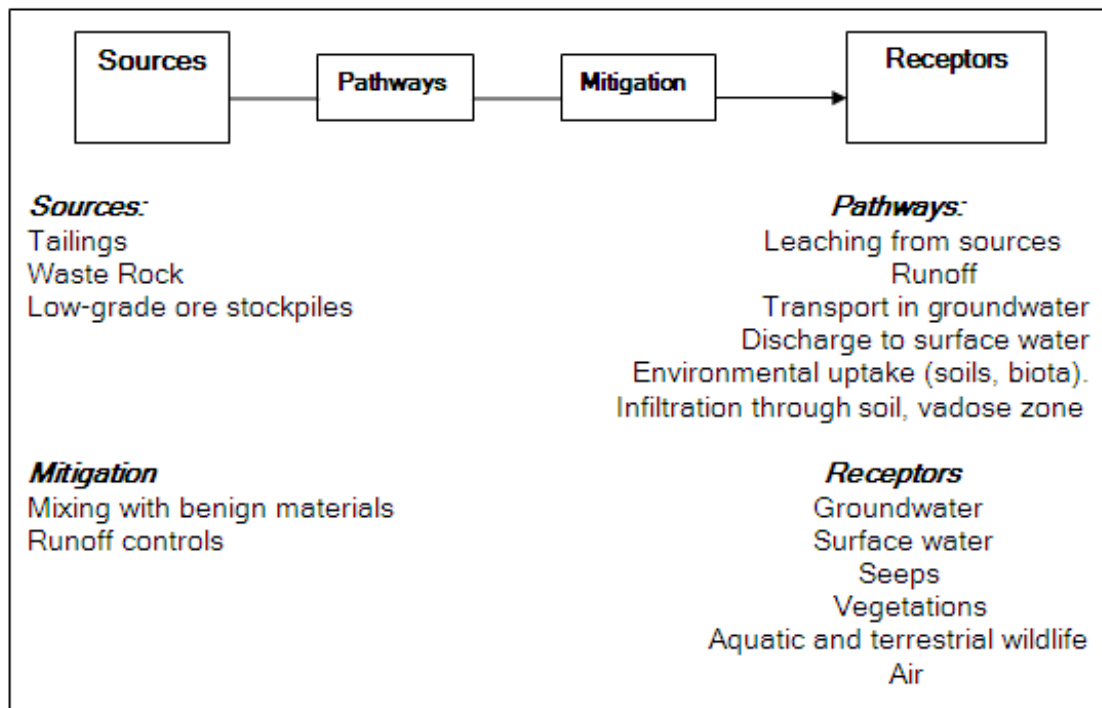


Figure 5-5: Generalized conceptual model of sources, pathways, mitigation and receptors at PMC.

## 6 RESULTS AND DISCUSSION

After all analysis were performed, the results and the discussions are presented below. The discussion of results includes:

- Ø Acid-Base Accounting (ABA) on waste rock and tailings samples.
- Ø Mineralogy results/ interpretations/ conclusions.
- Ø Calculating concentrations of constituents that will be present during and after mining.
- Ø The on-site chemistry.
- Ø Groundwater results/ interpretations/ conclusions.
- Ø Identification of management options to minimize water quality deterioration and regional impacts.
- Ø Mine site conceptualization.
- Ø Salt loads estimations.

### 6.1 The Acid Base Accounting (ABA) results

#### 6.1.1 Waste samples

##### 6.1.1.1 Methodology

The samples arrived in the laboratory for analysis three days after all of them had been collected.

The initial pHs of the tailings samples were simply obtained by adding distilled water to 5g of each of them and then reading the values from the pH-meter.

Furthermore, to obtain an estimate of the final pH of the tailings dams after oxidation, a further 5g of soil were mixed with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), (NAG

testing). The following give an evolution of the pH with respect to the various waste facilities.

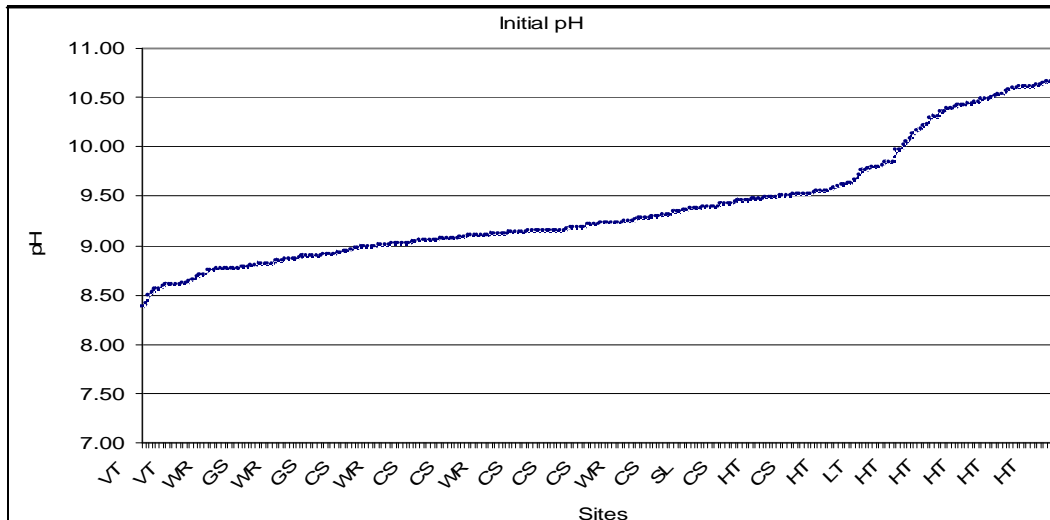


Figure 6-1: Initial pH of the waste facilities.

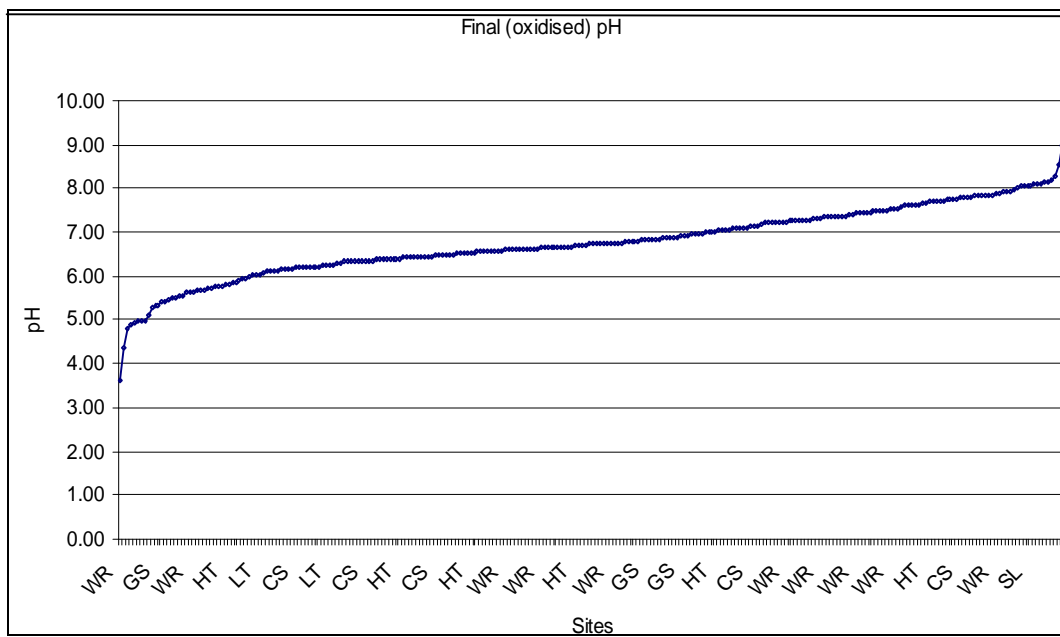


Figure 6-2: Oxidised pH of the waste facilities.

These figures speak for themselves:

- Ø Initially, no sample/site is acidic in terms of pH
- Ø HT is the most alkaline site

- Ø When oxidized, most sample/sites become acidic
- Ø The waste rock (WR) is the most “acidic”, followed by the titanium dumps and the copper sulfide dam
- Ø In addition, acidity here varies with specific sites on the facilities.

A significant majority of the samples have natural pH-levels at or above 8.5. This is only possible if the samples have sufficient or even excess base material available, which will prevent immediate acidification during the mining phase. The high pH-values indicate the presence of significant alkaline phases. Many samples have pH-values above 8.2. This suggests the presence of significant carbonate species. These are released through solution and represent the first line of acid neutralisation. This is also very much in line with the observed pH levels in the groundwater on the mine as shown in the 2007 data, for example.

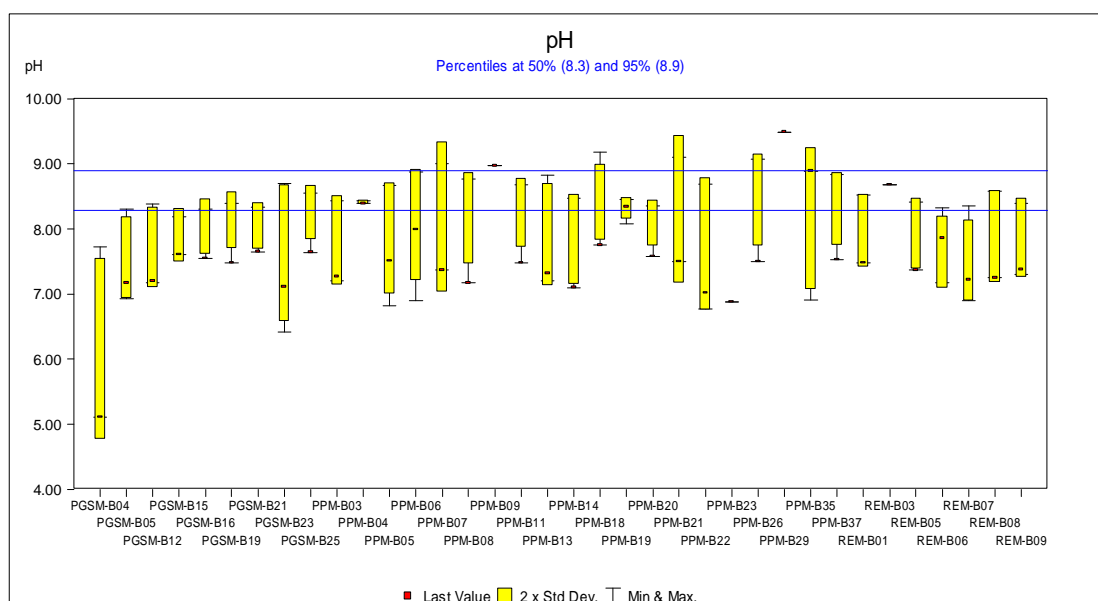


Figure 6-3: Groundwater monitoring data pH from 2007.

The implications of these might extend beyond simple similarities. It is very tempting to say that various types of carbonates dominate the geology of the mine, but also that the waste facilities and groundwater are related through leaching.

Two other ABA tests were performed on the samples. These are separate measurements of the acid and base potential contained in each of the samples. In these static tests, the amount of acid that can potentially be produced by each sample and the associated potential of each sample to counteract this acidity are determined separately. It is important to realize that these tests determine the maximum availability of the acid-producing minerals (usually sulphides) and of the neutralizing species (at pH-levels above 6.0, usually calcium/magnesium carbonates). The test methods are designed to utilize all the potential inherent in the sample.

In nature, carbonates are more reactive than the sulphides, resulting in base potential leaching by circulating groundwater, (Usher and Moukodi, 2008). This invariably results in an acid problem over the long term, when the neutralizing potential is closely matched to the acid- generating potential.

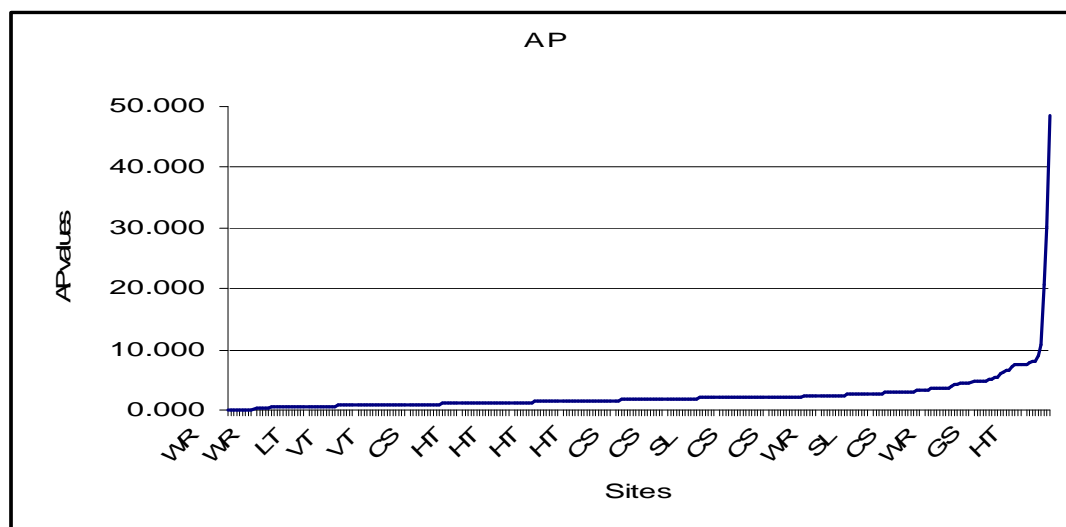


Figure 6-4: AP for the waste facilities.

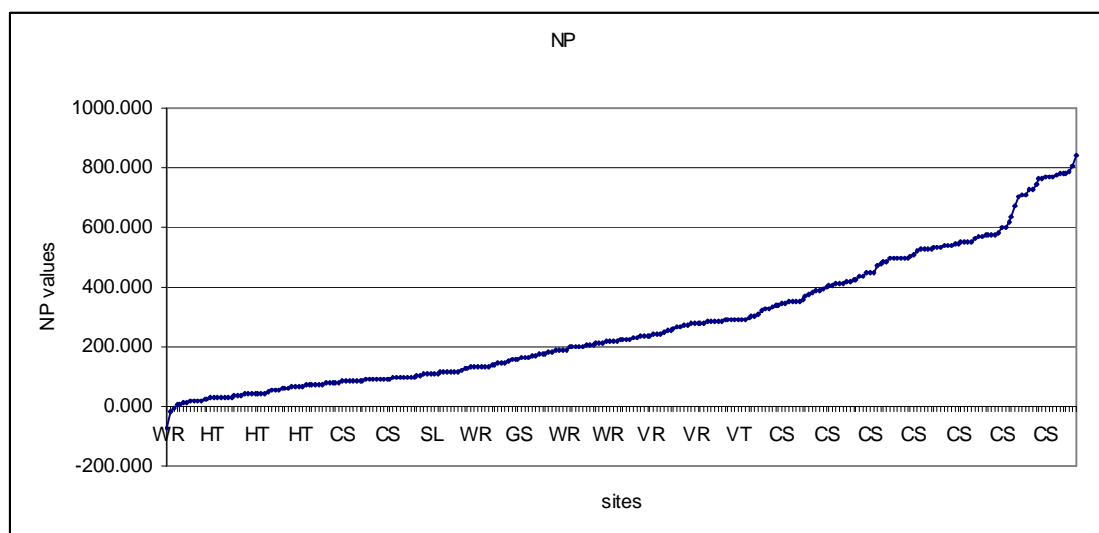


Figure 6-5: NP diagram of the waste facilities.

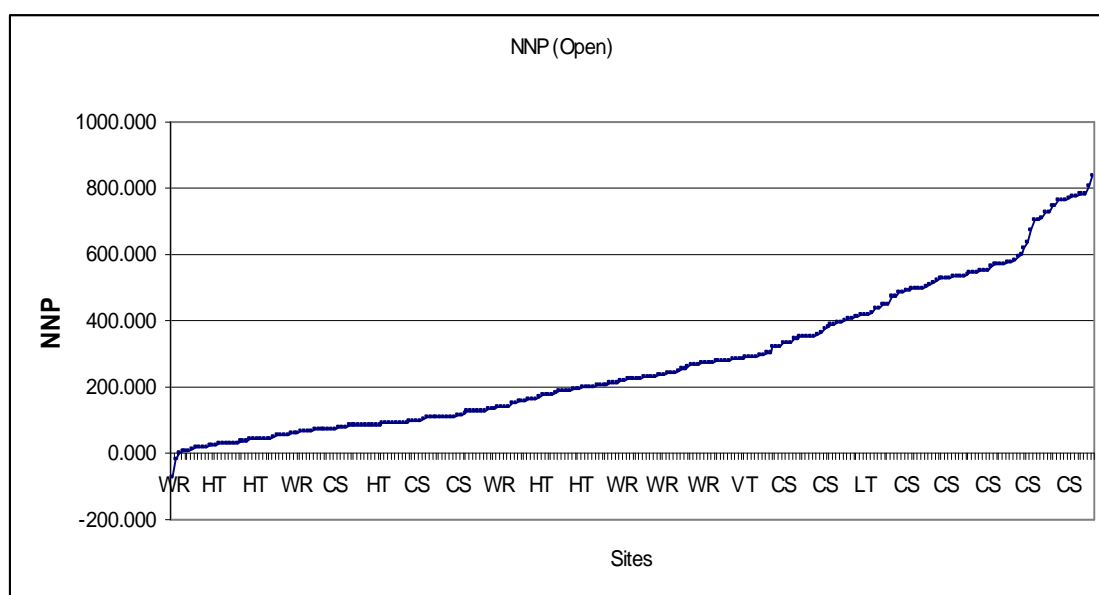


Figure 6-6: NNP diagram of the waste facilities.

As explained in the Methodology Section (3.1.4), the NNP is obtained by subtracting the AP from the NP.

Experimentally, if the Net Neutralising Potential for any sample is greater than zero (0), then the sample has the potential to neutralise acid.

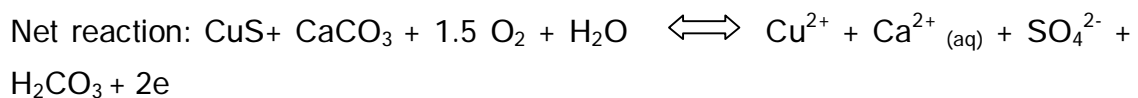
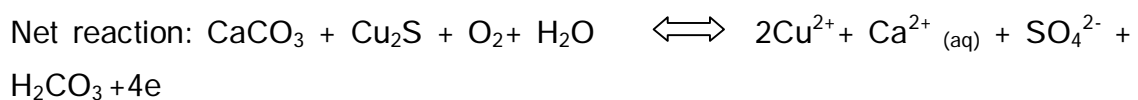
From the acid potential and neutralisation potential graphs, it is clear that across the tested waste material, the acid potential remains very low across the site, with very few exceptions, whereas there is a far greater proportion of NP in the different waste types.

In the above figure, more than 95% of the samples have NNP values far above the threshold value of zero (0) (83.5% actually have an NNP >20). The same percentage is evenly capable of potentially neutralising acidity.

This is further confirmed when comparing Figure 6-5 and Figure 6-6 above; it is noticeable that the site with the highest NP is also has the highest NNP values.

The site in question is the Copper Tailings (CS) main tailings dams.

These results have several very important implications, in terms of maintaining the neutral to alkaline conditions current found on the site. The following net reactions serve as explanations for the high neutralisation potentiality.



The results also indicate that the waste in general is low in sulphide content, and therefore the generation of acid mine drainage, sulphates and associated salts should be relatively low.

The average NP in the waste is in the order of 270 kg/t as  $\text{CaCO}_3$ , whilst the AP on average is in the order of 3 kg/t as  $\text{CaCO}_3$ , reflecting a sulphide content of less than 0.1% in all the waste on average.

The following conclusions are drawn:

- Ø In the calculations of acid potential and consequently NNP, a distinction is made between open and closed conditions. Under closed conditions, the base potential is halved due to the production of  $\text{CO}_2$ . The latter produces carbonic acid ( $\text{H}_2\text{CO}_3$ ) upon dissolution in the available water. This acid reacts with the carbonate species in the rock, thus increasing the overall acid potential. Under field conditions, it can be assumed that most of the



CO<sub>2</sub> ends up in the water. However, instances would certainly occur where some of the CO<sub>2</sub> is released into the air. A continuum between closed and open systems, which tends towards a closed system, is therefore likely in the tailings but unlikely in the waste rock. In the case of the PMC wastes, due to the low AP generally, this is not an important distinction to draw.

Ø A composite graph, showing the combination of natural and oxidised pH-levels as well as the results from acid and base determinations, is plotted in Figure 6-7. In that diagram, natural pH-levels are shown on the y-axis as diamonds and oxidised pH-levels as squares. On the x-axis, the NNP is plotted. Advantages of this plot are:

- The drop in pH as a result of oxidation for each sample can be demonstrated.
- A check on the accuracy of the analyses can be made. The position of acidification should approximately coincide with the zero NNP value. The conclusion is that the analyses appear to be accurate.
- The representative spread of values on both axes confirms adequacy in the number of samples analysed.

The latter plot shows that the overwhelming majority of samples remain neutral to alkaline, while those of which the pH does drop have negative NNP values.

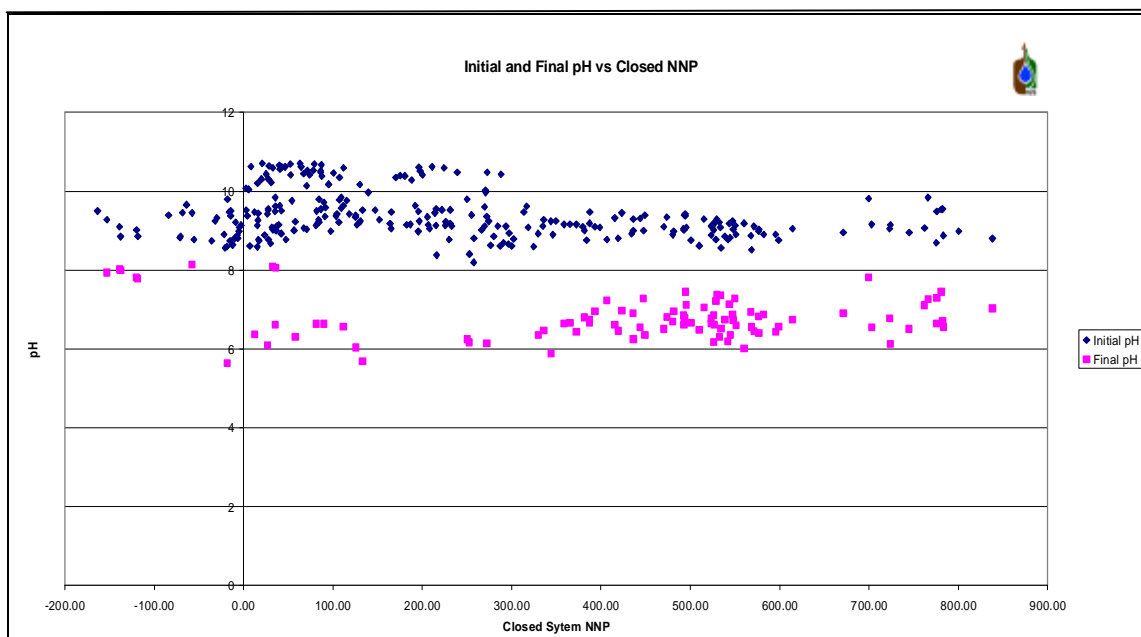


Figure 6-7: Initial and Oxidized pH vs. Closed NNP.

An additional graph to demonstrate the likelihood of long-term acidification is shown in Figure 6-8 below, using a graphical tool, Acid Base Accounting Cumulative Screening Tool (ABACUS), after Usher (2000). The Neutralizing Potential Ratio (NPR) is calculated from Base Potential/Acid Potential. The graph is divided into different sectors - the red sector with low NPR (0.3 - 1.0% S), is a field where long-term acidity is very probable. The green sector is an area where there should be enough neutralizing potential and too little sulphur for significant acidity to occur. Samples in this field will be likely long-term buffers in the system. The grey area on the chart represents samples with a low sulphide content but low neutralizing potential. These samples should not theoretically have enough sulphides for long-term acid generation, but can yield acidity in the short term until the sulphides have been depleted.

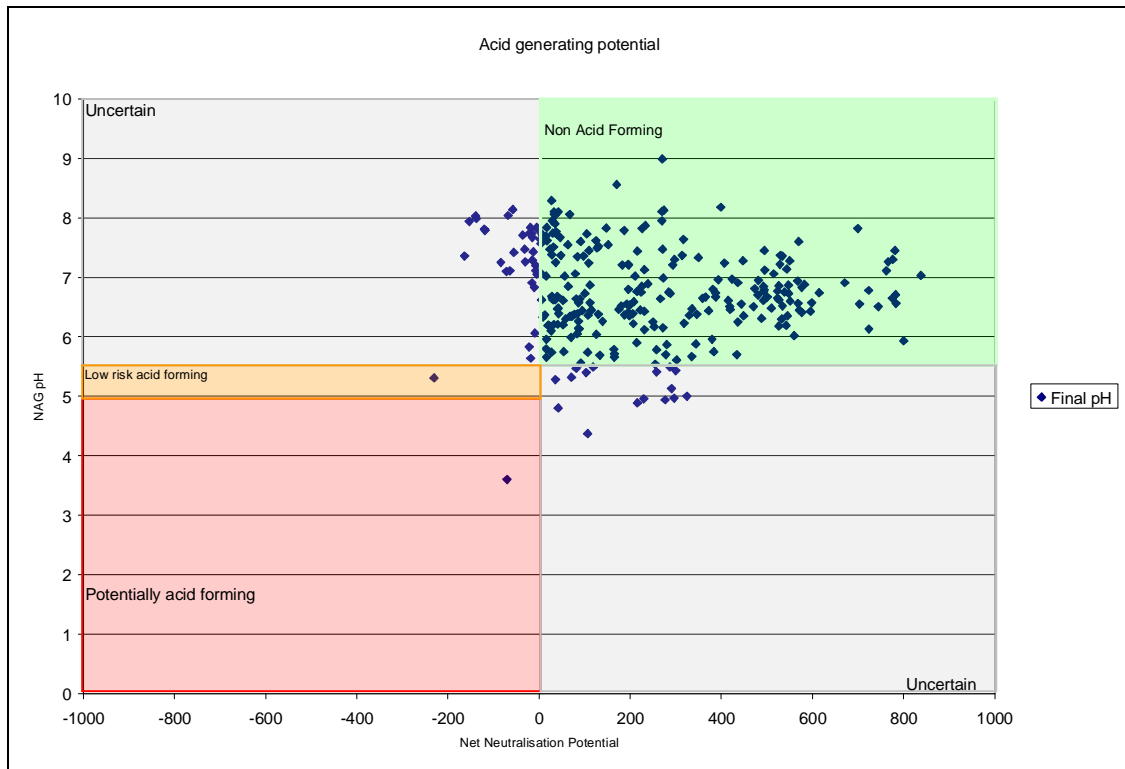


Figure 6-8: Acid-generating probability of the material, (AMIRA, 2002)

From this, it is evident that most of the samples are sufficiently non-acid forming to prevent the long-term generation of acidity, and that in fact the low sulphides should limit high rates of sulphate generation from the waste.

Comparisons of AP and NP shows that AMD-associated problems are considered highly unlikely at PMC.

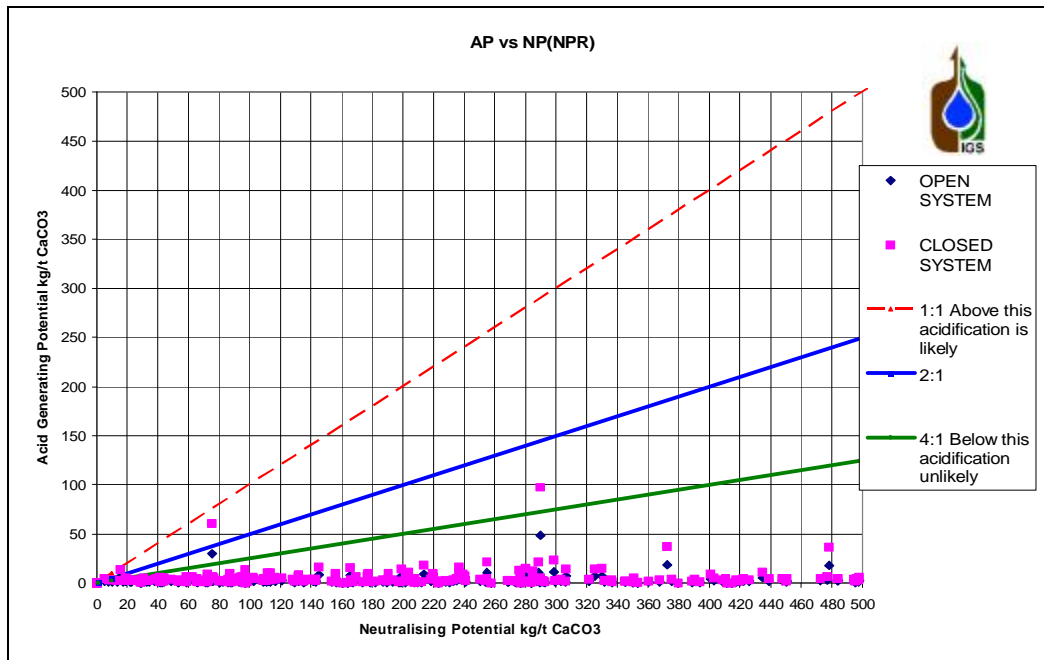


Figure 6-9: AP vs. NP for all waste.

The graph (Figure 6-9) shows that, despite different considerations (open vs. closed system), the outcome of the results is the same: Acidification at PMC is highly improbable.

An overview of the different waste types is shown below. It is clear that the AP values are consistently higher in the waste rock, indicating that this area is associated with elevated sulphates if the waste conditions are similar. It is also very clear that the sulphides have generally been removed by processing the tailings, but that significant NP still exists in these wastes. The vermiculite tailings are inert, with low AP or NP values, and the salts generated are due to weathering of the material, and not associated with sulphide oxidation reactions or the system's response to these reactions.

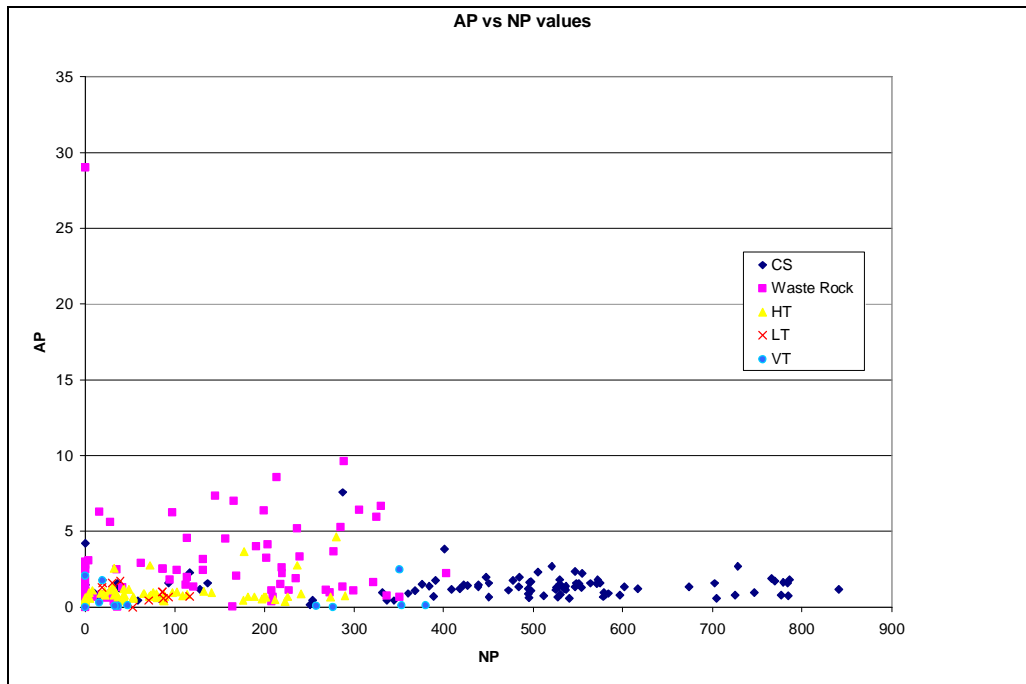


Figure 6-10: AP vs. NP from different types of waste.

All the graphical tools above only give the results of the analytic testing. A closer and deeper interpretation of these data as per facility would help understand the processes behind these results.

#### 6.1.1.2 Analysis per facility

On site, nine dams' types and construction are present, together with the giant hole known as the "copper pit".

However, the facilities that carry the more concern are those expected to generate significant salt loads. These include:

- Ø The Main copper tailings dam (CS);
- Ø The Waste Rock Dump (WR);
- Ø The magnetite tailings (HT and LT)

In order to get any estimate of the tonnages in terms of elements released from each waste site, the mine provided with the volume of all the facilities, and using the following formula, it was possible to obtain the corresponding tonnages.

$$\text{Mass (Tons)} = [\text{volume (m}^3\text{)} \times \text{specific gravity (kg/m}^3\text{)}] / 1000 \dots \dots \dots \text{Equation 6-1}$$

Table 6-1: Areas and volumes of different waste types (PMC, 2007).

Dam Type & Construction	Dam Dimensions	Volume of Dam	Material Stored in Dam
The Main copper tailings dam	Total bottom area 435.58 Ha. Total top area 288.76 Ha Active top area 255.71 Ha Active linear distance 6,851m	215,521,035 m <sup>3</sup>	Copper tailings
South Paddock copper tailings dam	Total bottom area 435.59ha	1,633,062.5m <sup>3</sup>	Copper tailings & Magnetite
The Hi-Ti Magnetite dam	Total bottom area 174.28 Ha. Total top area 71.12 Ha Active top area 36.17 Ha.	73,101,072m <sup>3</sup>	Magnetite
The magnetite infill dam	Total bottom area 20.68 Ha.	1,633,062.5m <sup>3</sup>	Magnetite
The lo-Ti magnetite dam	Total bottom area 43.22 Ha. Total top area 19,39 Ha. Active top are 9.69 Ha	7,557,350 m <sup>3</sup>	Magnetite
Copper tailings and all magnetite Dams *Total tailings dam area	Total bottom area 785.90 Ha. Total top area 504.81 Ha		

### 6.1.1.3 The Waste Rock dump

#### 6.1.1.3.1 The ABA

This site is located at the centre of the mine. 70 samples were collected from different positions of the waste rock dump. An excavator was used for sample collecting. A composite was created to be as representative as possible for the position, with fine material and coarse material combined in an estimated proportional weight percentage.

The sampling positions are shown on Figure 6-11:

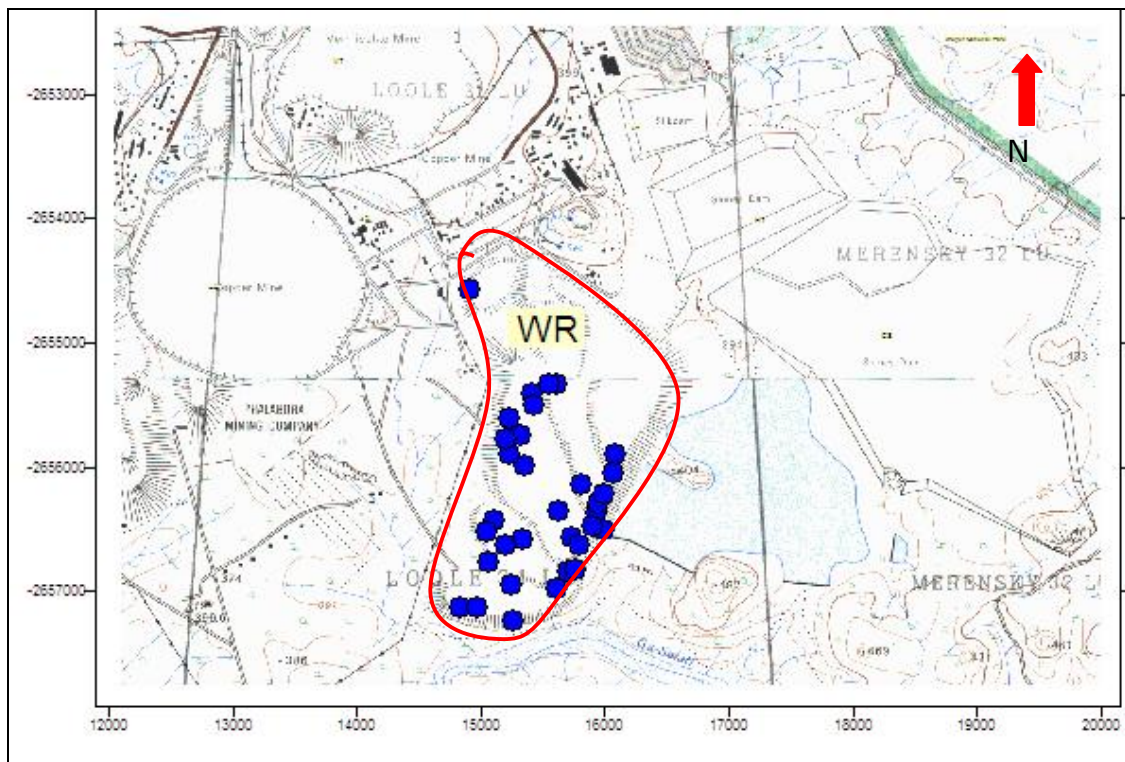


Figure 6-11: Waste rock sampling positions.

At each position, two samples were taken, considered to represent the rock at the point. When one views the average values there seems to be little variation. However, comparison of individual samples shows the tremendous variability in sampling waste rock particularly, as will be shown later in this section.

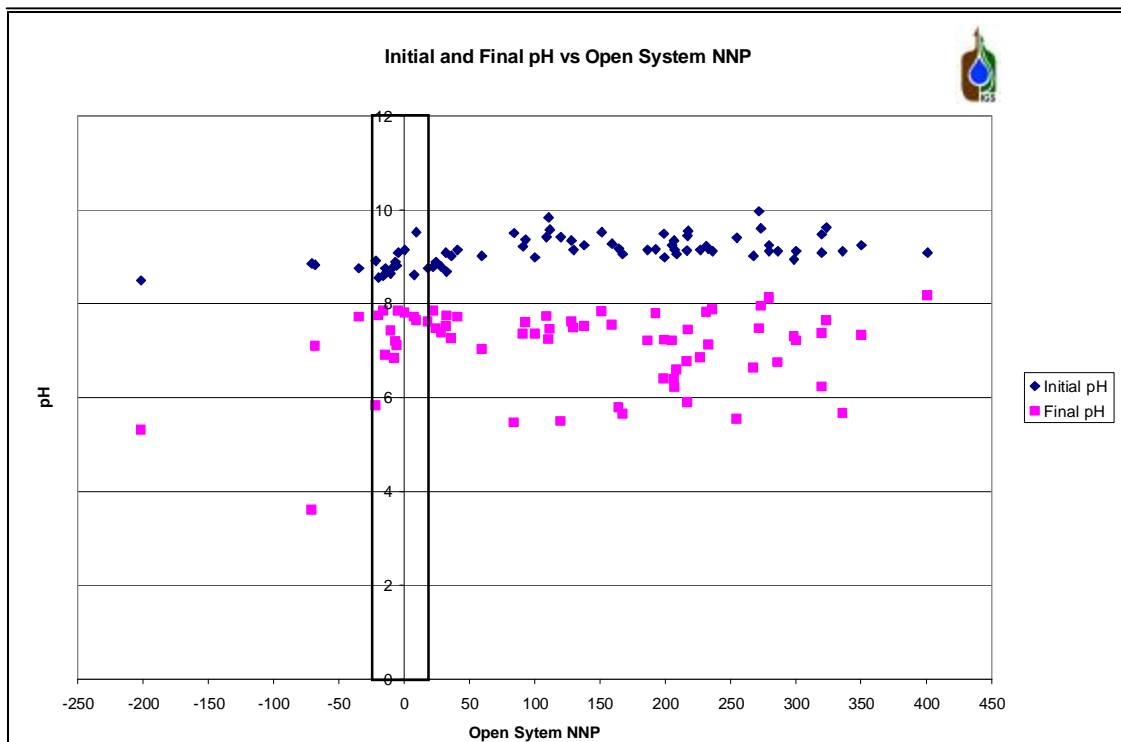


Figure 6-12: NNP vs. pH in Waste Rock.

If one considers the overall ABA nature it is clear that there are a few samples that contain significant sulphide in the waste rock. These are however, a minority of the samples obtained, and as can be seen on the NNP vs. pH plot, the large majority of the waste has a great excess of material which is net alkaline rather than potentially acid forming.

Statistically, samples having a paste pH of < 4.0 are considered potentially acid forming, and contain significant acidic sulphate salts (up to 30.1 kg  $\text{H}_2\text{SO}_4$ /t equivalent) that will immediately produce acid upon exposure to water. Samples with a paste pH of 4.0-5.0 are considered potentially acid forming as well, but have a lower stored acidic salt content (up to 9.0 kg  $\text{H}_2\text{SO}_4$ /t equivalent), (Weber *et al*, 2006).

This is confirmed by regarding the % S found in the rock with the NPR, showing that the majority will be expected not to acidify with a few uncertain samples in



between. The important aspect here too is the very low average sulphide content in the waste, as referred to previously.

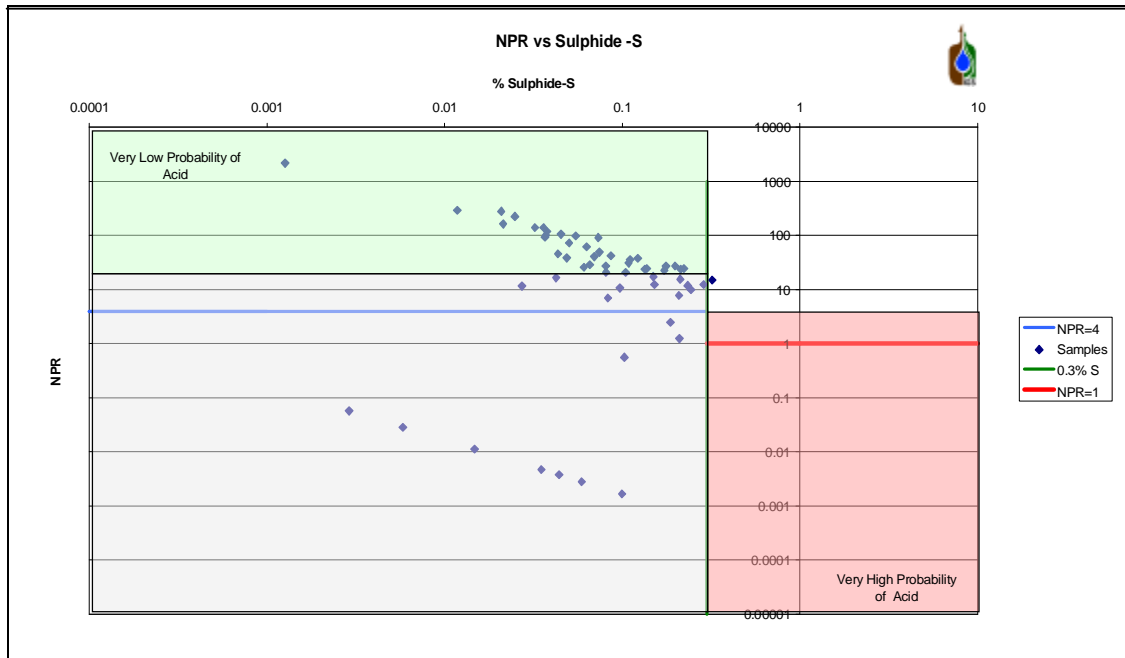


Figure 6-13: %S vs. NPR for Waste Rock.

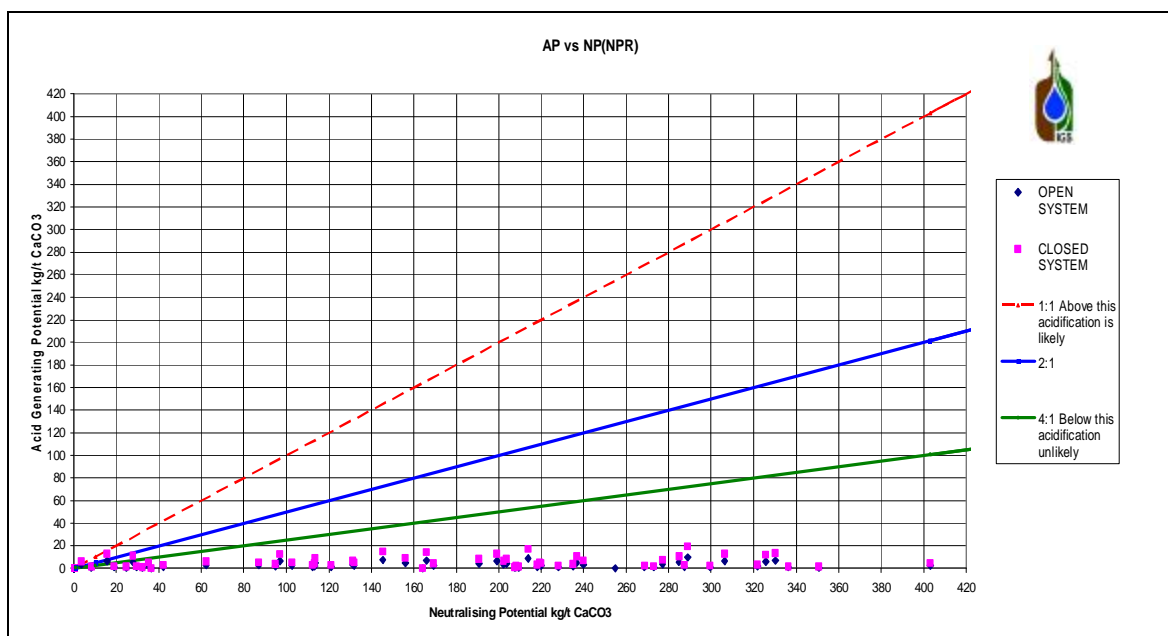


Figure 6-14: AP vs. NP.

The AP vs. NP therefore shows that there is a great excess of NP over AP and acidification is highly unlikely.

Statistically this can be seen as in the Table 6-2 below:

Table 6-2: Summary of acid vs. base potentials in the Waste Rock dump (kg/ton).

Samples	Acid (Open)	Acid (Closed)	Base	NNP (Open)	NNP (Closed)
AVERAGE	2.88	5.76	163.32	160.44	157.56
MAX VAL	9.62	19.24	403.07	400.87	398.67
STDEV	2.37	4.74	119.39	118.97	118.59

As with the tailings, the water soluble (Table 6-3) and oxidation liberated elements were also determined, (Table 6-4). It is very important here to point out that for the waste rock, that the values represent the maximum amount of each constituent that could be available or released under oxidation. Due to the nature of static testing, the waste rock is crushed to a very fine particle size for the testing and thus a far larger proportion of elements would rather be liberated by water particularly and oxidation than would occur in the field. Nonetheless, it is the finer material in the waste rock that would contribute the most to the salt generation, thus this provide an indication of this contribution. To scale this up using the entire mass of waste rock would therefore greatly exaggerate the waste rock dumps contribution to the salinity, and an estimate of the proportion of fine material as a weight proportion of the total would provide a better indication. Figure 6-15 shows the variation over sequential holes that were excavated.



Figure 6-15: Variation in waste rock samples obtained in sequential holes.

Table 6-3: Water liberated elements from the waste rock (kg/t).

Samples	Ca	Cu	Fe	K	Mg	Mn	Na	Sr	Ti	Pb	Zn	SO4
AVERAGE	0.1689	0.0003	0.0033	0.2510	0.0734	0.0003	0.0855	0.0045	0.0001	0.0002	0.0002	0.4327
MAX VAL	0.4989	0.0008	0.0195	0.5610	0.2045	0.0007	0.1671	0.0205	0.0007	0.0020	0.0010	1.4761
MIN VAL	0.0526	0.0001	0.0000	0.0853	0.0238	0.0000	0.0226	0.0001	0.0000	0.0000	0.0000	0.0402
STDEV	0.0822	0.0002	0.0040	0.1202	0.0351	0.0002	0.0319	0.0037	0.0001	0.0004	0.0002	0.3331

Table 6-4: Oxidized liberated elements from the waste rock samples (kg/t).

Samples	Ca	Cu	Fe	K	Mg	Mn	Na	Ti	Pb	Zn	SO4
AVERAGE	1.3364	0.0039	0.0040	0.4674	0.7722	0.0029	0.1756	0.0114	0.0002	0.0005	0.0003
MAX VAL	2.4031	0.0394	0.1343	1.5409	1.9083	0.0345	0.4502	0.0489	0.0029	0.0034	0.0009
MIN VAL	0.5062	0.0000	0.0140	0.0672	0.1493	0.0003	0.0363	0.0008	0.0003	0.0003	0.0004
STDEV	0.4648	0.0070	0.0200	0.3484	0.3396	0.0057	0.0866	0.0081	0.0006	0.0007	0.0003

The plot of the major elements liberated under oxidation (Figure 6-19) clearly shows that sulphate is the most significant within a range of pH conditions, with Ca, Mg and K being prominent. The relatively low and constant Na values are consistent with the Cl measured in selected samples, and point to the concentration effects that occur on site. It is significant that the released sodium or chloride is exceeded twenty-fold by the sulphate values in the liberation. High sodium and sulphate values in the groundwater therefore point to high rock: water ratios, with sulphate values being in greater excess. Metals are relatively low, due to neutral conditions, ( Figure 6-16).

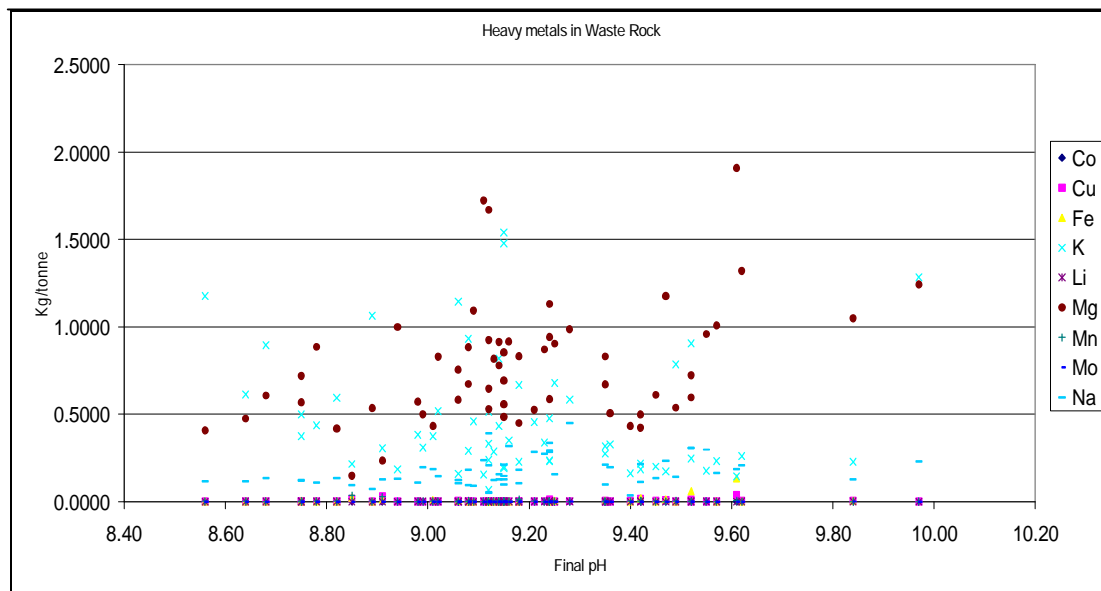


Figure 6-16: Heavy metals in WR samples (kg/tonne) with respect to pH.

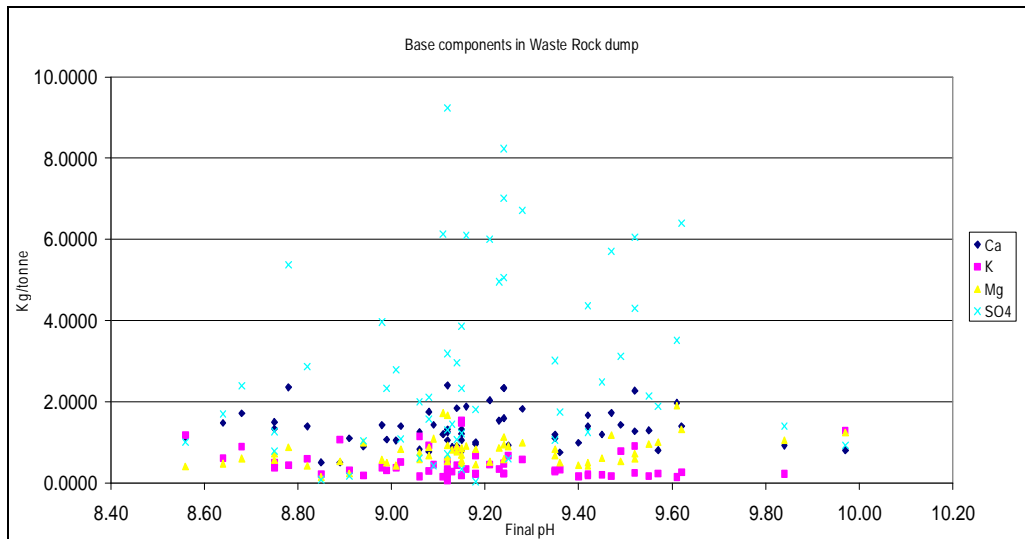


Figure 6-17: Base components in WR soil samples.

The clearest observation from Figure 6-17 is the high concentration of sulphate in waste rocks. This leads to an expectation of high salt loads. It is important to mention that the waste rock contains unprocessed rock, unlike the CS, which is a waste facility of processed waste.

However, there is a high level of base mineral content, which, in case of acidic formation, would counteract the reactions. These base minerals mainly originate from the plagioclase and Alumino-silicates, as indicated by mineralogy studies of the site, (Table 6-6 and Table 6-7).

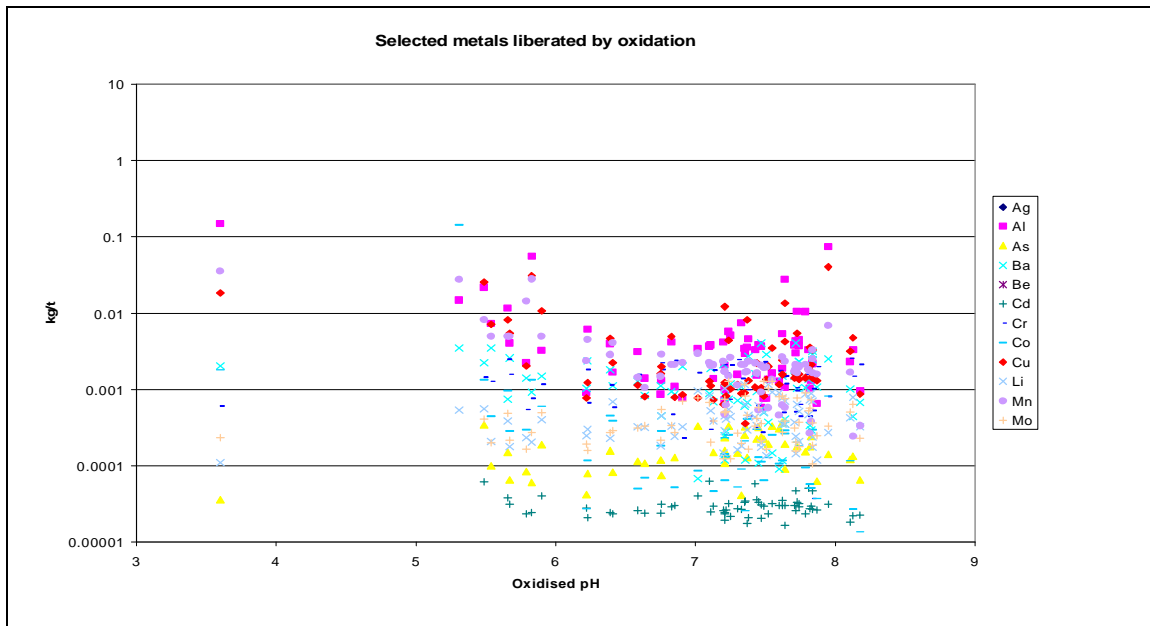


Figure 6-18: Other elements from WR.

The major elements liberated and the effect of oxidation can be shown graphically below, (Figure 6-19):

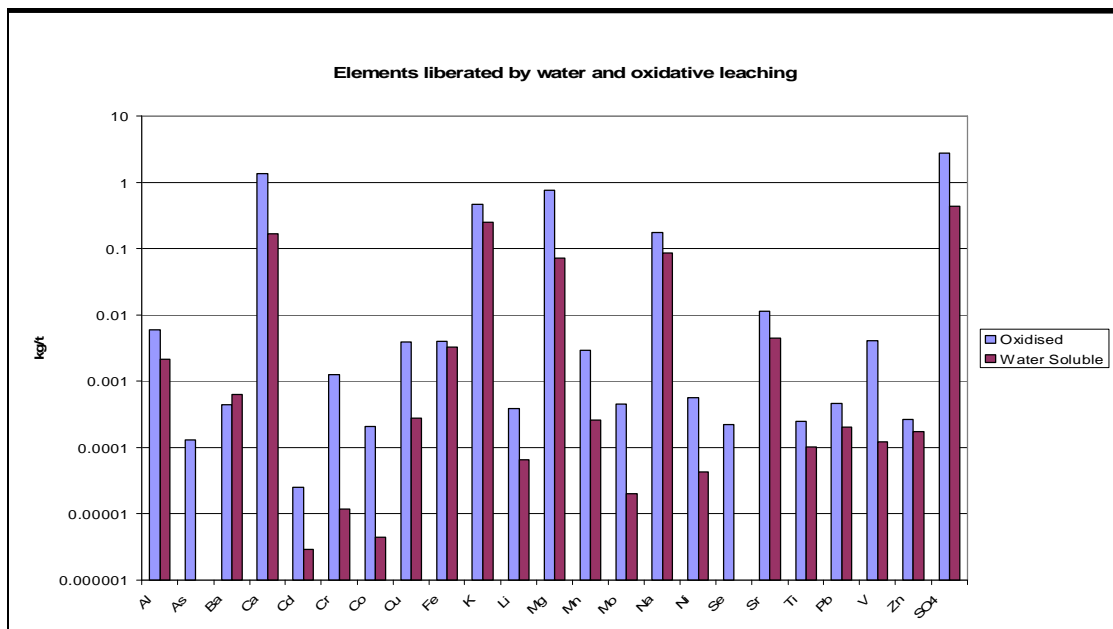


Figure 6-19: Graph of major elements liberated from WR.

#### 6.1.1.3.2 The Mineralogy of the Waste Rock

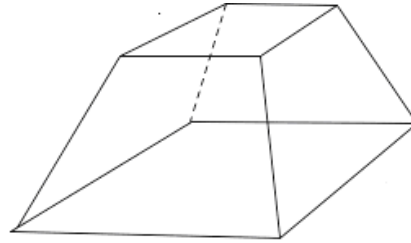
All the tested samples were submitted to the University of the Free State's Geology Department, with the request that they be investigated mineralogically and chemically. X-ray fluorescence and X-ray diffraction testing was undertaken. The Table 6-6 and Table 6-7 below give occurrences of various minerals, as well as percentages in terms of metal oxides at WR. The following are inferred from the mineralogy:

- Silicon oxide is highly present; this is a an indication of the weathered nature of the rocks.
- Iron (Fe) is largely represented as an oxide. However, no pyrite was detected in the XRD, thus Fe presence can be attributed to iron-bearing clays and silicates.
- Aluminium is equally present in the XRF. It is thought to emanate from the plagioclase.
- High calcium and magnesium represented as oxide are an indication of high potential of neutralising material.
- Eventhough calcium and magnesium oxides are present in non-negligible quantities; dolomite and calcite presence are still very negligible in the WR, (Table 6-7), thus their presence is attributed clays and other minerals like clinocllore, vermiculite for magnesium, and mainly ca-plagioclase for calcium.

In conclusion, the mineralogy indicates that the samples are dominated by iron-bearing and aluminosilicate minerals.

#### 6.1.1.3.3 Tonnages estimations of the Waste Rock

Unfortunately, no data was available for the tonnages present at the Waste Rock. In order to get any estimate of the tonnages in terms of waste in this facility, the mine provided surface areas for the top and the bottom footprint. This made it possible to estimate the volume of the facility using the following formula:



$V = \frac{1}{2} h \times (A + B)$ , (Couchoud, 1993).

where:

A= the area of the top footprint ( $m^2$ )

B= the area of the bottom footprint ( $m^2$ )

V= the overall volume of the dam, ( $m^3$ ), while h is the height (m).

Table 6-5: Physical parameters of the Waste Rock.

Area of the Dam ( $m^2$ )		Height (m)	Volume of waste ( $m^3$ )	Mass (Tons)
Top	3,000,000	103	6.71E+14 (calculated)	1.8E+15 (calculated)
Bottom	4,340,000		PMC estimations (N/A)	

With respect to the tailings, this formula assumes the following:

- That the facility has a trapezoid shape
- The facility is regular (square at both bottom and top bases)
- The formula does not take into account the tilt of the waste
- The formula does not consider any of the angles of the figure.
- The formula assumes both that bases are plane surfaces, thus the height is equal at all points at the top of the facility.
- The grains occupy the entire volume and space of the waste facility.



Table 6-6: XRF results obtained from WR samples.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>
Average	41.51	8.99	15.51	0.18	9.63	15.99	1.10	2.77	1.60	2.26
Max value	72.63	15.01	28.50	0.33	25.90	27.03	2.76	6.79	2.67	6.10
Min value	27.13	3.78	1.34	0.02	0.21	0.39	0.00	0.78	0.15	0.07
ST DEV	9.03	2.78	6.14	0.07	5.06	5.80	0.72	1.86	0.69	1.59
% occur (average)	41.70	9.03	15.58	0.18	9.67	16.06	1.10	2.78	1.60	2.26

Table 6-7: Mineral occurrences in WR as obtained by XRD.

Quartz	Phlogopite/vermiculite	Plagioclase	Clinochlore	Actinolite	Magnetite	Montmorillonite	Illite	Apatite	Dolomite	Calcite
accessory	minor	dominant	minor	accessory	minor	minor	major	minor	minor	minor

#### 6.1.1.3.4 Conceptual model of the Waste Rock

The aim of this conceptual model is depict all the physico-chemical processes happening on the Waste Rock from the deposition of the waste to the influence on the groundwater. The objectives of this model are:

- Explain the general processes on the waste facility at a smaller scale.
- Explain the hydrogeological processes.
- Explain the hydrochemical processes.

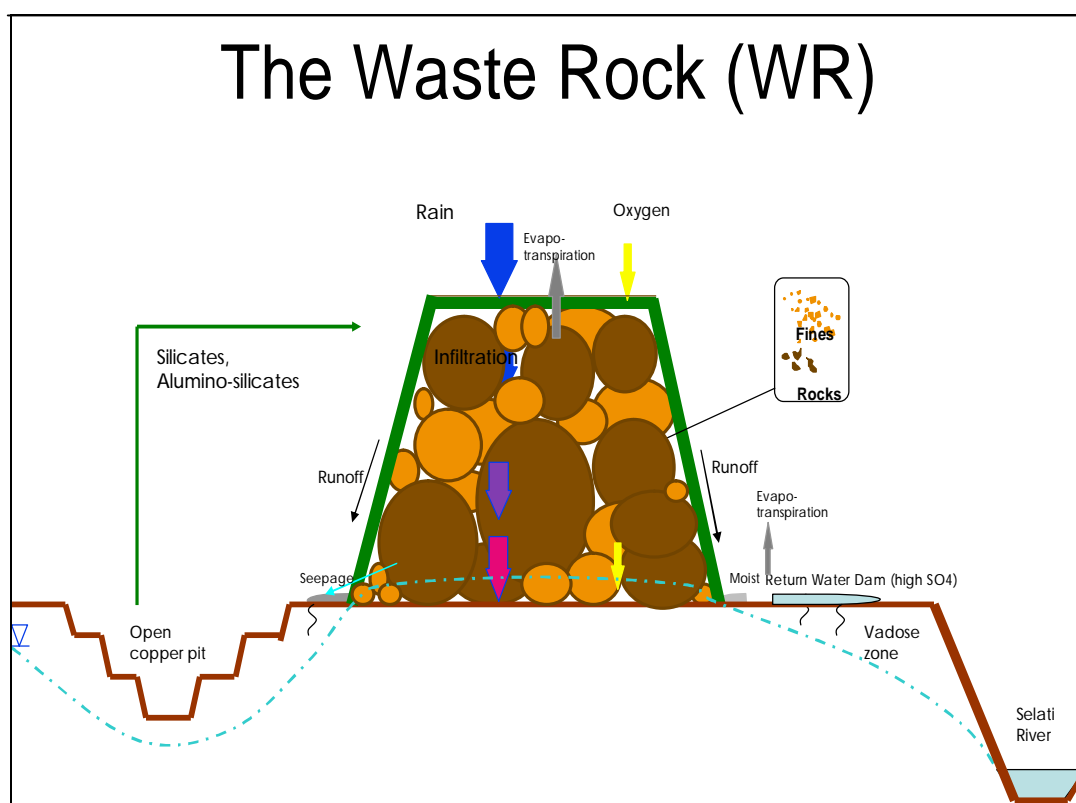


Figure 6-20: General conceptual model of the Waste Rock.

The general conceptual model (Figure 6-20) for the waste deposition is discussed below:

- the waste rock obtained from the now-called open copper pit is dumped at the Waste Rock Dump.
- The open copper pit waste rock is largely composed of relatively unmineralised dolerite, granite-gneiss, syenite and pyroxenite. These rock types are mostly plagioclase feldspar and aluminosilicates. They are exposed to atmospheric conditions such as rain, oxygen. Infiltration and evapo-transpiration occurs. The fine rock particles will react faster with rain water and oxygen than the rock particles liberate sulphate and silica.
- It is assumed that the water level is below the bottom of the open copper pit as it is permanently dry.

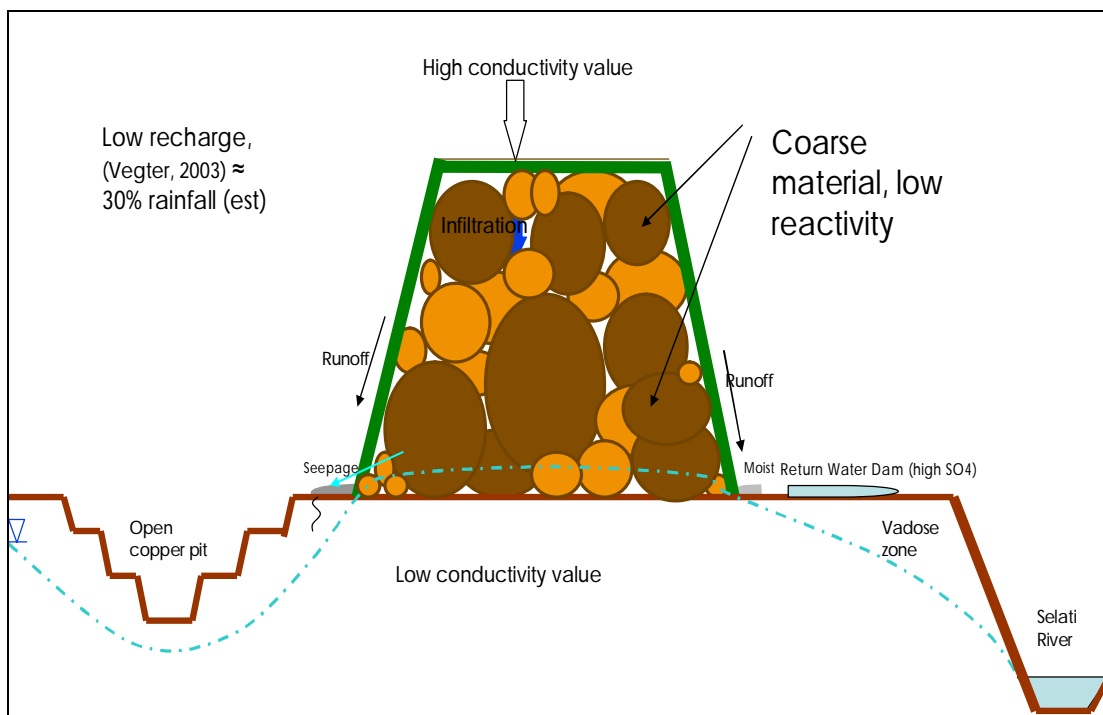


Figure 6-21: Hydrogeological conceptual model of the Waste Rock.

The hydrogeological conceptual model of the Waste rock is discussed as follows:

- the water level inside the dump is close to surface, thus the dump has higher conductivity value than the geological unit on which it sits

- 30% rainfall has been estimated to contribute to water input within the dump
- The material that composes the dump is coarse and has low reactivity in terms of surface area reactivity.
- Sizes of the particles vary from places to places, nevertheless, in the areas where high sulphates have been noticed, it is presumed that finer particles are present there.
- The seepage observed at some points of the dump show that water level is above ground level in the dump. However, the seepage do not extend to the open copper pit.

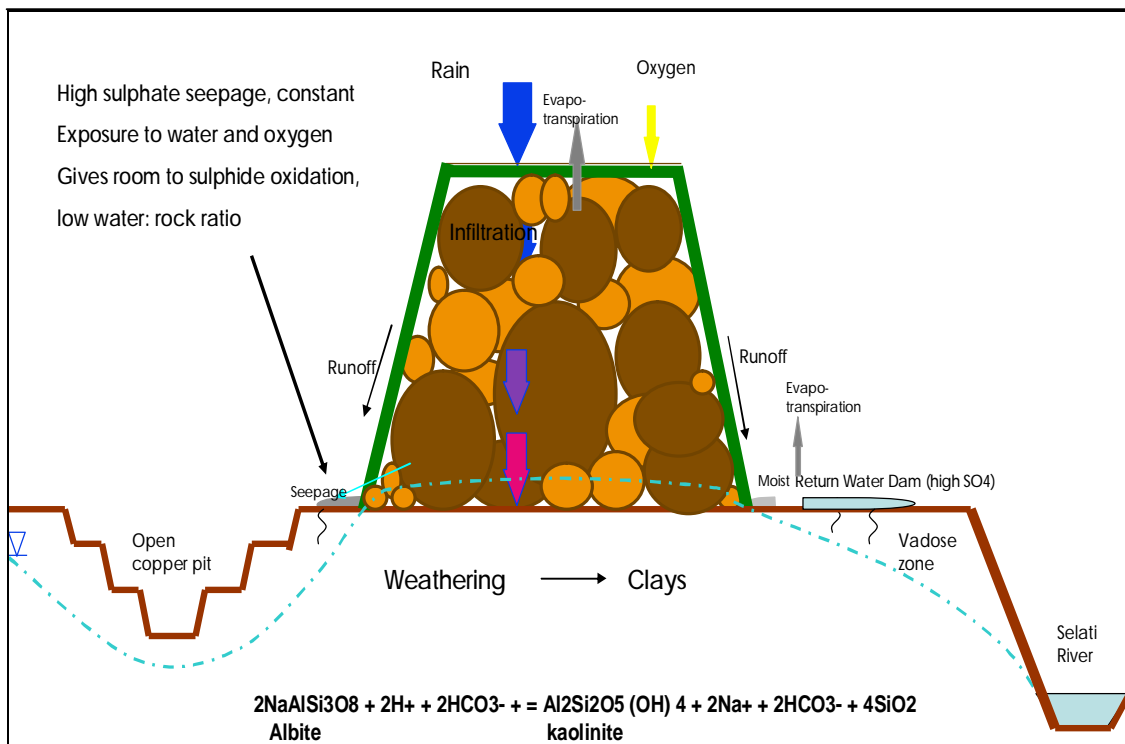


Figure 6-22: Hydrochemical conceptual model of the Waste Rock and its activities.

The hydrochemical conceptual model is discussed as follows:

- in general, plagioclase feldspar (Anorthite, K-feldspar, albite) weather with atmospheric conditions to form kaolinite.

- The marginal ore which is also dumped on the same facility contains high sulphides from contamination from the dolerite. Because of low water-to-rock ratio, and constant exposure to atmospheric conditions, these sulphides react to form sulphates. High sulphate values have been observed in water from the Return Water Dam and seepages from the Waste Rock which extend to the Return Water Dam.
- Silica from silicates minerals is an indication of some acidity. However, silicate minerals in the waste material will slowly dissolve therefore consuming some acidity and thereby introducing elements such as aluminium, silica, sodium and potassium in the groundwater.
- High sulphates have been picked up as well in some borehole water very close to the Selati River, an indication of the flow from the surface seepage to the groundwater.

In conclusion, because the feldspar components of syenite is alkaline, (PMC, 2007). it is therefore expected that the overall pH values of the water be within the slightly-alkaline range.

#### 6.1.1.4 The Copper Tailings dump

The approach to sampling at the copper tailings was to use an auger rig to drill to a depth of approximately 4m along various benches of the dam. It must be noted that at the time of the investigation, tailings deposition had been resumed on this dam, and it was not possible to sample across the extent of upper elevation of the dam. The sampling positions can be seen on the Figure 6-23 below.

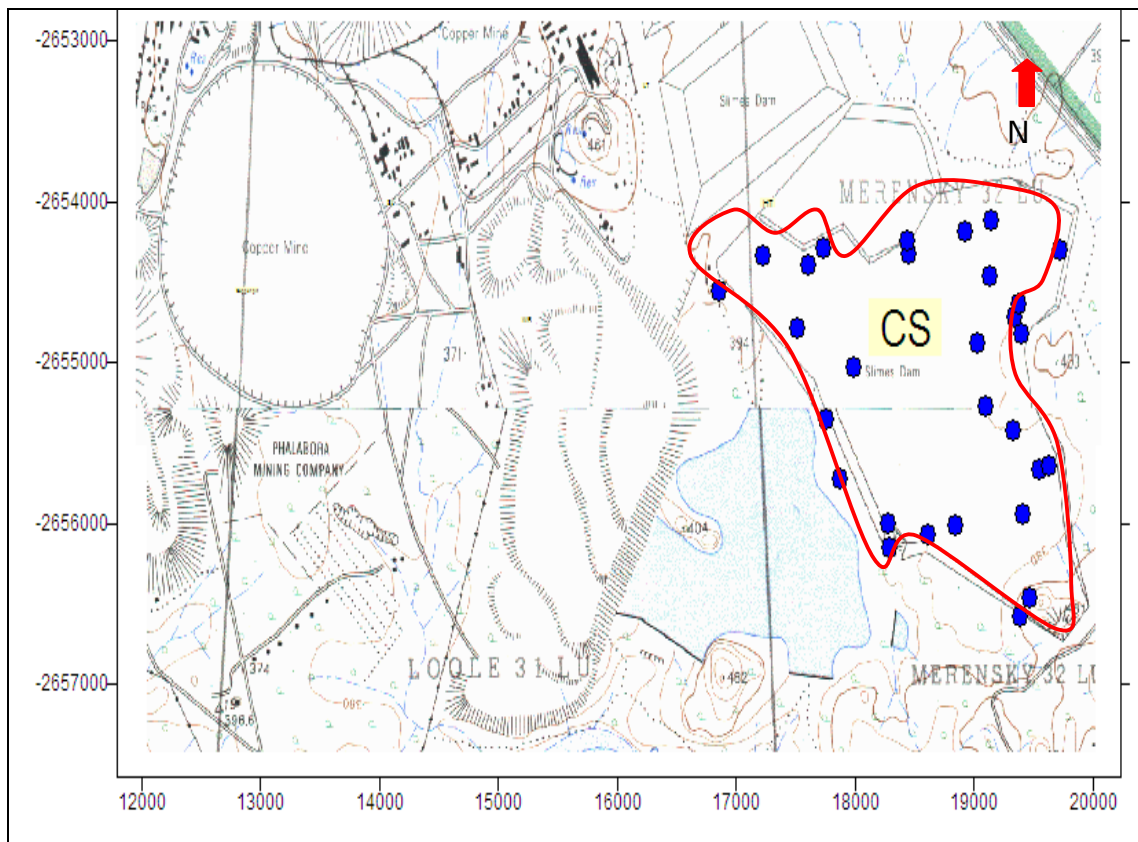


Figure 6-23: Waste sampling locations on CS.

As its name indicates, this dump is the waste facility of processed rocks with no further use. The Copper Tailings are predominantly derived from carbonatite ore from which most of the sulphides have been removed by floatation. Ninety-four (94) samples were collected from this site.

#### 6.1.1.4.1 Acid-Base Accounting

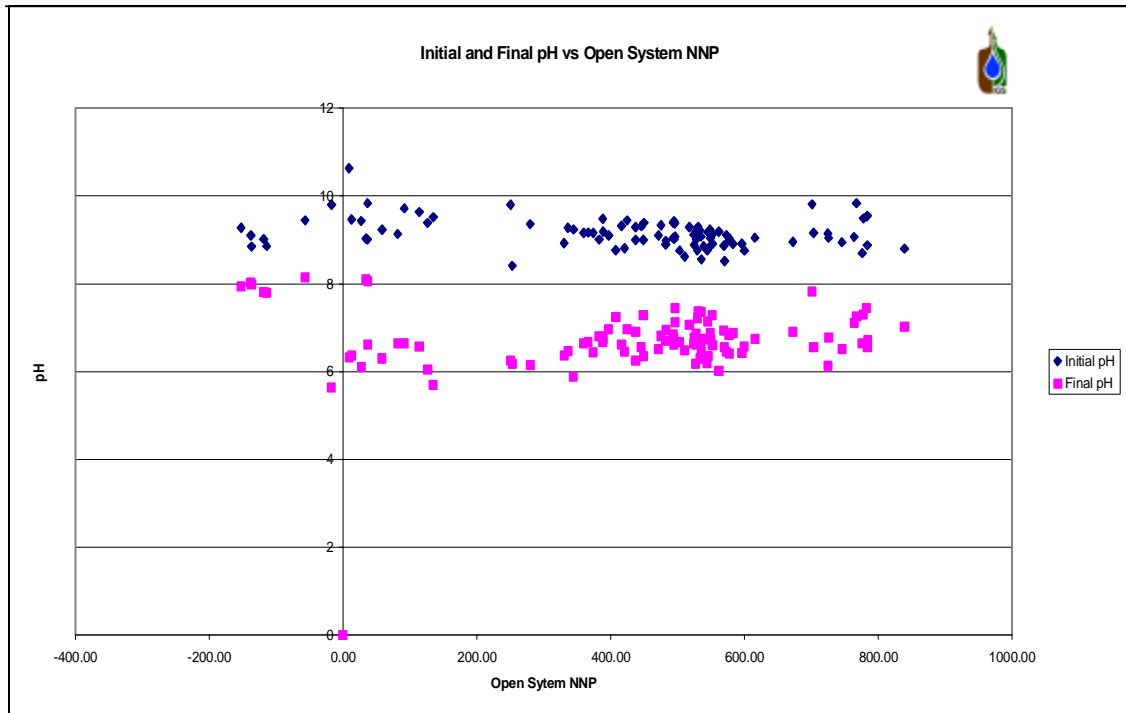


Figure 6-24: NNP vs. pH for CS.

The ABA data shows that the majority of the samples in general are very high in neutralising potential with low AP (Figure 6-24) resulting in a large excess or high NNP.

This is reiterated by plotting the AP vs. NP, (Figure 6-25) showing few that are not likely to be net neutral or alkaline in nature.

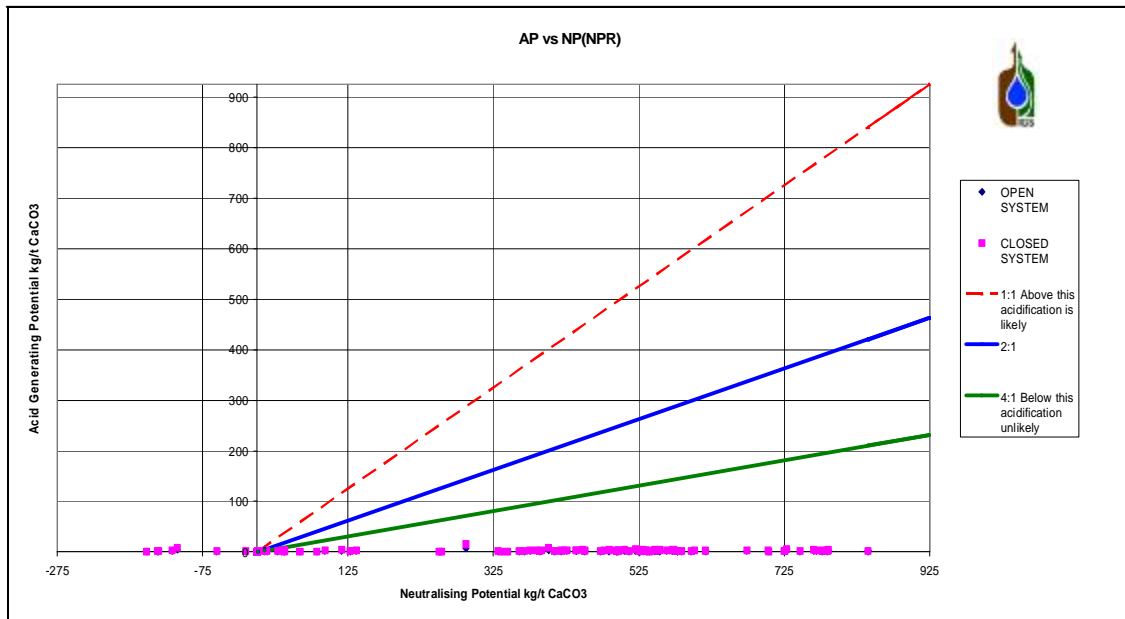


Figure 6-25: NPR diagram of CS.

It is believed that since the mine exploits copper more than any other mineral, this waste facility is also predominantly a copper sulphide's waste deposit, as its name indicates.

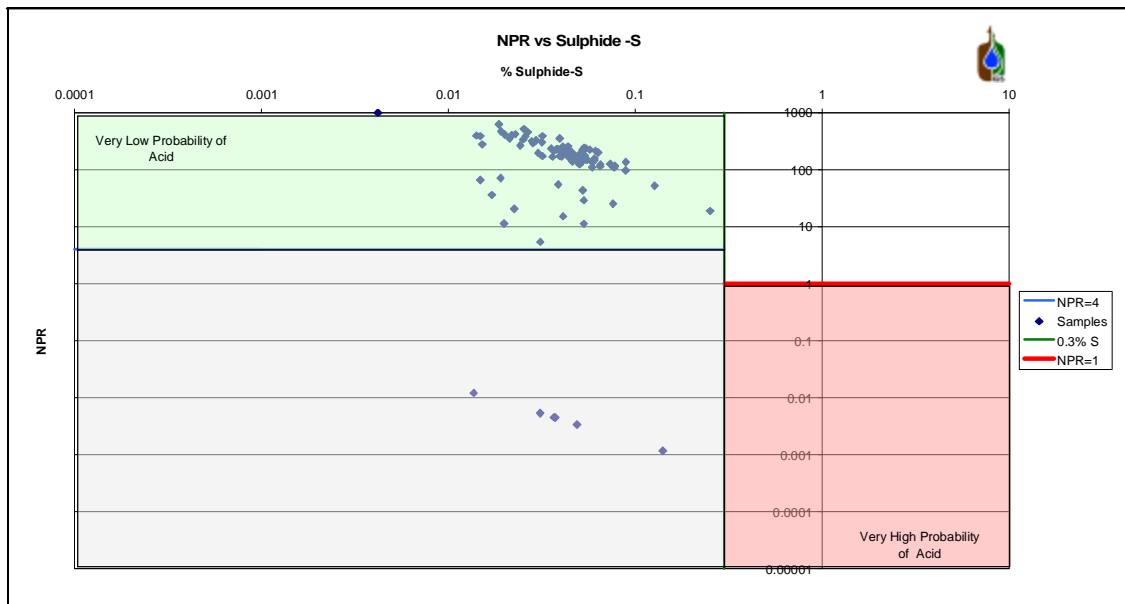


Figure 6-26: Acid-generating probability of CS material.



Consideration of the elements liberated shows similar trends to those highlighted previously. The samples have a sulphide content that is too low to produce acidity, (Figure 6-26) this is because there is excess neutralizing material present as can be seen on the Figure 6-27 below.

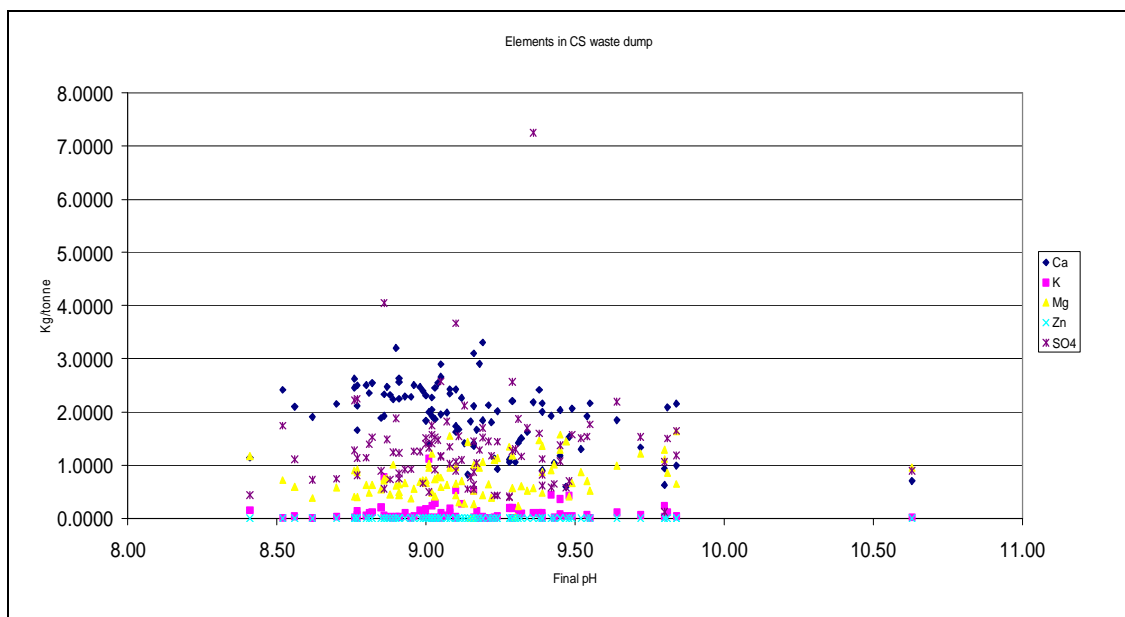


Figure 6-27: Base metals in CS tailings.

This graph (Figure 6-27) shows how some major base elements like calcium and magnesium control sulphate. Because they occur in carbonates, they tend to buffer any acidity that could be left or formed after processing the ore mineral.

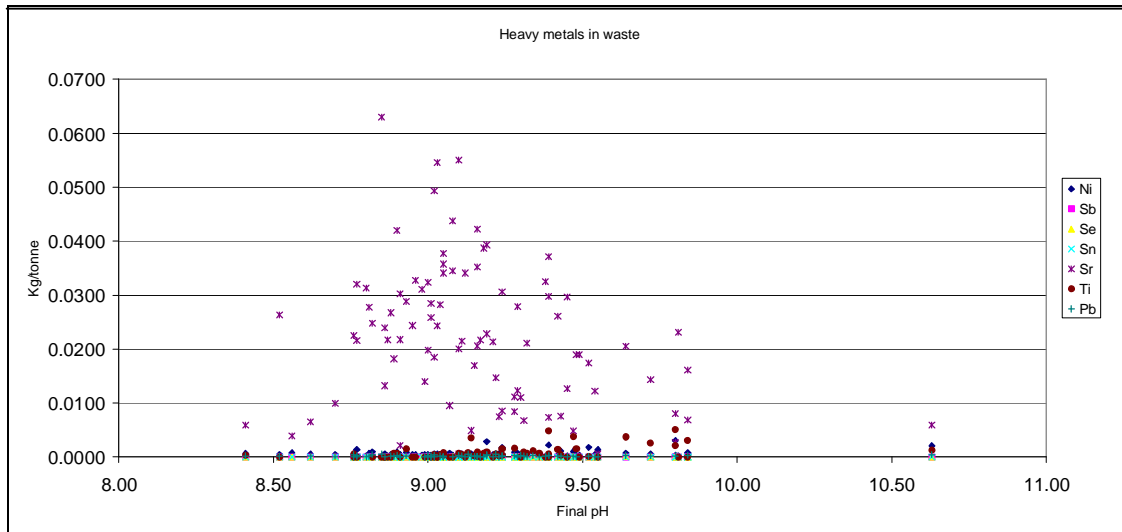


Figure 6-28: Heavy metals in CS waste dump.

Among the heavy metals, strontium dominance is clearly noticeable. Many samples have pH-levels above 8.2. This suggests the presence of significant carbonate species.

Strontium commonly occurs in nature, averaging 0.034% of all igneous rock and is found chiefly as the form of the sulfate mineral celestite ( $\text{SrSO}_4$ ), and the carbonate strontianite ( $\text{SrCO}_3$ ), (BGS, 2005). Of the two, celestite occurs much more frequently in sedimentary deposits of sufficient size to make development of mining facilities attractive. Strontianite would be the more useful of the two common minerals because strontium is used most often in the carbonate form.

Due to the elements being sufficiently similar chemically, strontium behaves in groundwater as if it were calcium. However, no water quality guideline is available for strontium. This point is brought forward to emphasize on the high carbonates presence in CS, and thus its ability to auto-neutralize acidity.

However, there should be huge concern about the quantities of this element in the waste should it find its way in the groundwater.



Figure 6-29: A view of the CS tailings dam.

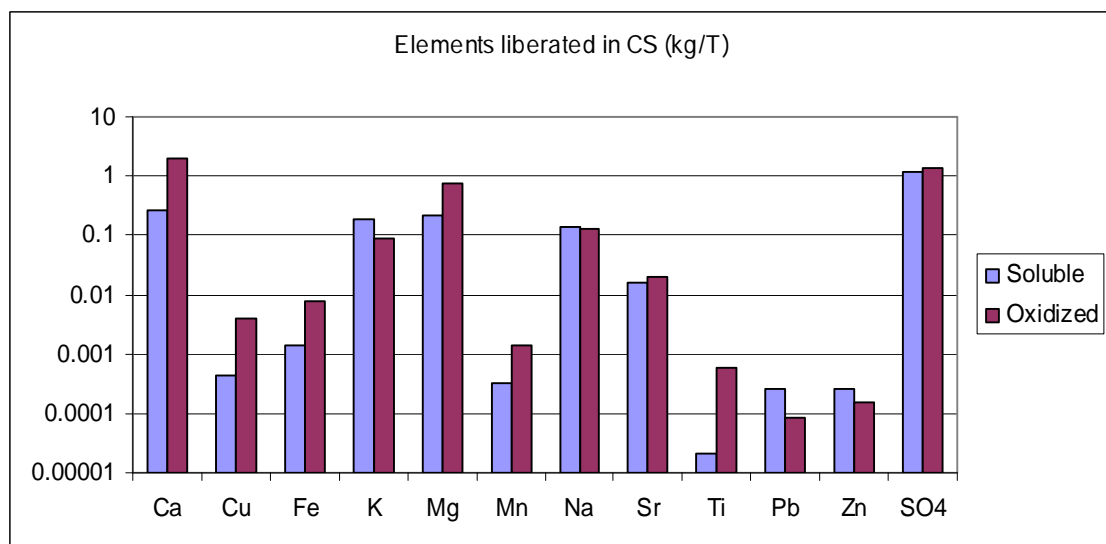


Figure 6-30: Total amount potentially released per element per kg per ton of waste for CS.

Figure 6-30 is a plot of an estimate of the elements already naturally released, against the amount from further oxidation, according to the tonnage of the waste. One obvious observation is the increase in the amount of the majority of the elements as they tend to be oxidised in the compounds where they are found. In general, during oxidation, the final pH is expected to fall, and thus more metals are usually liberated. However, the graph indicates that the final pH did not drop considerably (and therefore did not turn acidic) after the samples were oxidised, and thus the difference in the amount metals released is not significant.

#### 6.1.1.4.2 The Mineralogy of CS

All the tested samples were submitted to the University of the Free State's Geology Department, with the request that they be investigated mineralogically and chemically. X-ray fluorescence and X-ray diffraction testing was undertaken. The Table 6-8 and Table 6-9 below give occurrences of various minerals, as well as percentages in terms of metal oxides at CS.

The following can be inferred from the XRF/XRD results:

- Calcium oxide (CaO) was reported as the major oxide with 37.23%. this indicates the potential of neutralising material that can be expected from the CS waste facility.
- Magnesia (MgO) is also present in considerable amount, thus it is expected that dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) rather than calcite ( $\text{CaCO}_3$ ) dominates the neutralising materials as confirmed in Table 6-9.
- Iron oxide and alumina were also reported in considerable amounts. It is an indication that of the weathered material.

Table 6-8: XRF results obtained from CS waste samples.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	
Average	14.55	2.01	12.55	0.18	25.05	36.73	0.25	0.59	0.90	5.89	98.65
Max value	39.09	3.95	16.55	0.27	20.32	57.01	0.65	2.24	3.08	10.87	
Min value	0.67	0.72	8.03	0.09	14.22	1.64	0.00	0.05	0.32	0.41	
ST DEV	7.31	0.88	22.75	0.03	13.46	15.56	0.14	0.54	0.72	2.92	
% occur (average)	14.74	2.03	13.35	0.18	12.72	37.23	0.25	0.59	0.91	5.96	

Table 6-9: Mineral occurrences in CS obtained by XRD.

Quartz	Phlogopite/ vermiculite	Plagio- clase	Clinochlore	Actinolite	Magnetite	Montmorillonite	Illite	Apatite	Dolomite	Calcite
accessory	major	traces	traces	traces	minor	rare	minor	major	> major	dominant

The Phlogopite/Vermiculite  $[(\text{MgFe,Al})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$ , which is largely produced as a by-product at PMC, can account for the high silica (quartz) and magnesium oxide on the facility. Calcium oxide occurs in significant quantities; it is assumed that it comes from the mineral Apatite  $[\text{Ca}_5(\text{PO}_4)_3(\text{F/Cl/OH})]$ , which in this case is assumed to have the OH-group attached at the end. Dolomite  $[(\text{CaMg}(\text{CO}_3)_2)]$  is not present in WR at all, but the carbonatite minerals in general dominate the mineral occurrences, thus adding the amount of carbonates, together with carbonate strontianite ( $\text{SrCO}_3$ ), that neutralise acidification.

Even though the oxidation reactions of the sulphides of copper released some acidity, no sign of acidity was observed on site. The results of the X-ray fluorescence of the samples are presented below:

Table 6-10: Overall XRF results of Copper Tailings only.

	First batch	Second batch	Average
% of $\text{CaCO}_3$ (Calcium Carbonate) <sup>1</sup>	60.72	61.28	61
% of $\text{CaMg}(\text{CO}_3)_2$ (Dolomite) <sup>1</sup>	25.08	25.89	25.49
% oxides and sulphates <sup>1</sup>	9.35	9.75	9.55
% silicates and alumino-silicates <sup>2</sup>	4.85	3.08	3.96

<sup>1</sup>calculated using XRF keys by Norrish & Hutton technique.

<sup>2</sup>calculated using ABATES software.

Table 6-9 above is a combination of two techniques aiming at determining the acid or alkaline contents of samples. While the Norrish and Hutton technique is a universal method for mineral analysis of solid samples, the second is a tool that provides geochemical analysis. It stands for Acid-Base Accounting Tools Earth Systems (ABATES). This table provides with the percent composition of the waste samples obtained from the Copper Tailings. Based on these results, it was

possible using the ABATES software to estimate the Net Acid Producing Potential (NAPP), (Australian guidelines) from the weight percent mineralogical data.

The following assumptions were made in the settings of the software:

1. Estimates of the Acid Producing Potential (APP) and the Acid Neutralising Capacity (ANC) can be made from mineralogical data.
2. This tool produces a good estimate of the Net Acid Producing Potential of various rock types based on accurate and comprehensive mineralogical data. However, it does not intend to replace chemical analysis or kinetic tests.
3. In practice, some reactions may not go to completion or uniform mixing of acid generating and acid neutralising materials may not occur.
4. The Acid Neutralising Capacity (ANC) estimated with this tool is equivalent to a titration to an endpoint of 9.5. Hence, both acid and acidity generation are included in the NAPP estimate.

Table 6-11: NAPP results using the ABATES software.

Totals	Kg H <sub>2</sub> SO <sub>4</sub> per tonne material
Acid Producing Potential (APP)	0.00
Acid Neutralising Capacity (ANC)	868.91
Net Acid Producing Potential (NAPP) = (APP-ANC)	-868.91

Although the final numerical result is not the same compared to the Acid-Base Accounting Cumulative Screen tool (ABACUS), (Usher, 2000) that was used to interpret most of the results and draw the graphs, the final outcome is the same: there is enough or excess neutralising potential present on site.

#### 6.1.1.4.3 Tonnages estimations of the Copper Sulphide

Table 6-12: Physical parameters of the Copper Sulphide dam

Area of dam (m <sup>2</sup> )		Height(m)	Specific gravity(kg/m <sup>3</sup> )	Volume of waste(m <sup>3</sup> ):
Top	2.96E+06	42	1760	2.17E+08 (PMC estimations, 2008)
Bottom	4.35E+06			mass of waste(Tonnes)
				3.82E+08

#### 6.1.1.4.4 Conceptual model of the Copper Tailings dam

The aim of this conceptual model is depict all the physico-chemical processes happening on the Copper Tailings from the deposition of the waste to the influence on the groundwater. The objectives of this model are:

- Explain the general processes on the waste facility at a smaller scale.
- Explain the hydrogeological processes.
- Explain the hydrochemical processes.



# The Copper Tailings (CS)

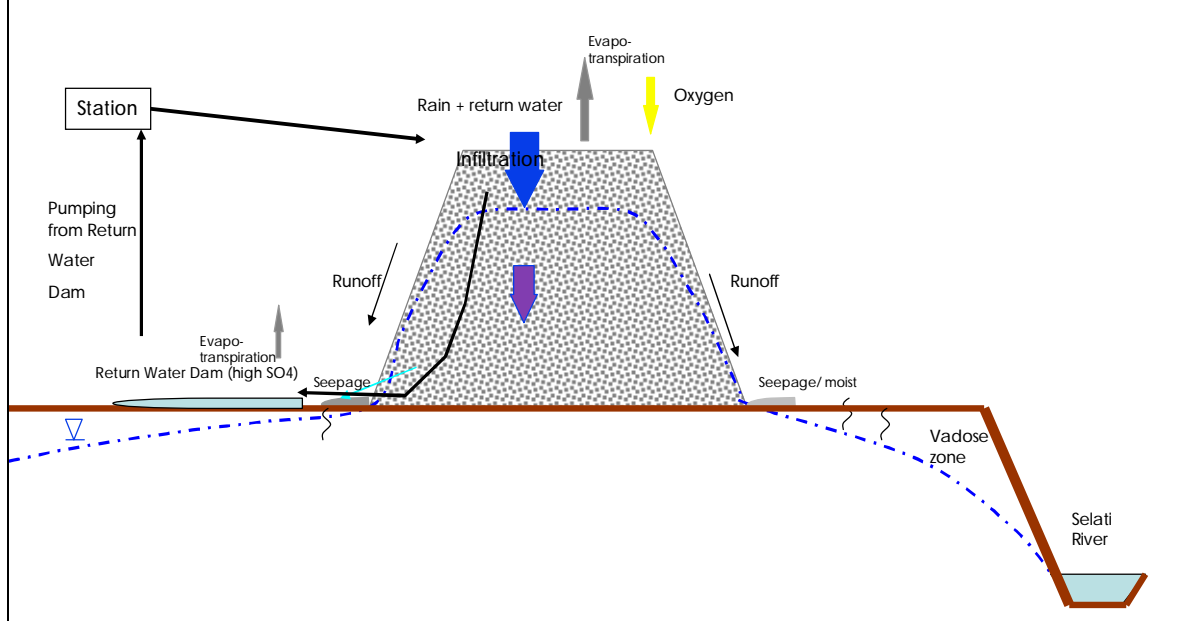


Figure 6-31: General conceptual model of the Copper Tailings.

The general conceptual model for the Copper Tailings is discussed as follows:

- These tailings are derived from the carbonatite ore that has had most of the sulphides removed by floatation processes. Therefore, there is abundant neutralisation potential in the dump.
- However, available sulphur analysis for the tailings had a content of at least 0.2%.
- To deposit the tailings, water is pumped from the Return Water Dam, passes to a station, then to the tailings, then back to the Return Water Dam.

- Seepages are observed on the sidewalls, and therefore it can be assumed that there is high piezometric level within the tailings dam.
- Sulphate values are expected to be high or low depending on the characteristics of the ore dumped at a particular location of the tailings.

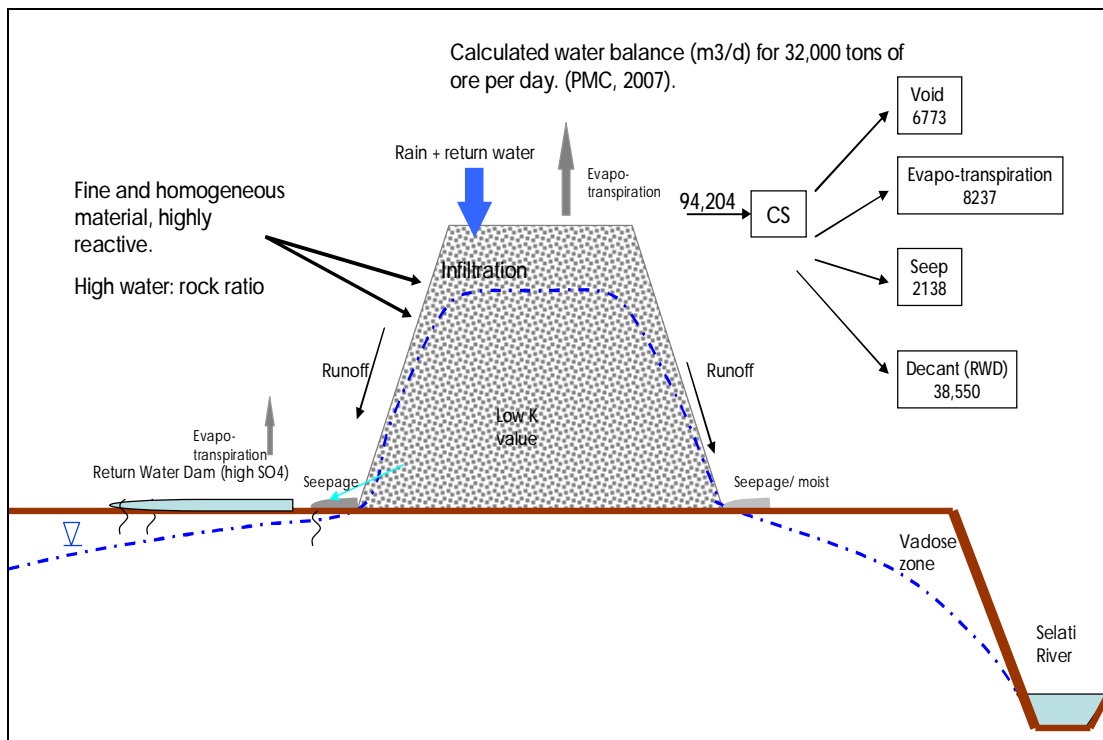


Figure 6-32: Hydrogeological model of the Copper Tailings.

The hydrogeological conceptual model is discussed as follows:

- The tailings is permanently supplied with water, thus it is very unlikely that a vadose zone exists between the tailings and the surface. However, it is expected that this water level decreases when supply stops.
- As seen on the water balance, decant is very important, an indication that should water supply stop, the water level should decrease accordingly.

- The waste material is very fine and also very reactive in terms of surface reactivity.
- The tailings is constructed in such a way that some of the seepages that can be channelled through toll drains should go to the Return Water Dam.
- The topography of the surface is southwards towards the Selati River, thus over time, these tailings are expected to influence the quality of the water in the river.

Attention should be brought to the fact that different kind of waste is produced daily out of the 32,000 tons of ore produced per day, and thus each waste facility receives only a portion accordingly.

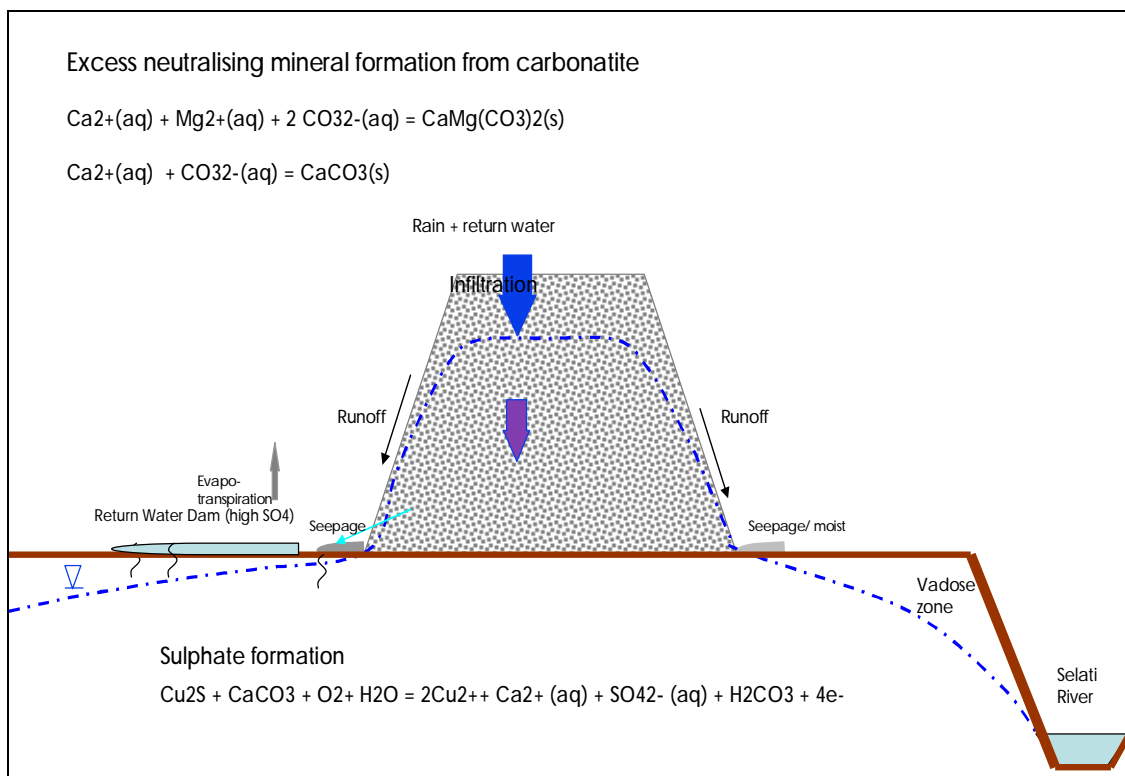


Figure 6-33: Hydrochemical conceptual model of the Copper Tailings.

The hydrochemical conceptual model of the Copper Tailings is discussed as follows:

- Copper sulphide waste is deposited on these tailings.

- Because it is obtained from the carbonatite ore body, high calcium content has been observed in the tailings.
- Calcite and dolomite are the carbonates responsible for the neutralisation.
- High sulphate values are expected where the ore source had a high sulphides content. This is evident from the results of the groundwater samples taken from boreholes close to the tailings dam.
- Because calcium is expected to be present in large amount, together with sulphates, the water is also expected to be saturated with gypsum (hydrated calcium sulphate).
- Since dolomite and calcium control the quality of the water, pH values are expected to range between 7.5 and 9.5, values at which these two minerals reach saturation in the water.
- Due to the chemically reactive nature of the tailings material, high in sulphate content is observed in the tailings return water.

#### 6.1.1.5 The Magnetite Tailings (HT, LT) dams

The approach to sampling at both magnetite tailings was to use an augur rig to drill to a depth of approximately 4m along various benches of the dams. It must be noted that at the time of the investigation, tailings deposition had been resumed on these dams as well, and it was possible to sample across the extent of upper elevations of the dams.

#### 6.1.1.5.1 The High-Titanium (HT) dam

The sampling positions can be seen on the Figure 6-34 below.

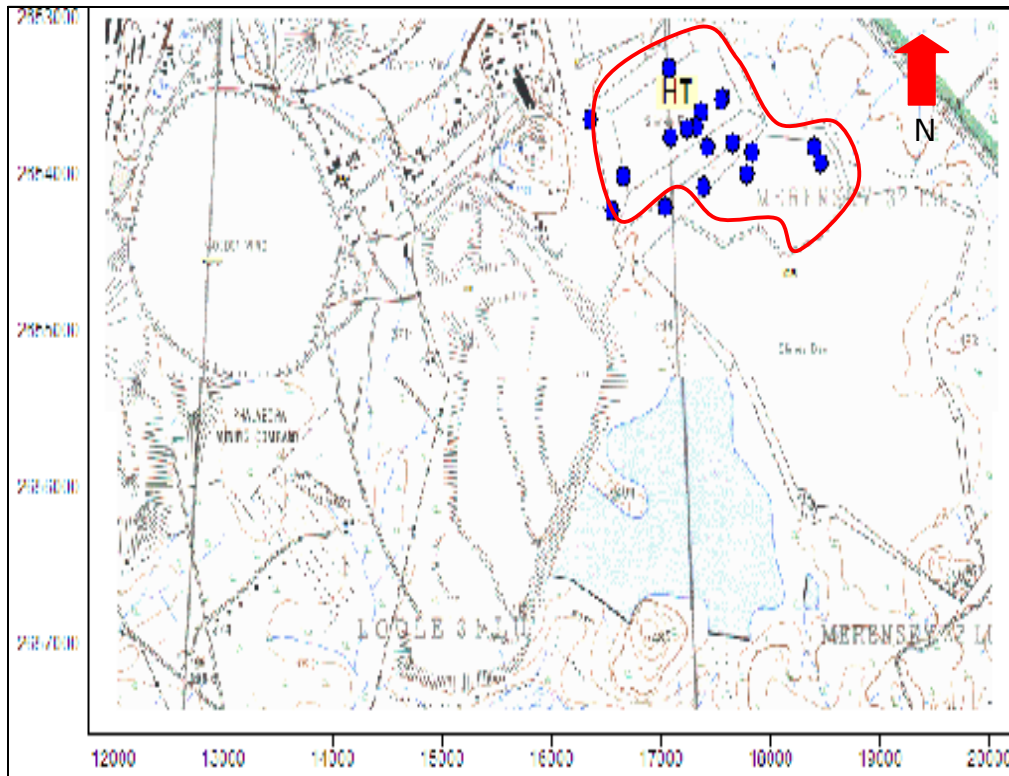


Figure 6-34: Sampling points at HT (PMC 2007).

#### 6.1.1.5.2 The Acid-Base Accounting of the High-Titanium dump

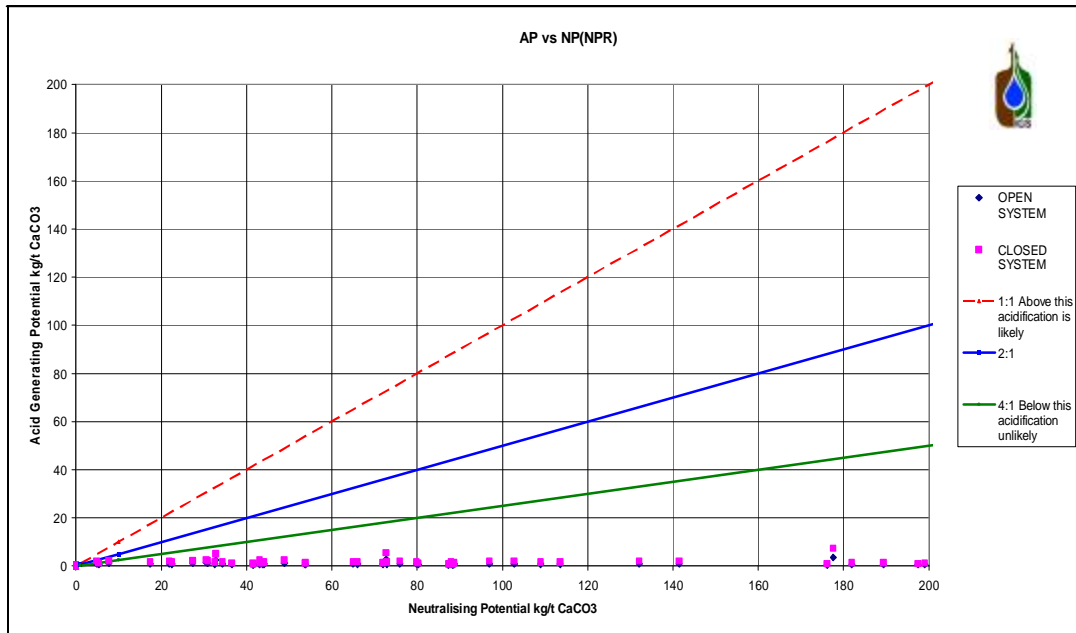


Figure 6-35: AP vs. NP of HT dam.

Acidification from this dam is very unlikely. The mineralogy of the dam shows that iron (III) occurs as the major oxide compound, (84.23%), (Table 6-13). Iron oxidizes to iron(III) oxide and oxygen is reduced forming iron(III) oxide as  $4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$ . However, the black color of the tailings is due to magnetite. The mineral magnetite itself is neither acid forming, nor reactive to atmospheric conditions. Iron is only released under oxidation at low pH, however, the final pH values after oxidation are still high enough for metal release, (Figure 6-39).

Nevertheless, iron does occur with gangue mineral that are susceptible to reacting with atmospheric conditions; but these are in very minute amounts, (Figure 6-36), thus responsible for some negative values of the Net Neutralization Potential.

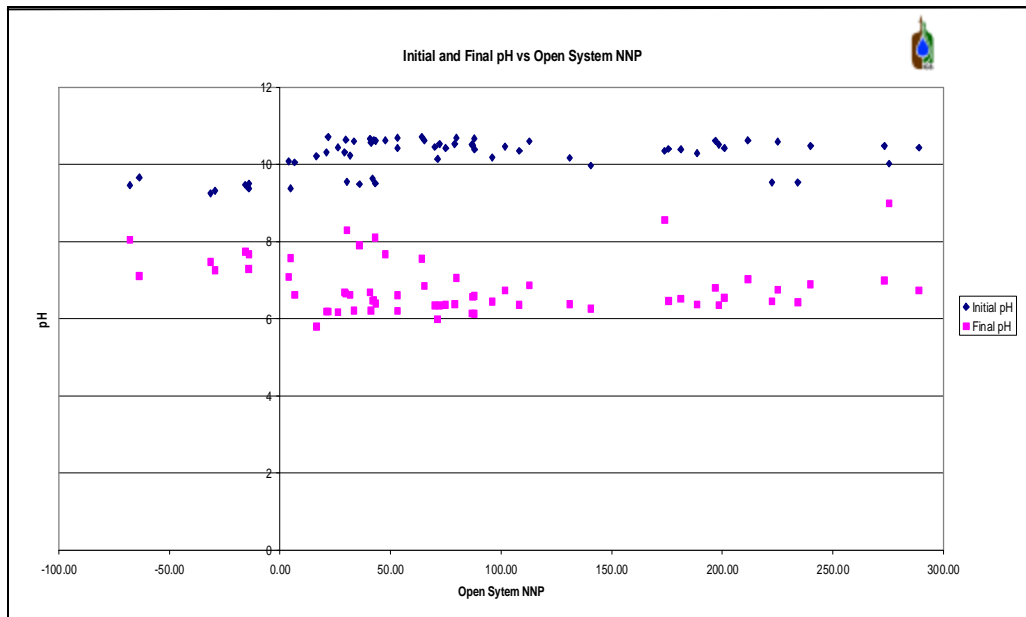


Figure 6-36: pH vs. NNP diagram for HT

The final pH values are within the near-neutral-neutral range, (Figure 6-36). This has a lot to do with the “inert” metals that are present on the waste dam.

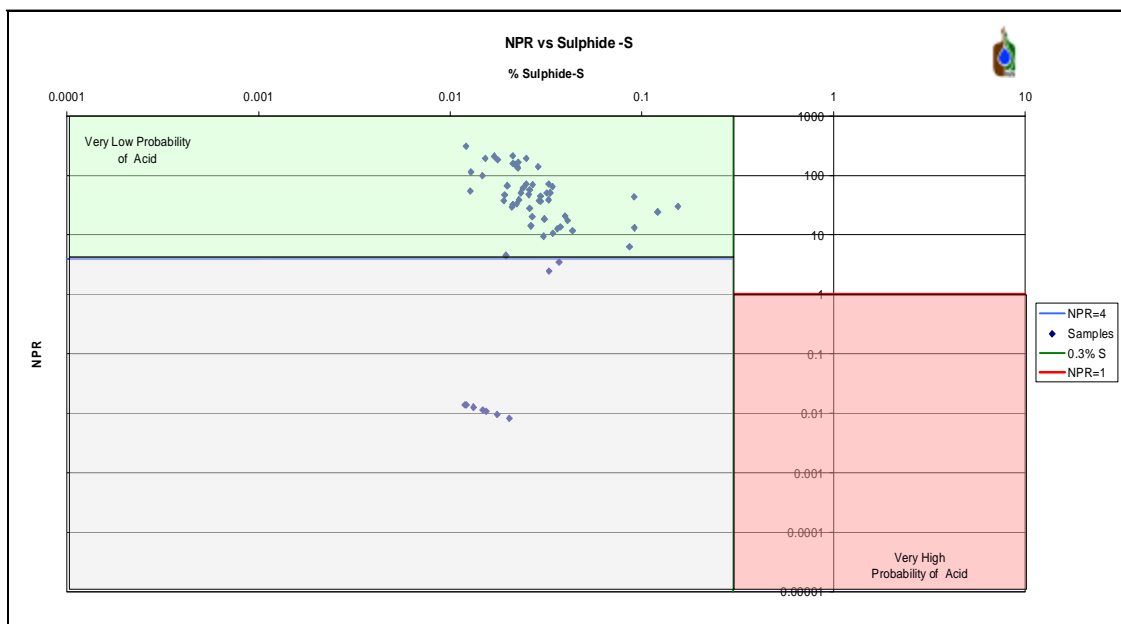


Figure 6-37: NPR vs. Sulphide diagram for HT.

This graph (Figure 6-37) confirms that acid generation is unlikely, the amount of sulphide present cannot sustain acidity.

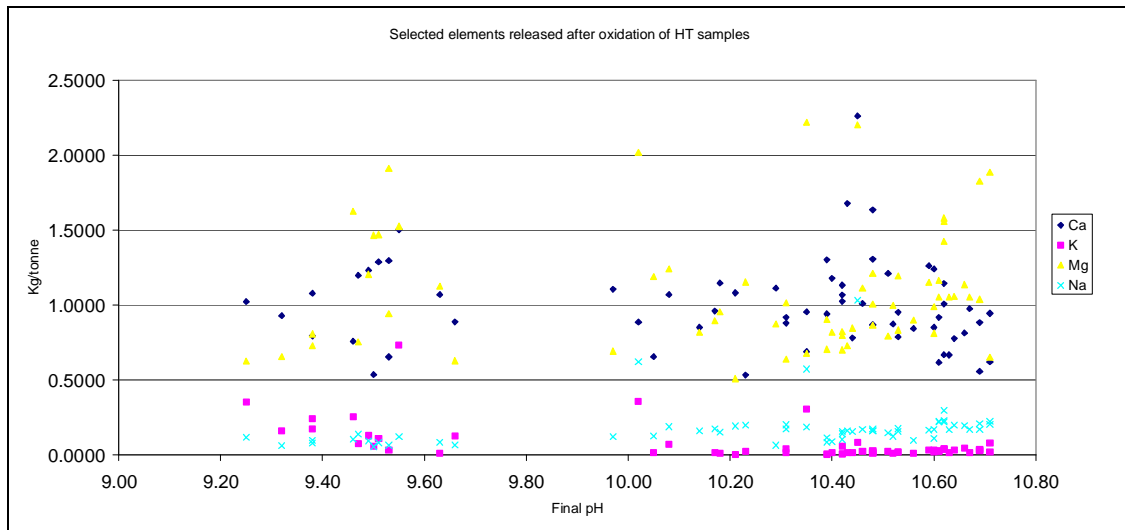


Figure 6-38: Elements released after oxidation in HT waste samples.

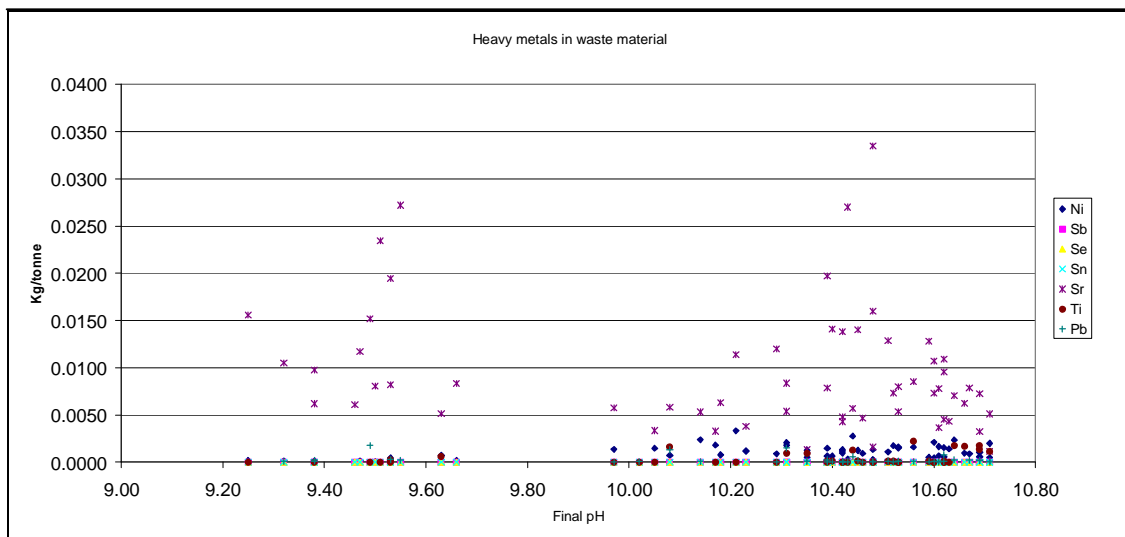


Figure 6-39: Heavy metals in HT (notice Strontium).

The more inert nature of the magnetite tailings will be reflected in the associated boreholes, (Section 6.3.3 below). However, here these graphs firstly show lower



sulphate domination and a roughly equal contribution from calcium, magnesium and strontium in the waste material, two of the most important sources of carbonates with dolomite and strontianite.

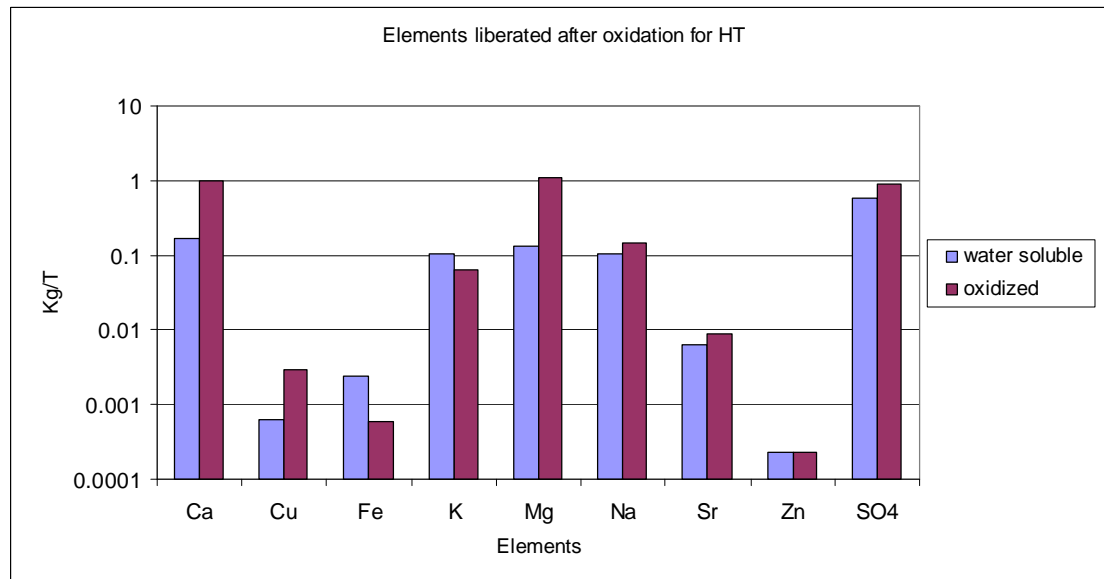


Figure 6-40: Oxidized vs. water-liberated elements for HT.

Only the “alkaline” species are liberated in noticeable amounts. All other elements which could participate in the acidification are thus damped by these “alkaline” species. A lot of metal are released, but in very negligible quantities.

#### 6.1.1.5.3 The Mineralogy of HT

The results from mineralogy of HT gives an idea of the dark colour of the site, and a reason why the 1:1 v/v waste from HT is heavier than the same proportions of the other waste deposits.

Table 6-13: XRF results obtained from HT waste samples.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	
Average	1.89	0.91	84.23	0.24	4.97	4.15	0.16	0.10	2.19	0.77	99.65
Max value	5.14	1.78	91.62	0.32	7.12	8.76	0.51	0.38	3.87	1.93	
Min value	0.08	0.10	77.05	0.18	3.24	1.25	0.00	0.00	0.82	0.11	
ST DEV	1.20	0.27	4.26	0.0	1.11	2.57	0.15	0.08	0.56	0.48	
% occur (average)	1.90	0.91	84.53	0.24	4.99	4.17	0.16	0.10	2.20	0.77	

Table 6-14: Mineral occurrences in HT , obtained by XRD.

Quartz	Phlogopite/ vermiculite	Plagio- clase	Clinochlore	Actinolite	Magnetite	Illite	Apatite	Dolomite	Calcite
accessory	minor	minor	accessory	accessory	dominant	minor	accessory	minor	minor

The following conclusions were drawn from the mineralogy of the Hi-Ti:

- Iron was reported as the overwhelming oxide in the sample. Though it was reported as haematite, the facility is actually a magnetite dump. This is confirmed by the XRD results.
- Other elemental oxides are very limited. This contributes to the inactiveness of the tailings.



Figure 6-41: Sampling at HT. Notice the colour of the waste.

#### 6.1.1.5.4 Tonnages estimations of the Hi-Ti

Table 6-15: Physical parameters of the Lo-Ti waste facility.

Area (m <sup>2</sup> )	Top	710000
	bottom	1740000
Height (m)	52	
Specific gravity (kg/m <sup>3</sup> ) of grains	2620	
Volume of waste (m <sup>3</sup> ) PMC estimations	7.47E+07	
Mass (Tons) estimated	1.96E+08	

#### 6.1.1.5.5 The Low-Titanium (LT) dam

The low-titanium (LT) dam is very similar to the HT, but, according to the mine staff, the concentration of titanium waste is of smaller scale compared to HT. This dump is the closest to the Kruger National Park (KNP), and thus its sampling was of great importance, despite the dam being the smallest of all the facilities. The material being fine, it is constantly blown to the KNP during windy conditions. However, a binder was placed at the top of the tailings to suppress the magnetite dust from getting to the KNP.

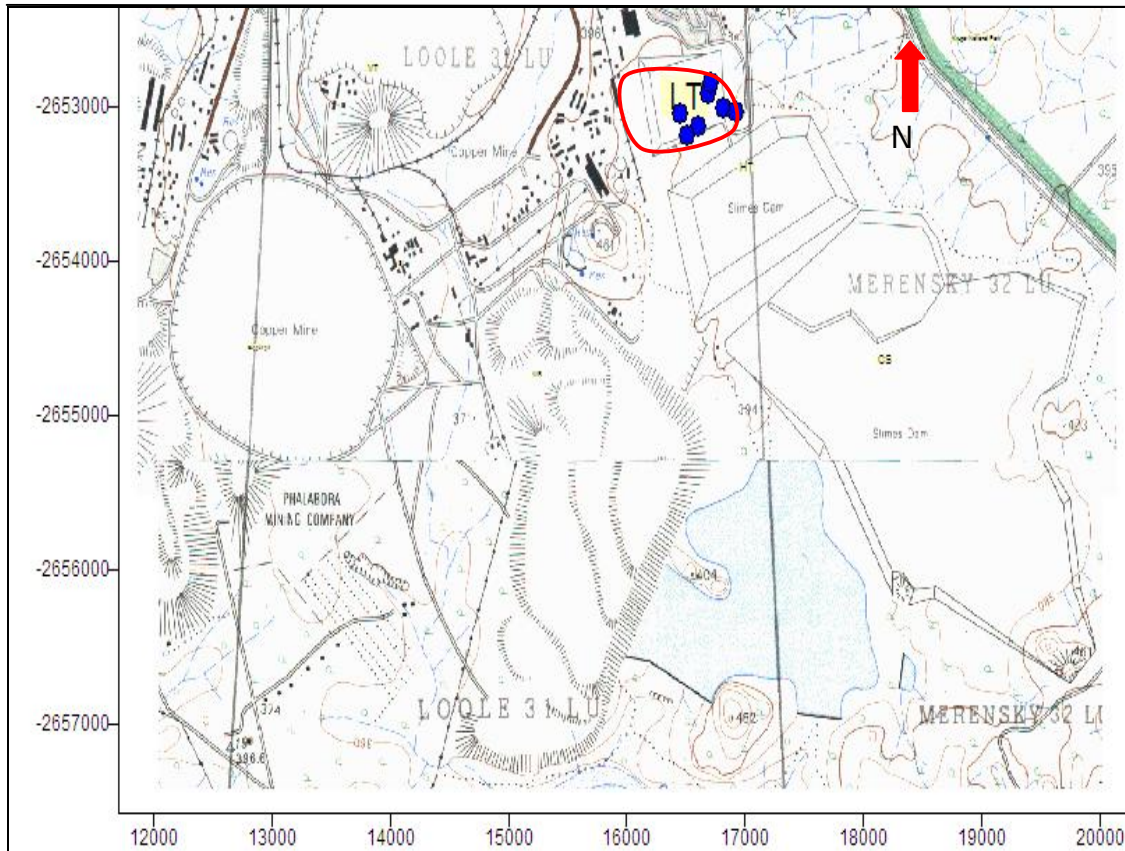


Figure 6-42: Sampling points on LT.

#### 6.1.1.5.6 The ABA of LT

Due to the size of the dam, only few samples were collected. However, these samples were extensively analysed and the analyses were satisfactory enough to give an assessment of the chemical activities happening at LT.

As can be seen on the Figure 6-44, the all the samples' final pH values fall within the circum-neutral range after oxidation, thus one could expect the dam to release a non significant amount of acidity, and the NPR vs. %S diagram below asserts that the probability of acidity is very low.

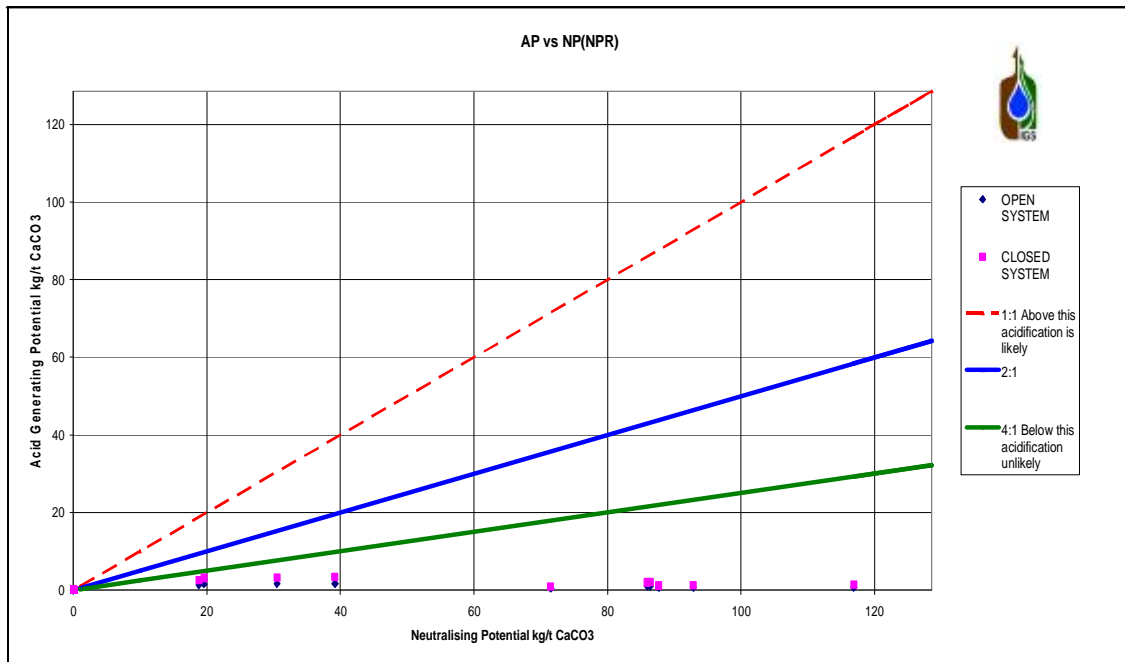


Figure 6-43: NPR diagram of LT.

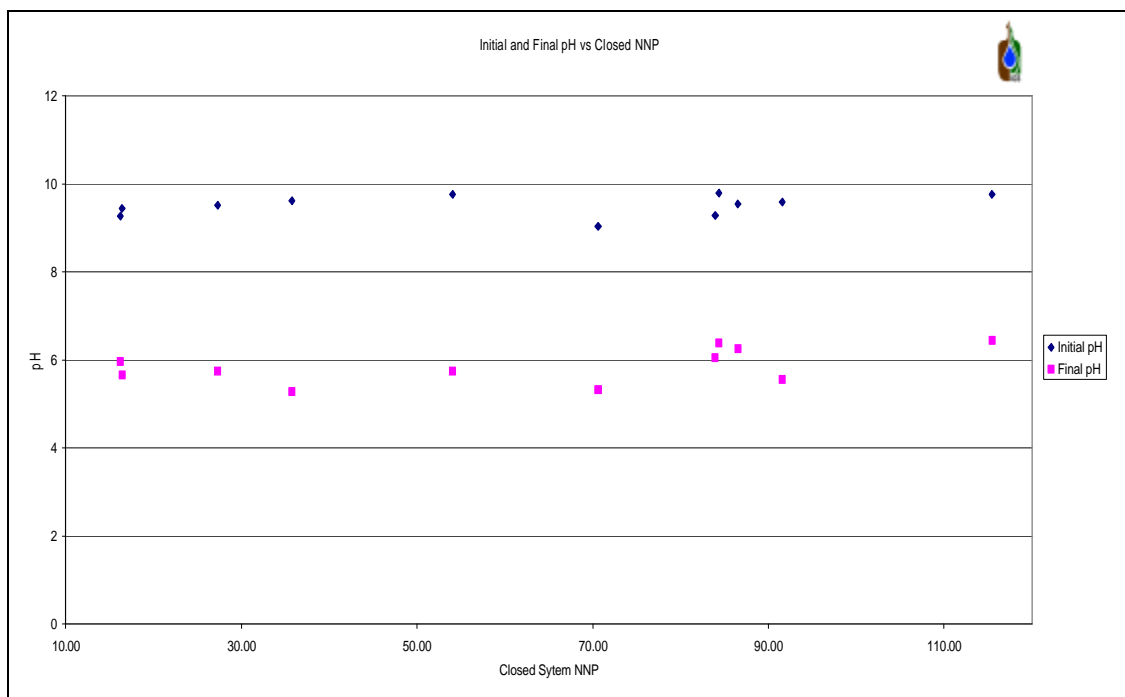


Figure 6-44: Final vs. initial pH diagram for LT.

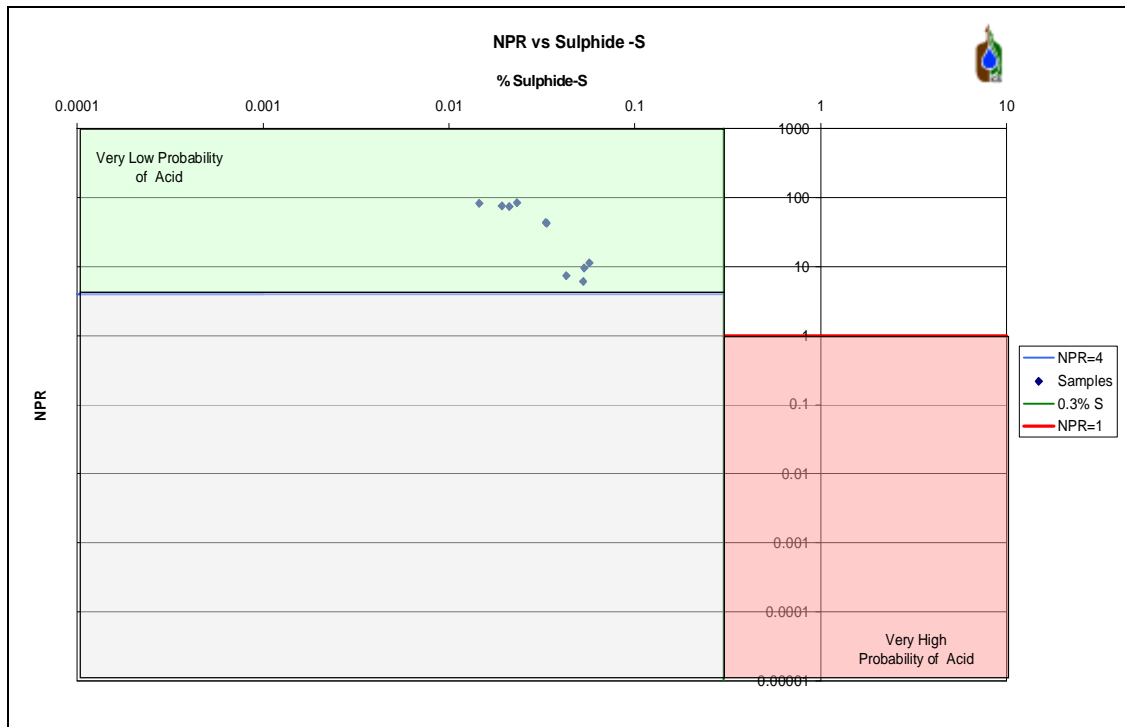


Figure 6-45: NPR diagram of LT.

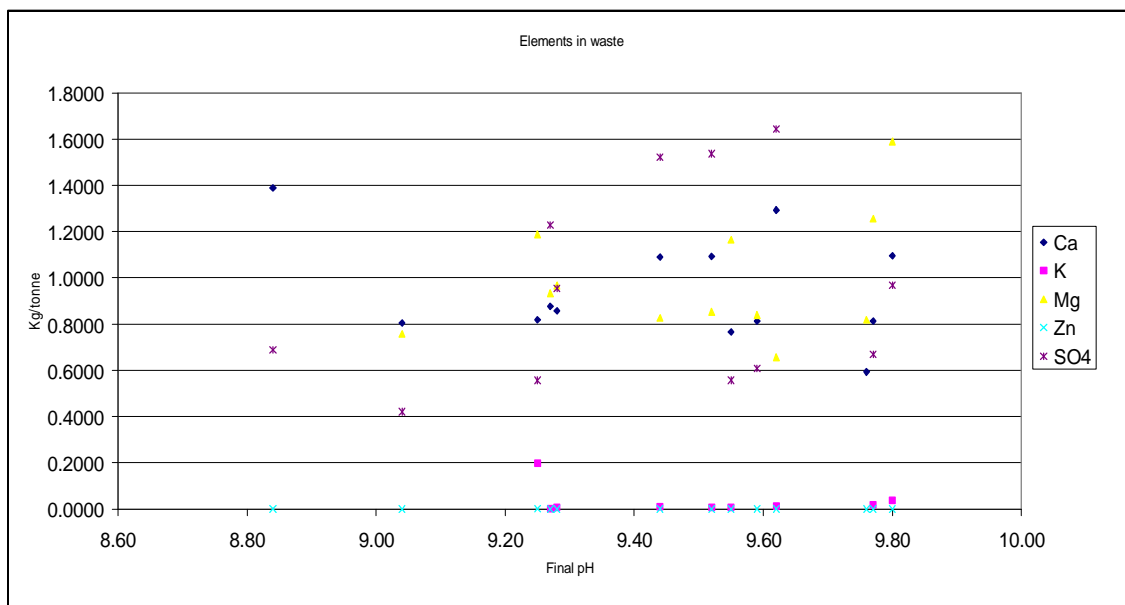


Figure 6-46: Elements in LT waste after oxidation.

When considering Figure 6-46, it is noticeable that calcium and magnesium are among the elements released after oxidation, although in minute amounts.

However, sulphides were not in sufficient quantities to participate in any acidification process, (Figure 6-45).

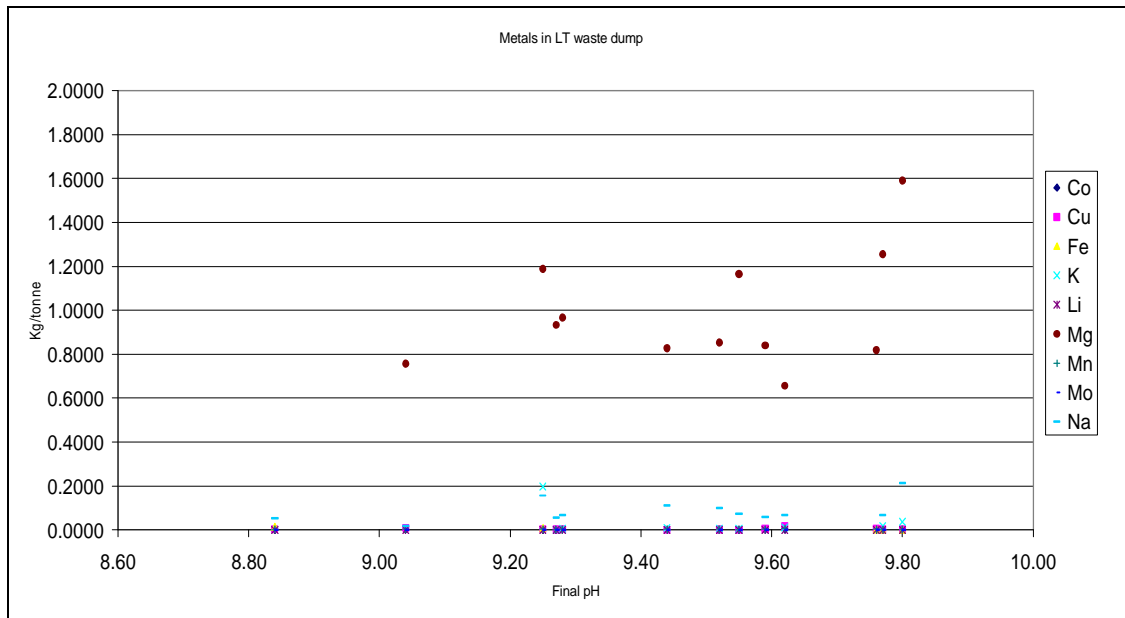


Figure 6-47: Metals in LT waste material.

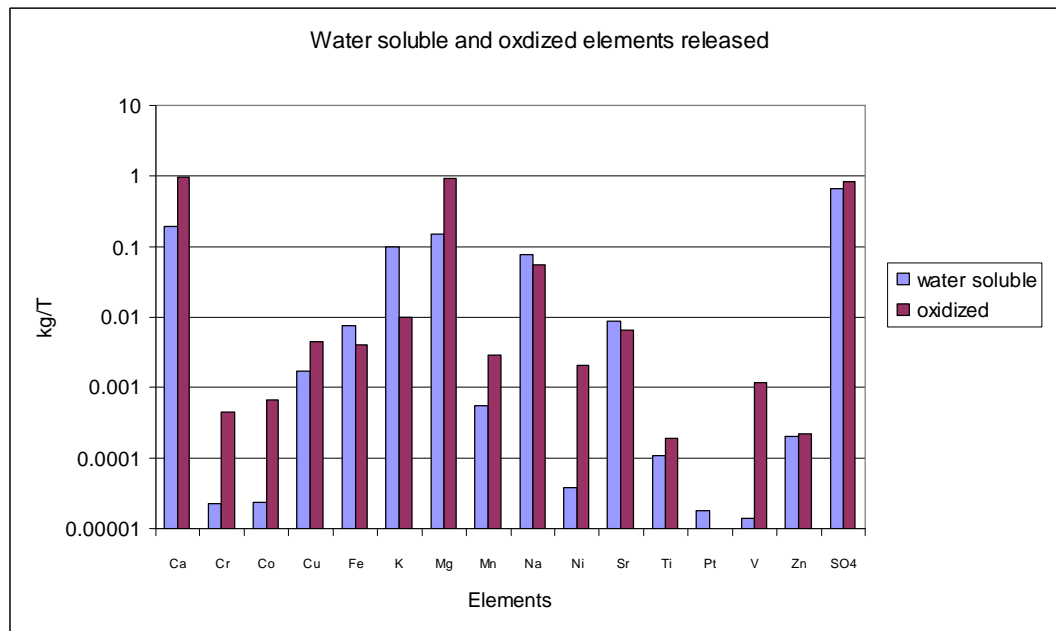


Figure 6-48: Elements released after further oxidation for LT waste material.



Elements are released in very small quantities after oxidations, this confirms the inert characteristic of the dump, Figure 6-48.

#### 6.1.1.5.7 The Mineralogy of LT

Both HT(High-Titanium and magnetite) dam and LT (Low titanium and magnetite) dam obtained their names from the iron oxide and titanium present in the waste dumps. Quantitatively, LT is relatively small and the tailings material inert, when compared to the other dumps.

The following conclusions were drawn from the mineralogy of the Lo-Ti:

- Iron was reported as the overwhelming oxide in the sample. Though it was reported as haematite, the facility is actually a magnetite dump. This is confirmed by the XRD results.
- Other elemental oxides are very limited. This contributes to the inactiveness of the tailings.

Table 6-16: XRF results obtained from LT waste samples.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	
Average	1.10	0.59	89.53	0.23	3.87	1.85	0.25	0.05	1.76	0.35	99.56
Max value	1.27	1.02	92.44	0.26	4.67	2.68	0.58	0.08	2.63	0.74	
Min value	0.83	0.13	86.06	0.20	3.41	1.10	0.00	0.00	0.92	0.11	
ST DEV	0.19	0.45	2.91	0.02	0.59	0.68	0.24	0.03	0.94	0.29	
% occur (average)	1.09	0.59	89.92	0.22	3.88	1.85	0.25	0.04	1.76	0.34	

Table 6-17: Mineral occurrences in LT obtained by XRD.

Quartz	Phlogopite/ vermiculite	Plagio- clase	Clinochlore	Actinolite	Magnetite	Montmorillonite	Illite	Apatite	Dolomite	Calcite
N/A	minor	N/A	N/A	N/A	dominant	N/A	traces	traces	traces	N/A

#### 6.1.1.5.8 Tonnages estimations of the Lo-Ti

Table 6-18: Physical parameters of the Lo-Ti waste dump.

Area of dam (m <sup>2</sup> )		Height (m)	Specific gravity(kg/m <sup>3</sup> )
TOP	200000	38	2540
BOTTOM	430000		
Volume of waste(m <sup>3</sup> )			
PMC estimations : 7.56E+06			
mass of waste(Tonnes): 1.92E+07			

#### 6.1.1.5.9 Conceptual model of the Magnetite Tailings

The aim of this conceptual model is depict all the physico-chemical processes happening on the Magnetite Tailings in general from the deposition of the waste to the influence on the groundwater. The objectives of this model are:

- Explain the general processes on the waste facility at a smaller scale.
- Explain the hydrogeological processes.
- Explain the hydrochemical processes.

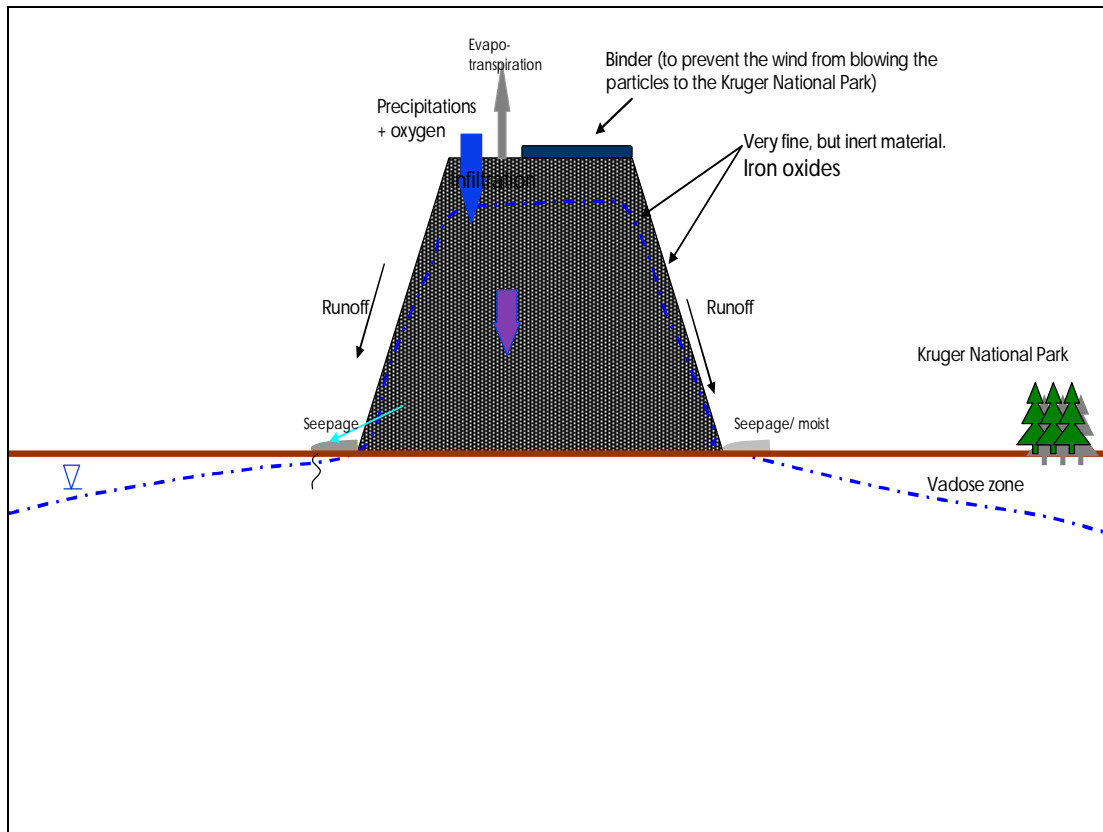


Figure 6-49: General conceptual model of the Magnetite Tailings.

The general conceptual model of the magnetite tailings is discussed as follows:

- The particles are so fine, a chemical binder was put at the top of the tailings to prevent the particles from reaching the Kruger National Park when the wind blows.
- Though the particles are fine, they are chemically inert as magnetite does not react with atmospheric conditions.
- High sulphate seepage have been observed though, and this is due to leakage from a refinery built upstream of the tailings.
- Permanent water pumping onto the tailings maintained the water level high enough, and low hydraulic conductivity of the grain is also expected.
- Any borehole located upstream the tailings has acceptable levels of sulphate concentrations unlike the boreholes downstream. This is an indication of the flow direction.

- Particles also have high surface reactivity as they very fine.
- The tailings are almost entirely black due to the presence of magnetite.

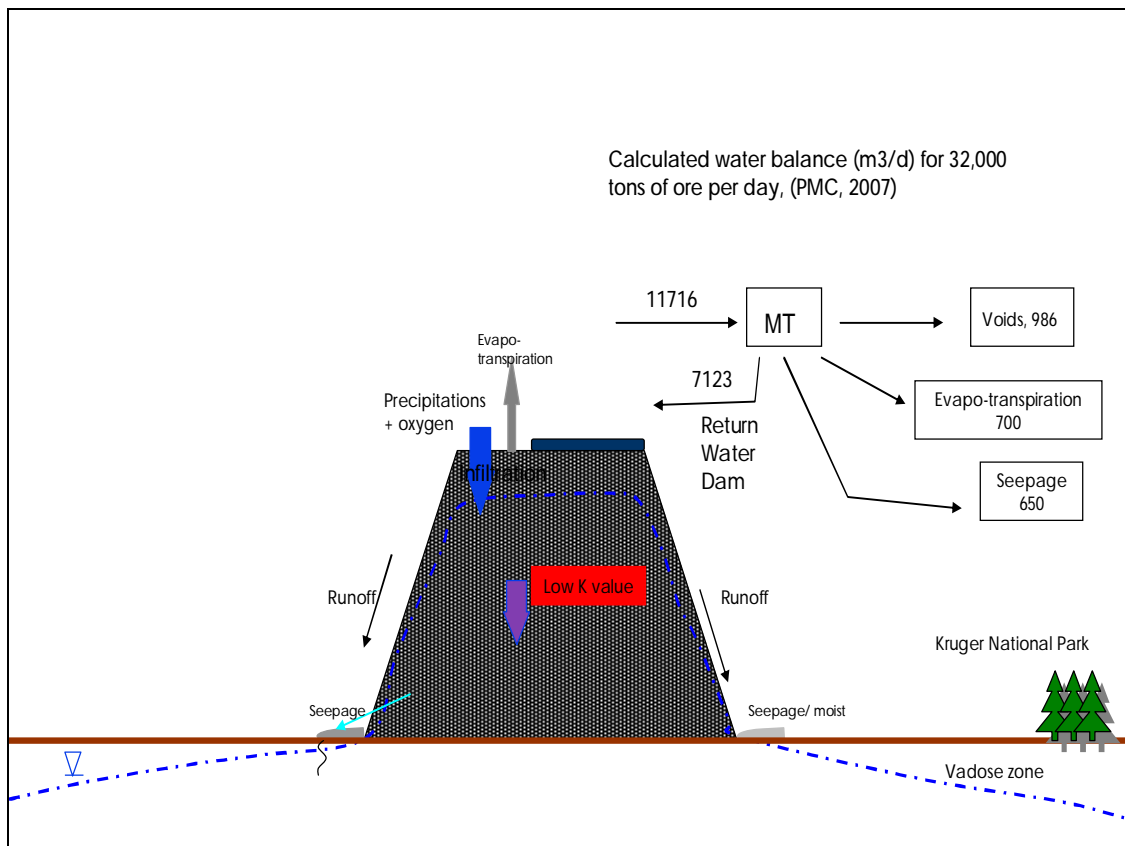


Figure 6-50: Conceptual model for the Magnetite Tailings.

Recently, the mine has been exporting the Magnetite Tailings to foreign buyers. Furthermore, some vegetation has been observed onsite and it is believed that a positive outcome (i.e. vegetation) is possible after mine closure.

## 6.2 X-Ray Diffraction/Fluorescence, investigation of rock samples (summary for all facilities)

The mineral composition of a sample will ultimately determine the contribution of different species in the system as a whole. Particularly where assessments that are more detailed are required and geochemical modelling is used, mineralogical determinations are a vital component in the evaluation. Ambiguities on the interpretation of ABA results can also be greatly reduced by including mineralogical results (Paktunc, 1999).

### 6.2.1 Introduction

All the tested samples were submitted to the University of the Free State's Geology Department, with the request that they be investigated mineralogically and chemically. X-ray fluorescence and X-ray diffraction testing was undertaken.

#### 6.2.1.1 Method of investigation

Some of the samples were already finely ground, while others were chip samples. In order to conduct an X-ray diffractometric investigation of the samples, the latter were also crushed and ground to a grain size of minus 50 micron for semi-quantitative X-ray diffraction analysis. The powdered samples were analysed with a Siemens D-5000 X-ray diffractometer using monochromatic  $\text{CuK}\alpha$ -radiation and the PC-PDF2 computer programme for mineral identification.

##### 6.2.1.1.1 Results

Table 6-19: Summary of mineral oxides on the waste facilities.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MnO}$	$\text{MgO}$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{TiO}_2$	$\text{P}_2\text{O}_5$
HT	1.90	0.91	84.24	0.24	4.98	4.16	0.16	0.10	2.19	0.77
CS	14.55	2.01	25.01	0.18	12.55	36.73	0.26	0.59	0.90	5.89
WR	41.51	8.99	15.51	0.18	9.63	15.99	1.10	2.77	1.60	2.26
LT	1.10	0.59	89.53	0.23	3.87	1.85	0.25	0.05	1.76	0.35
VR	44.86	3.73	5.53	0.08	26.00	16.72	0.06	2.07	0.50	0.37
VT	39.11	6.57	6.70	0.07	22.21	15.77	0.13	3.41	1.06	4.63

Table 6-20: Summary of mineralogy on the waste facilities

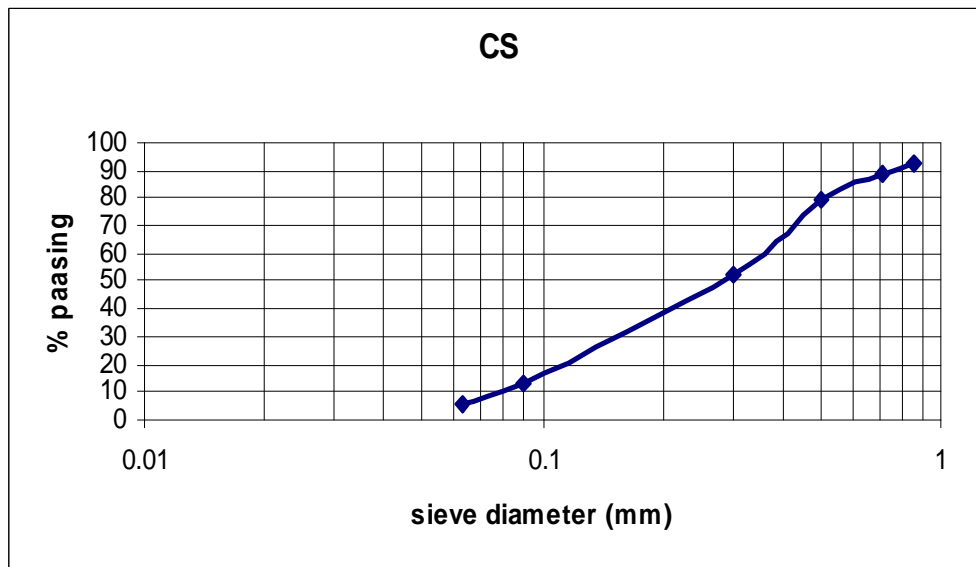
	Quartz	Phlogopite/ vermiculite	Plagio- clase	Chlinochlore	Calcite	Hematite	Montmo- rillonite	Illite	Apatite	dolomite
HT	Accessory	Minor	Minor	Accessory	Minor	Dominant	n/a	Minor	Accessory	minor
WR	Accessory	Minor	Dominant	Minor	Minor	Minor	Minor	Major	Major	minor
CS	Accessory	Major	Traces	Traces	Dominant	Minor	Minor	Minor	Major	> major
LT	n/a	Minor	n/a	n/a	n/a	Dominant	n/a	Traces	Traces	Traces
VR	Accessory	Dominant	Accessory	Minor	Rare	n/a	Minor	Minor	n/a	Rare
VT	Accessory	Major	Minor	Minor	n/a	n/a	Minor	Major	Rare	n/a

Dominant > 40%  
 Major 10-40%  
 Minor 2-10%  
 Accessory 1-2%  
 Rare/traces <1%

#### 6.2.1.1.2 Particle Size Analyses and Estimates of Surface Area

Several samples for the finer grained materials, namely the copper tailing and Hi-Ti and Lo-Ti tailings, were selected for sieve analysis to obtain the average particle size distribution.

The average results for these are provided on the graphs below:



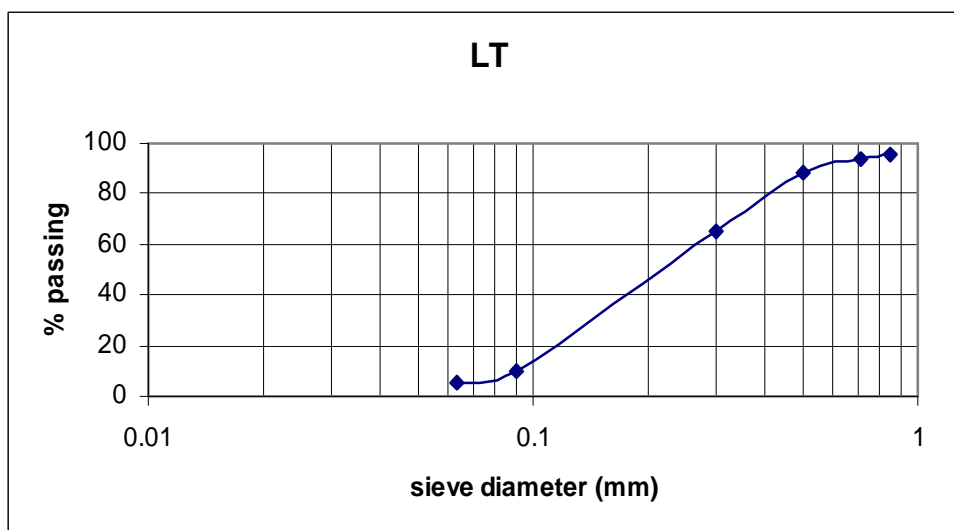
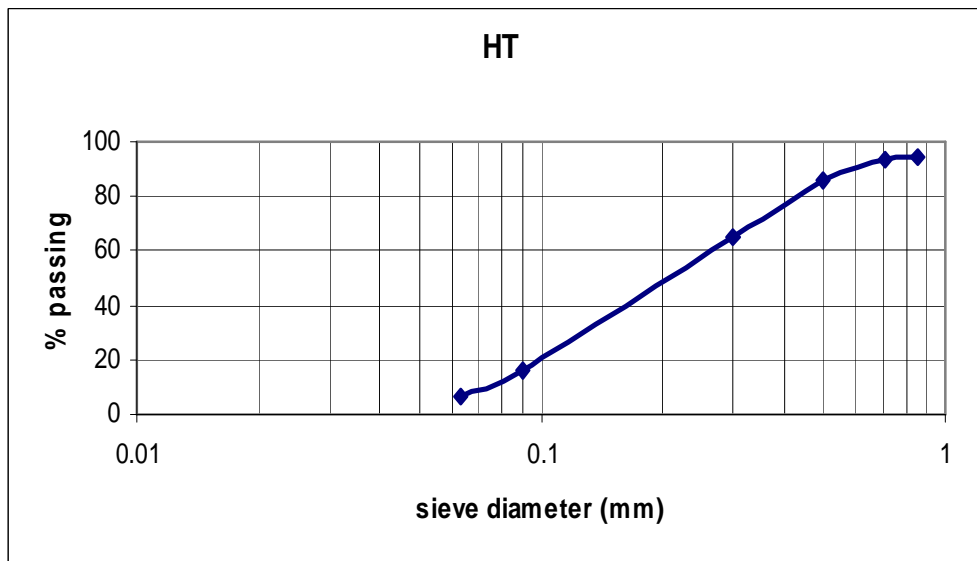


Figure 6-51: Average sieve analysis results for fine-grained material.

From this, the estimated reactive surface areas were estimated. This estimate was obtained using the Grain 3.0, a spreadsheet to calculate grain-surface area from sieve analyses (MDAG Publishing, [www.mdag.com](http://www.mdag.com)). For the waste rock, visual estimation was used to suggest a starting point for particle size distribution. The bulk density of each waste was also estimated in the samples tested, using volumetric estimations.



Table 6-21: Estimated grain surface areas (m<sup>2</sup>/kg) for major waste types.

Waste Rock	0.20
Hi-Ti	5.06
Lo-Ti	5.27
Copper Tailings	6.59

Not all the waste facilities have the same reactivities. Bulky coarse materials like those dumped on the Waste Rock react slowly. According to Table 6-20, one (1) kilogram of Copper Tailings waste will react in a corresponding area of 6.59 square metres, whereas the same mass of Waste Rock will react only in 0.20 square metres, a reactivity that is thirty-three (33) times smaller than that of the Copper Tailings. Table 6-20 above classifies the waste facilities in increasing order of reactivity.

### 6.3 Groundwater monitoring

The water analysis from the mine was taken during various intervals of years.

The boreholes locations vary across the site, (Figure 5-2).

A proper study of the geology of the terrain is a better parameter of appreciating the physico-chemical parameters of natural groundwater, as this latter depends on:

- rock types
- source recharge/characteristics
- flow path, (residence time of water in formation).
- vegetation types

To assist in understanding the effect of the waste on the groundwater resources, the monitoring data as collected by PMC was used; PMC has been undertaking sampling at various as early as 1993. All together, more than 1700 groundwater samples have been collected from 87 sampling sites for the 15-year period. Within the same period and area, over 2600 surface water samples were collected from 42 different sites on the streams flowing within the mine, and on the Olifant River flowing to the south of the mine.

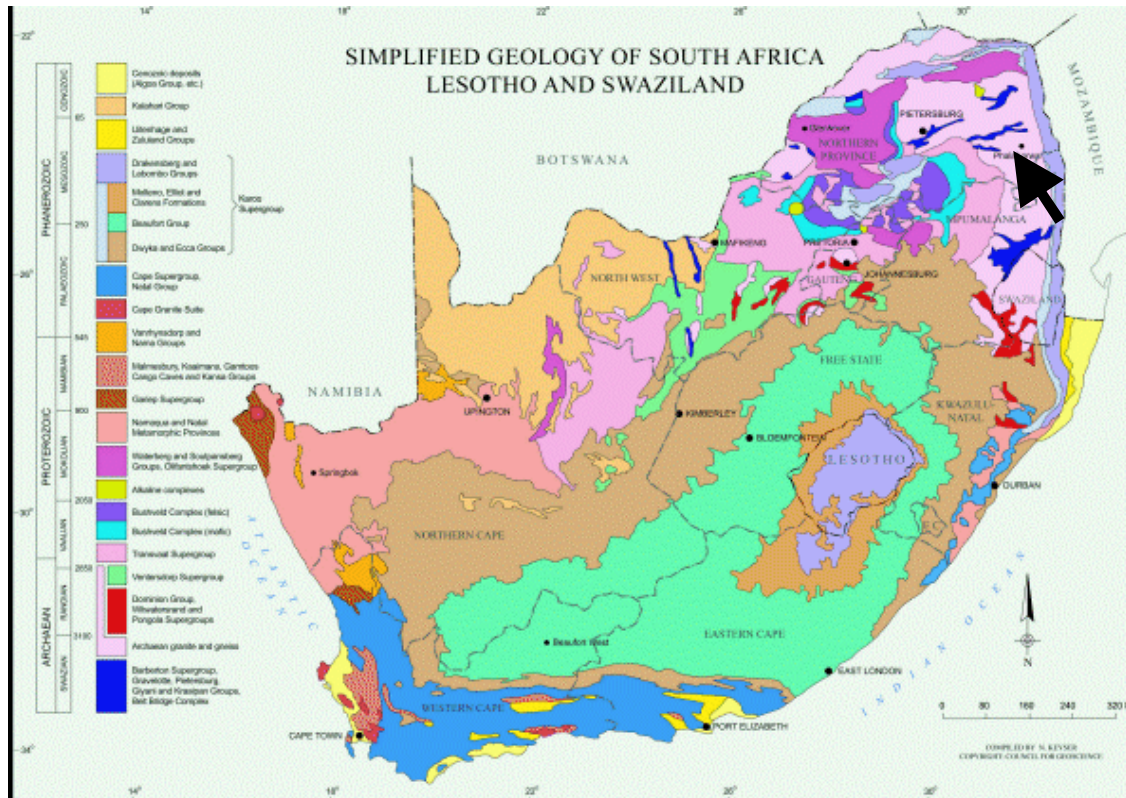


Figure 6-52: Simplified geology of South Africa, (Wilson and Anhaeusser, 1998).

According to Figure 6-52 above, Phalaborwa lies on a Granite-gneiss formation. Moreover, analysis within the area attributed the water to a dolomitic environment, which naturally contains high TDS values.

To address the problem in a proper manner to highlight the mechanisms involved, it is important that the entire area be dissected. This will give a better understanding of the whole unit. The boreholes were carefully selected with respect to their proximity to the tailings, and the corresponding groundwater analyses were partly attributed to the tailings.

Out of the seven waste facilities, four (4) are of particular interest in the sense that they contain the largest tonnages of waste within the mine, i.e. WR, CS, HT, LT; and the best way to monitor their impact on groundwater was to drill boreholes around them.

**Total dissolved solids**

Percentiles at 50% (1980.0) and 95% (6613.0)

TDS (mg/l)

15000  
10000  
5000  
0

6613.0

2 x Std. Dev. Min & Max.

PGSM-B01 PGSM-B02 PGSM-B03 PGSM-B04 PGSM-B05 PGSM-B06 PGSM-B07 PGSM-B08 PGSM-B09 PGSM-B10 PGSM-B11 PGSM-B12 PGSM-B13 PGSM-B14 PGSM-B15 PGSM-B16 PGSM-B17 PGSM-B18 PGSM-B19 PGSM-B20 PGSM-B21 PGSM-B22 PGSM-B23 PGSM-B24 PGSM-B25 PGSM-B26 PGSM-B27 PGSM-B28 PGSM-B29 PGSM-B30 PGSM-B31 PGSM-B32 PGSM-B33 PGSM-B34 PGSM-B35 PGSM-B36 PGSM-B37 PGSM-B38 PGSM-B39 PGSM-B40 PGSM-B41 PGSM-B42 PGSM-B43 PGSM-B44 PGSM-B45 PGSM-B46 PGSM-B47 PGSM-B48 PGSM-B49 PGSM-B50 PGSM-B51 PGSM-B52 PGSM-B53 PGSM-B54 PGSM-B55 PGSM-B56 PGSM-B57 PGSM-B58 PGSM-B59 PGSM-B60 PGSM-B61 PGSM-B62 PGSM-B63 PGSM-B64 PGSM-B65 PGSM-B66 PGSM-B67 PGSM-B68 PGSM-B69 PGSM-B70 PGSM-B71 PGSM-B72 PGSM-B73 PGSM-B74 PGSM-B75 PGSM-B76 PGSM-B77 PGSM-B78 PGSM-B79 PGSM-B80 PGSM-B81 PGSM-B82 PGSM-B83 PGSM-B84 PGSM-B85 PGSM-B86 PGSM-B87 PGSM-B88 PGSM-B89 PGSM-B90 PGSM-B91 PGSM-B92 PGSM-B93 PGSM-B94 PGSM-B95 PGSM-B96 PGSM-B97 PGSM-B98 PGSM-B99 PGSM-B00

## Results



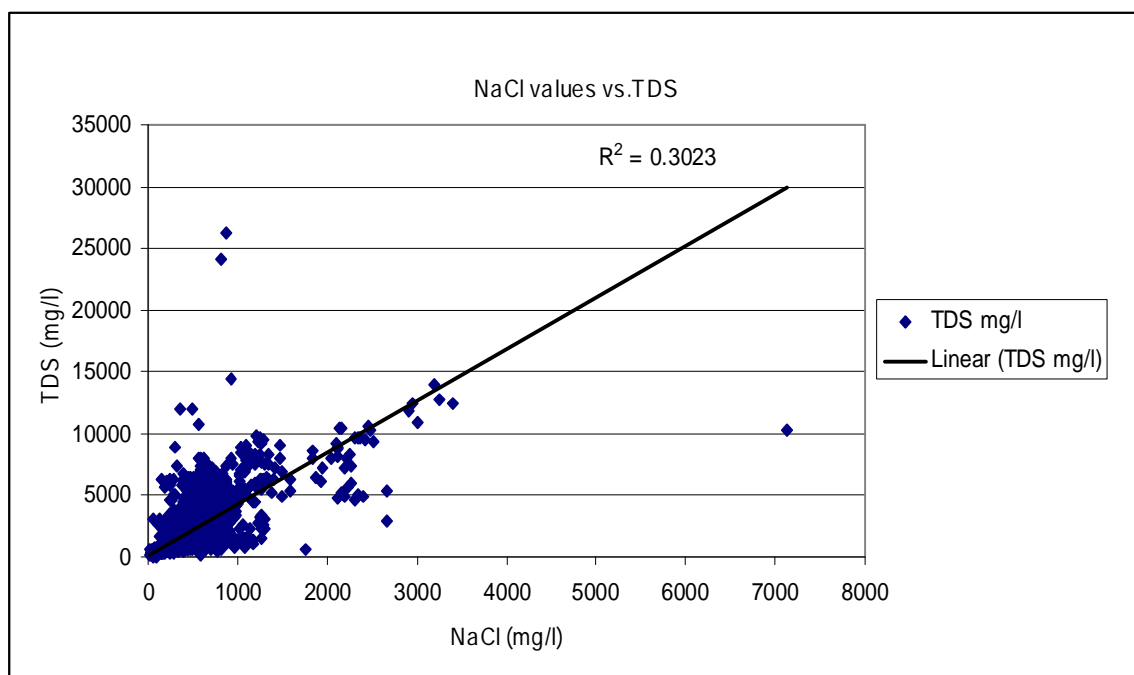


Figure 6-55: % NaCl in TDS in all monitoring boreholes.

Two aspects can be highlighted, namely that in general the trends in Cl are mirrored in sodium concentrations, and secondly that the sum of these two ions contribute a significant proportion, averaging at around 30%, of the overall TDS in most boreholes and salinity of the groundwater, (Figure 6-55).

Although this suggests that the usual drivers on mine water quality, namely sulphate domination may not be as prominent, it is clear from plots such as the Durov diagram of the entire period of monitoring (15 years), that the highest values for the total dissolved solids (TDS) are associated with sulphate dominated waters.

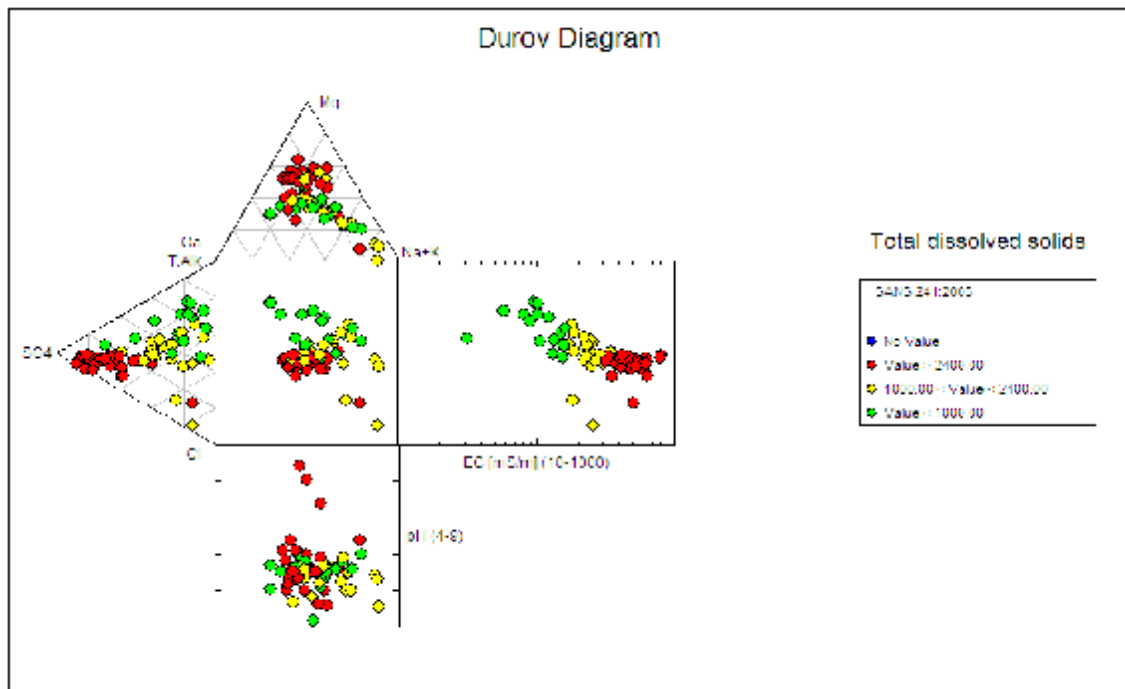


Figure 6-56: Durov diagram for all boreholes, (average values).

The responses of the groundwater system around each waste facility can be briefly discussed in the sections that follow.

### 6.3.1 Waste Rock Monitoring 2000-2008

Several sites surrounding the waste rock dump were sampled until 2008. Only the last nine years' data are considered as a general understanding of the interactions.

The groundwaters do not always have similar quantities in their chemical compositions. In fact, some analyses have shown differences between very close boreholes.

Geographically, we expect boreholes from the south of WR to be similar to the south of CS, but very different from the north of WR as the marginal ore was dumped in that northern part of WR, (PMC, 2007).

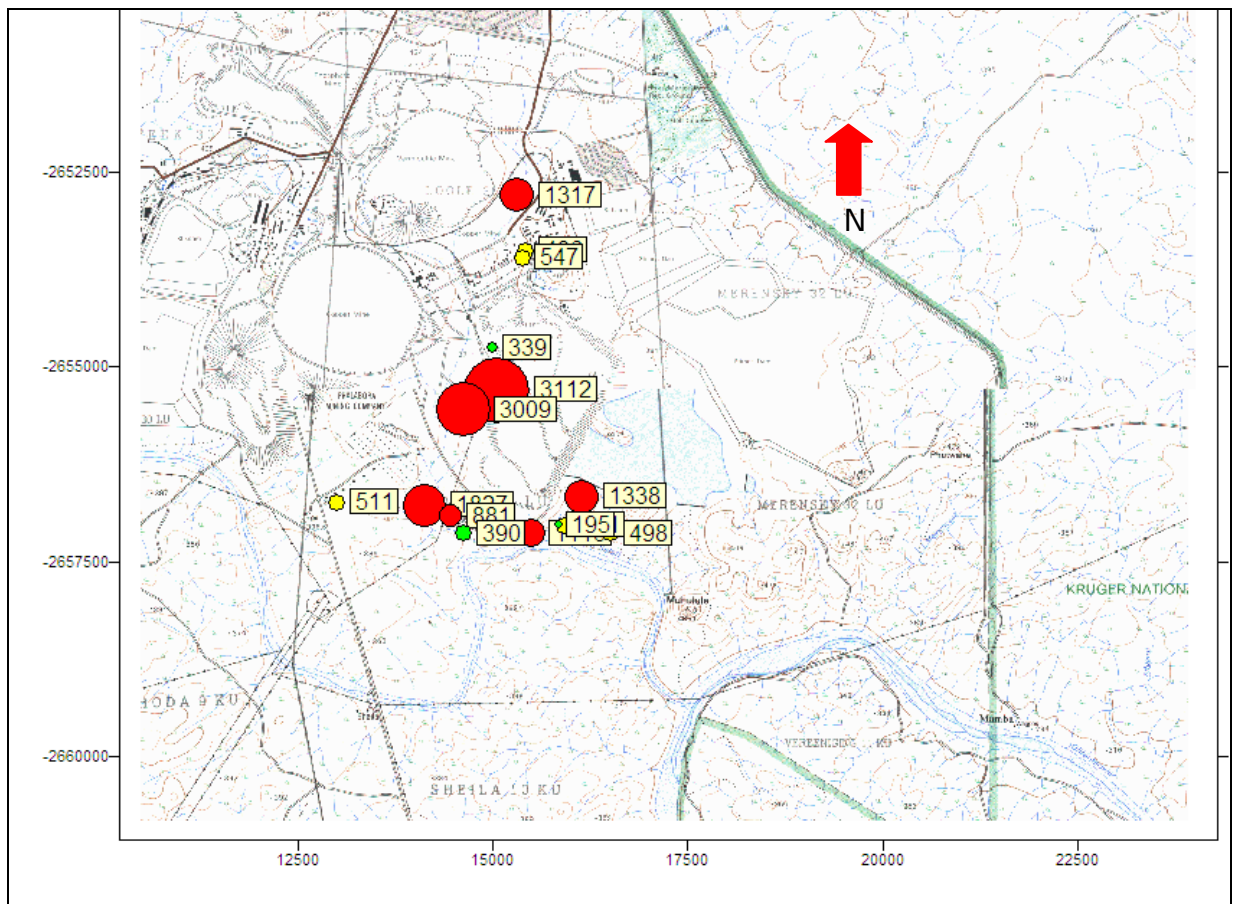


Figure 6-57: Sulphate concentrations of boreholes around WR.



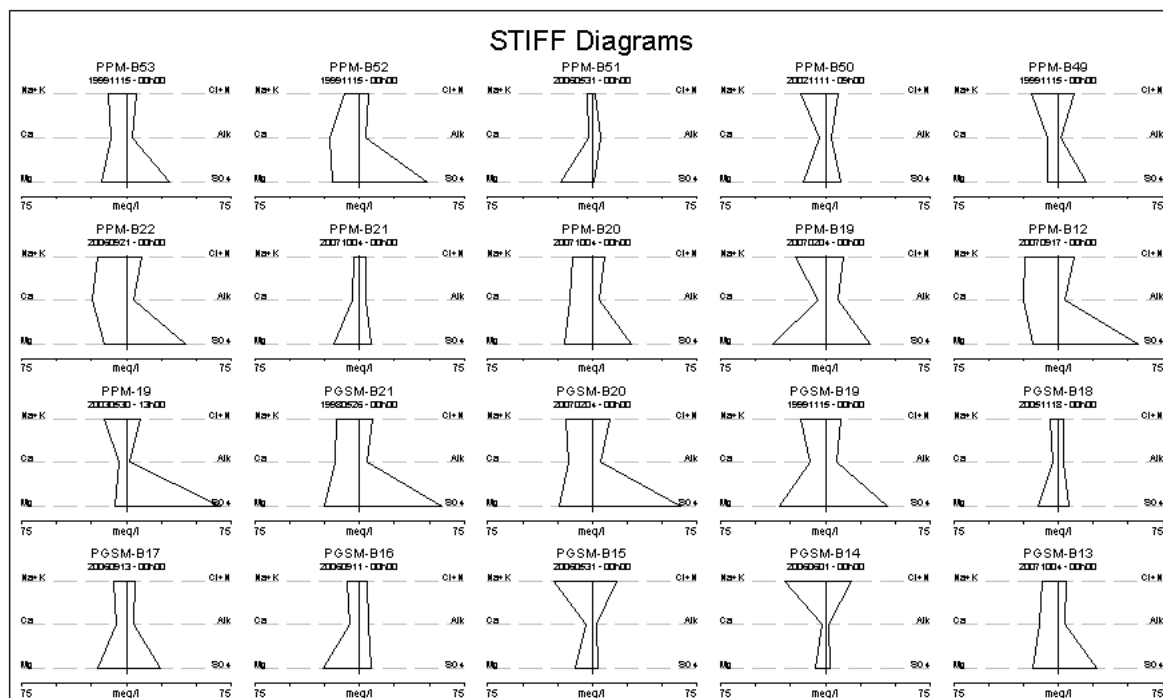


Figure 6-58: Stiff diagram of WR.

Above is another example to support the statement regarding an eventual flow path of the groundwater. Looking at PGSM-B20, PGSM-B21, PGSM-B19, and then PPM-B22, PPM-B12, these boreholes locations could tell a lot about the leachate flow path from WR for the first set of boreholes.

## Bicarbonates

A helpful observation is the presence of plagioclase ( $\text{NaAlSi}_3\text{O}_8$ ,  $\text{CaAl}_2\text{Si}_2\text{O}_8$  and  $\text{KAlSi}_3\text{O}_8$ ) dominantly in WR.



Albite

kaolinite

## Equation 6-2

Where  $\text{H}^+$  comes from  $\text{CO}_2$  (atmosphere) +  $\text{H}_2\text{O}$  (rain) =  $\text{H}_2\text{CO}_3$  (carbonic acid).

Equation (6) produces Kaolinite by the weathering of feldspar, and could also account for additional  $\text{HCO}_3^-$  content in the groundwater, and silica in the mineralogy.

In general, the weathering of silicate minerals is a relatively slow process compared with the reaction of carbonates under acidic conditions. Thus in most cases, the acid neutralization capacity of the solid phase of an aquifer is due to its carbonate mineral content.

However, kaolinite was not observed in the mineralogy, the reason being that it a very unstable clay mineral, and depending on whether calcium or sodium is the sole exchangeable cation in the system, or partial pressure or other thermodynamic components, kaolinite decomposes to montmorillonite, which has indeed been observed in the mineralogy, though in minute quantities. Kaolinite decomposes according to the following reaction:

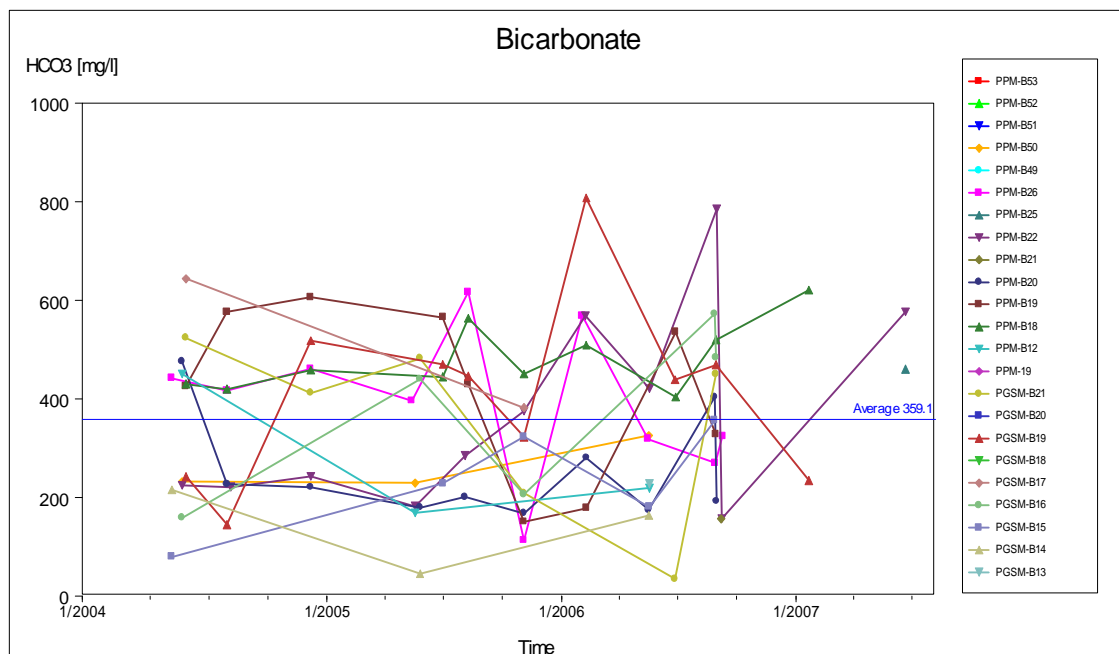
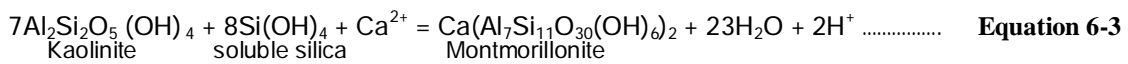


Figure 6-59: Bicarbonate concentration at WR-related boreholes. Note the average value

The effects of this control of the acidity is clearly seen on CS and WR where Ca-Na-HCO<sub>3</sub> waters (pH 7.5 - 8) would lose all Ca and Mg to form dolomite, and the waters would become NaHCO<sub>3</sub> groundwater with pH 9 - 10.5 over depths of

200m, (Gascoyne and Kamineni, 1994). Chapter 7 shows that dolomite is saturated in the groundwater between pH 7.5 and pH 8.5.

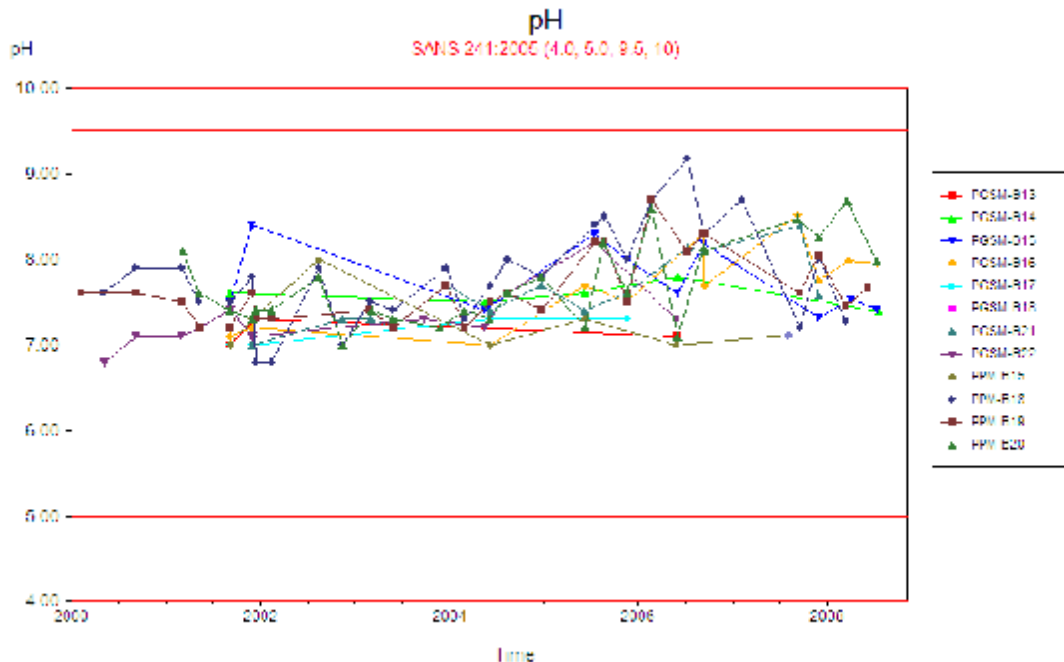


Figure 6-60: pH values for WR-related boreholes, (2000-2008).

While in the last nine years (2000-2008), the pH of the boreholes surrounding the Waste Rock have registered an increase in values, they however remain in the slightly alkaline range. Chapter 7 on the saturated indices of minerals shows that there are many minerals dissolved in the groundwater of the monitoring boreholes at PMC. These minerals are mostly alumino-silicates minerals, and they control the pH of the groundwater as they get saturated at pH values around pH 9.5, thus have an influence of buffering eventual low pH values, ( $5 < \text{pH} < 9.5$ ). Moreover, leachate from WR come from rainwater, which is also alkaline and contributes to buffering fairly low pH values.

The data from this monitoring indicates that pH levels are relatively neutral, that the highest TDS is associated with sulphate dominance, and there is a significant Cl contribution to the elevated TDS values.

It is also clear that borehole PGSM-B21 has significantly higher values in terms of chemical composition than the other boreholes. This is regarded as somewhat anomalous, based on the waste rock characterisation, and other reasons for this need to be found.

The Stiff diagrams show variation in content and composition, and that despite the high sulphate dominance in the high TDS samples, Cl is relatively high. This is important, as stated in the preceding section, since it points towards high rock: water ratios or low flow rates relative to the mass of rock contained on site.

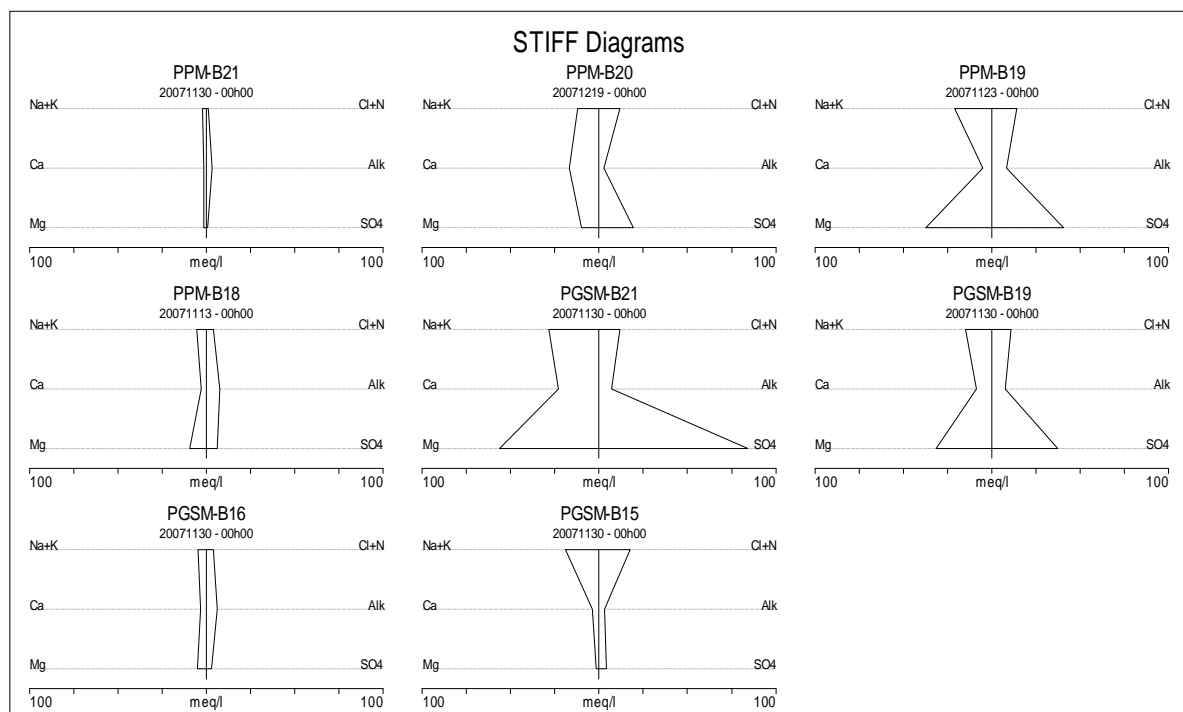


Figure 6-61: Stiff diagrams from the borehole near the waste rock dump.

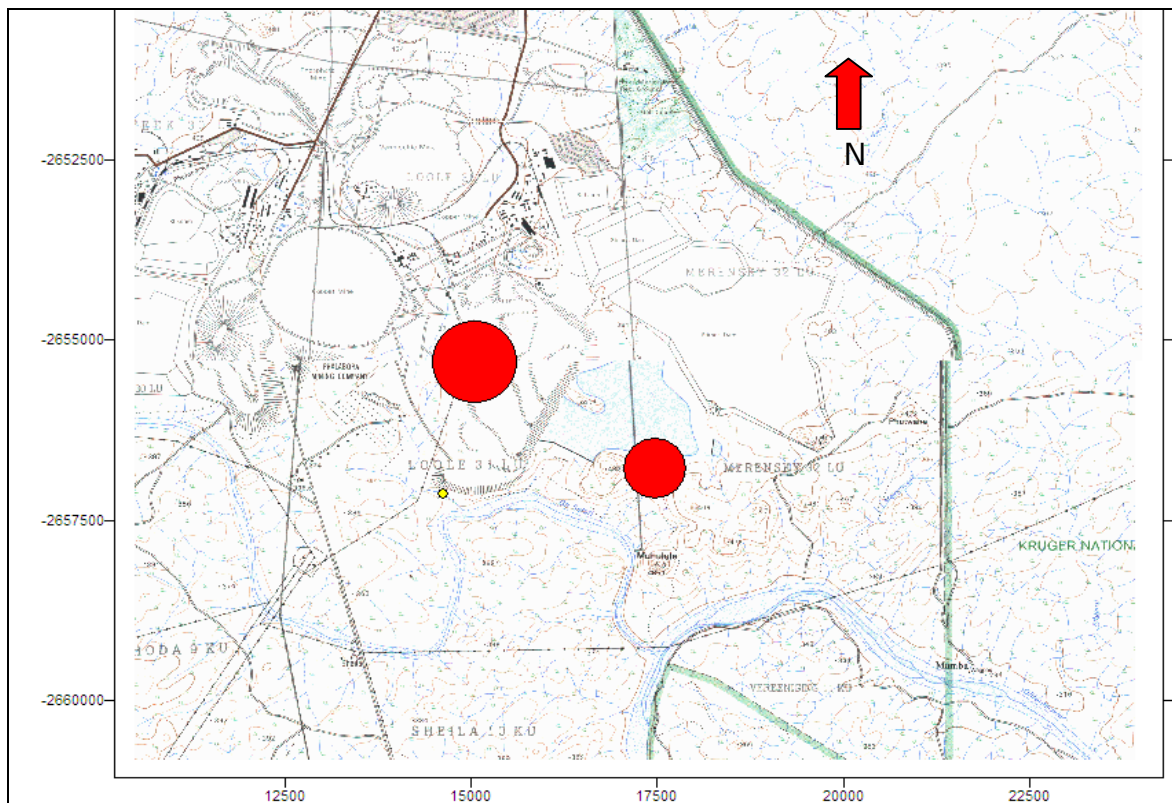


Figure 6-62: Positions of some Boreholes with their corresponding TDS values.

Sulphate ( $\text{SO}_4^{2-}$ ) concentrations and the electrical conductivity were monitored at three randomly selected boreholes over the years, to assess the content of sulphate in groundwater. Results are presented in Figure 6-63.

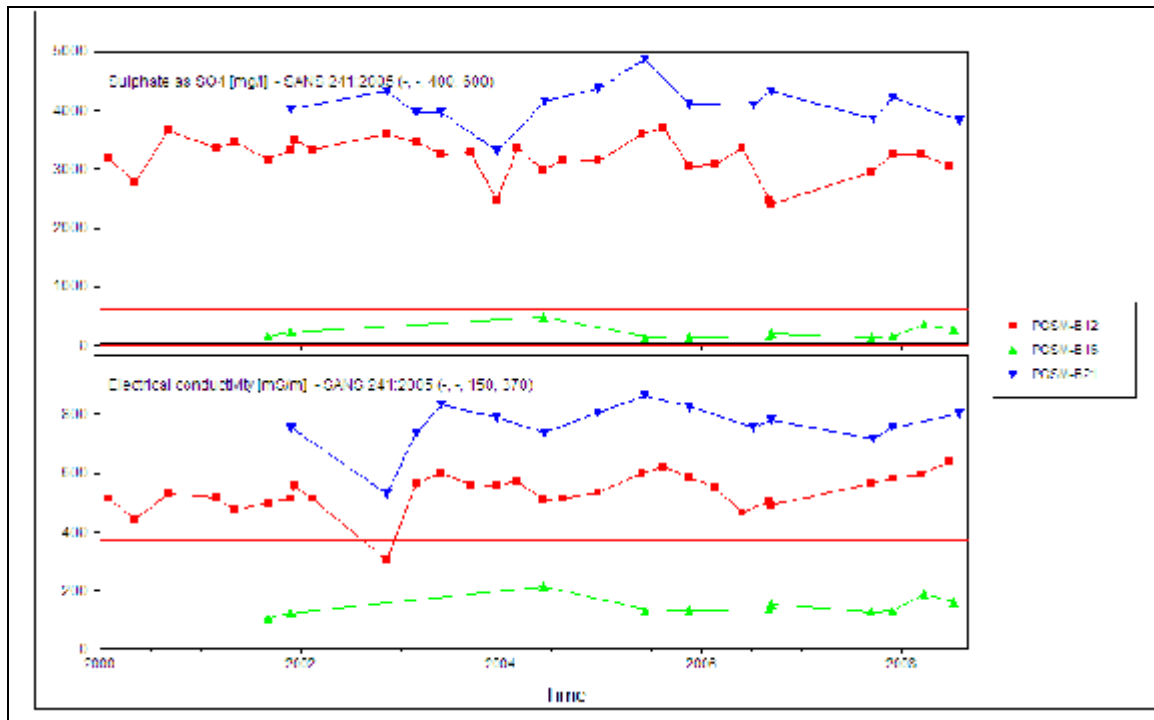


Figure 6-63: EC vs. SO4 of the three boreholes.

This exercise is useful in the sense that it helps in the direct observations of the influence of the wastes facilities in groundwater. This also proves that the seeps from the waste dumps do indeed find their way in the groundwater.

From the plots, only one borehole has its EC and sulphate values that comply with the standards of the South African Bureau of Standards for drinking water, (SANS).

As seen on the above Figure 6-63, PGSM B-16 is located at the foot of the Waste Rock (WR) dump. Unlike PGSM B-12, which is located at the foot of the Copper Tailings (CS), its corresponding values are well within the limits because the waste material dumped on that particular location is the unprocessed waste rock. That material from the WR is coarse and bulky, therefore reacts slower compared to materials from the Copper Tailings.

Meanwhile, PGSM-B12 and PGSM-B21 share similarities in their concentrations. The reason is quite obvious. According to the history of the mine, the very first processed ore mineral was dumped in the early sixties (1960s) at the location where PGSM-B21 was drilled; later on, waste dumping ceased on that site and

the Copper Tailings (CS) was then built. From the processing of the ore mineral, copper sulphide waste dump (CS) was built and is believed to form the absolute majority of CS, thus the name of the Copper Tailings also known as the Copper Sulphide waste dump. These tailings (CS) are predominantly derived from the carbonatite ore which has had most of the sulphides removed by floatation process. While the unprocessed ore mineral is known to be lowly reactive to oxygen, the processed ore mineral and copper sulphide reacts very effectively with atmospheric conditions of water, moist and oxygen. As previously stated at the beginning of this study, the two forms of copper sulphides present on site are Chalcocite ( $\text{Cu}_2\text{S}$ ), and Covellite ( $\text{CuS}$ ).

The sulphide is normally oxidized to sulphate. These sulphides of copper themselves do not produce acids, but they do liberate soluble metals and sulphate. This is confirmed by the Stiff diagrams below for PGSM-B12 and PGSM-B21, (Figure 6-64).

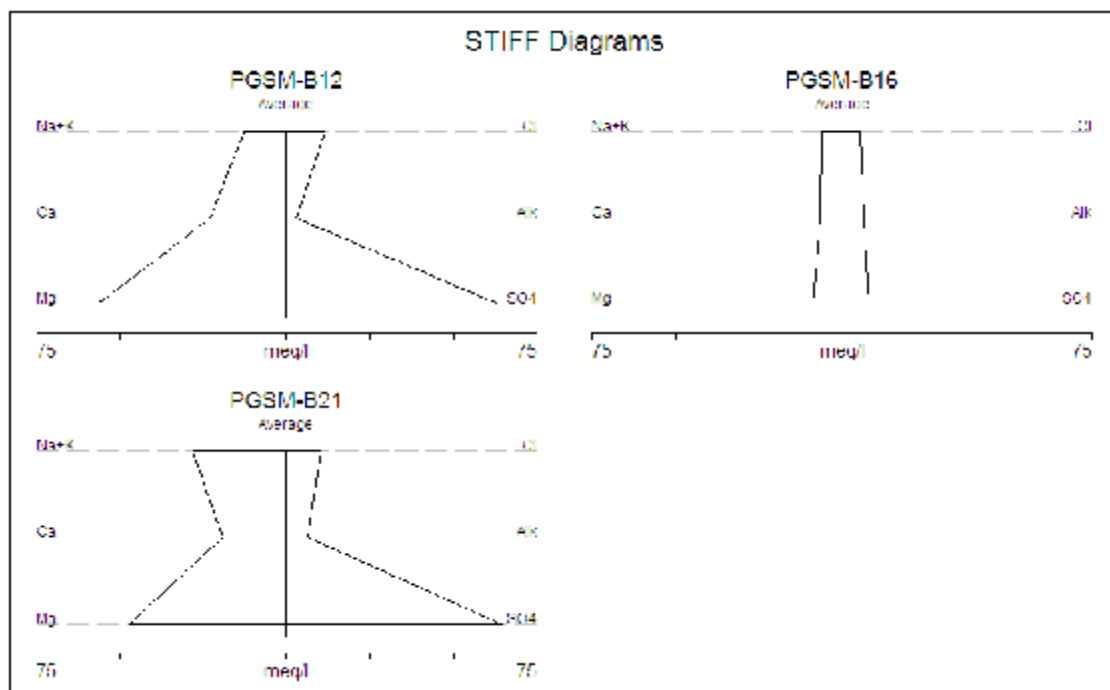


Figure 6-64: Stiff Diagram of borehole PGSM-B12, PGSM-B16, and PGSM-B21 (average values).

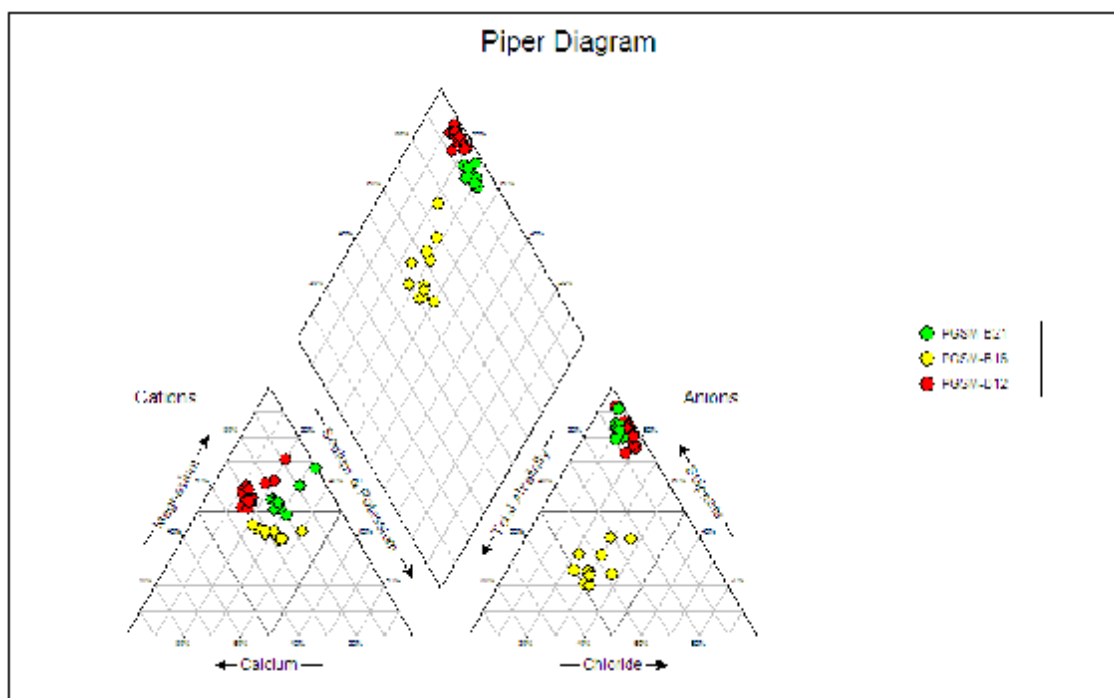


Figure 6-65: Piper diagram of the three different groundwater.

The marginal ore, which forms a section of the Waste Rock dump is predominantly composed of foskorite with copper content of about 0.1 to 0.15%, (PMC, 2007). This material likely has higher sulphide content than the run-of-mine waste rock from the copper pit. This explains why PGSM-B21 which was drilled by the side of the location where the marginal ore is stored contains high sulphate compared to PGSM-B16. The latter was drilled next to the waste material from the copper open pit, which is composed of un-mineralized dolerite, granite gneiss, syenite and pyroxenite, (PMC, 2007).

However, it was noticed that the pH remain within acceptable range. It is believed that the carbonates, mostly calcite and dolomite, together with the aluminosilicates control the pH.



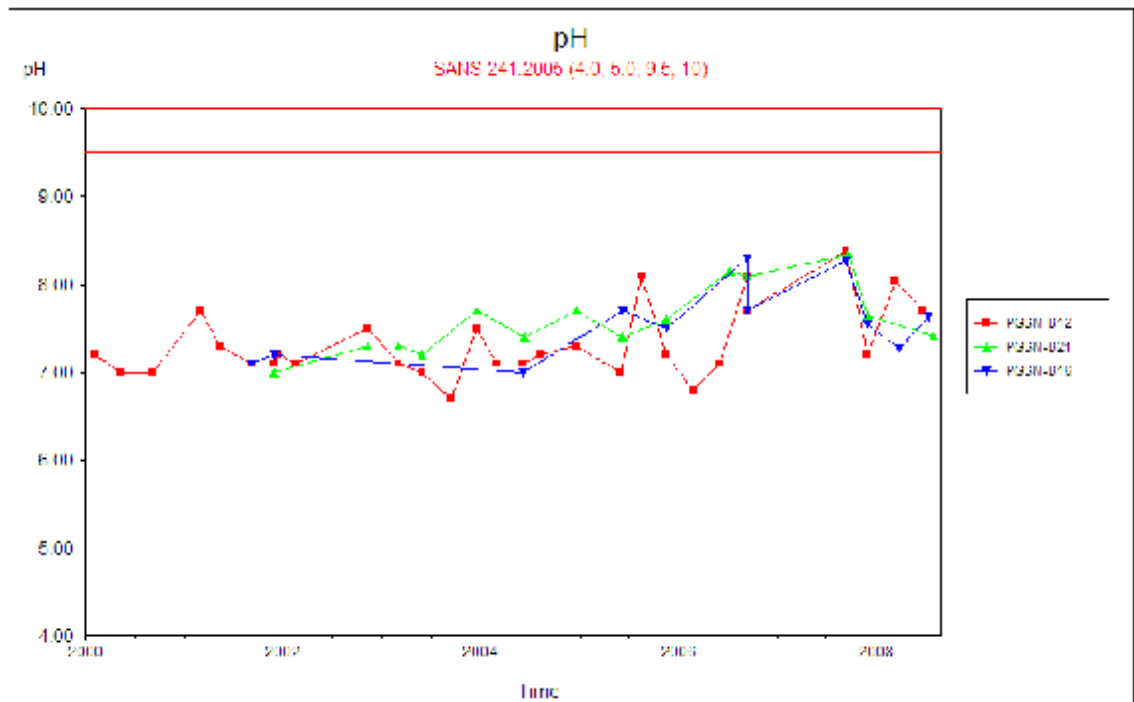


Figure 6-66: pH of the selected boreholes.

### 6.3.2 Monitoring the Copper Sulphide tailings 2000-2008

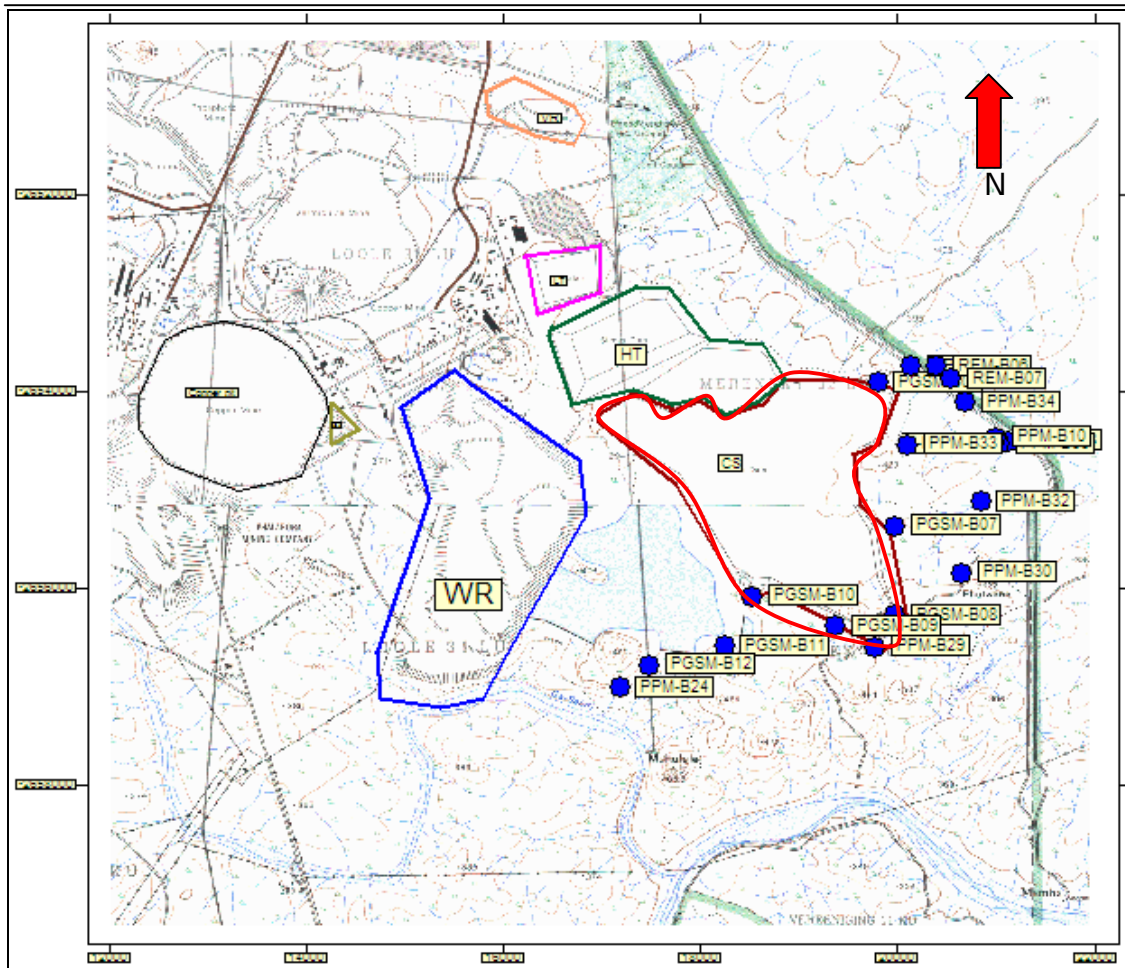


Figure 6-67: CS-related boreholes.

The Copper Tailings were built for the purpose of dumping waste from the processed rock containing the copper ore. To elaborate on the chemical differences more briefly, comparisons between CS and WR waters were to determine the specific influences on groundwater.

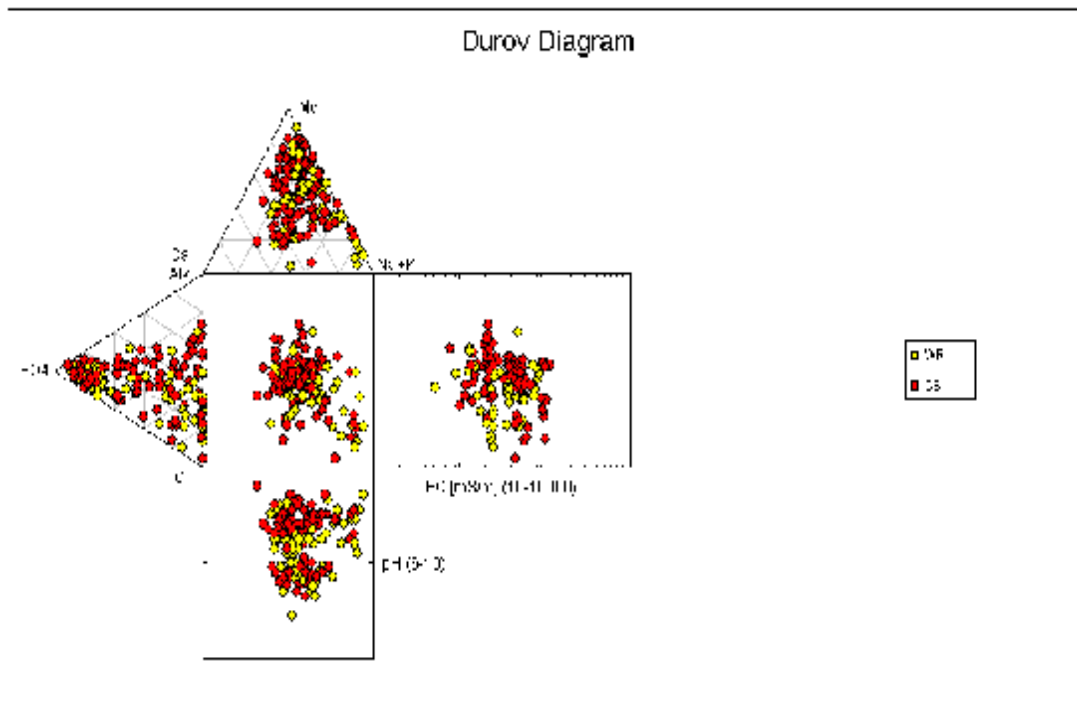


Figure 6-68: Durov Diagram of CS and WR related groundwater (2000-2008).

Despite being on different facilities, both waters emanating from these tailings interestingly have very high sodium and potassium content. The Stiff Diagram below confirms this. However, PPM-B08 and PPM-B34 are located at the boundary between the mine and the Kruger National Park, whereas PPM-B12 and PPM B21 are located around the Selati River. These last two boreholes show similarities in their sodium content only, but not on their sulphate content. This is possible if PPM-B12 (with higher sulphate) receives more influence from the Return Water Dam as it is the closest source of elevated surface, (see Section 6.4).

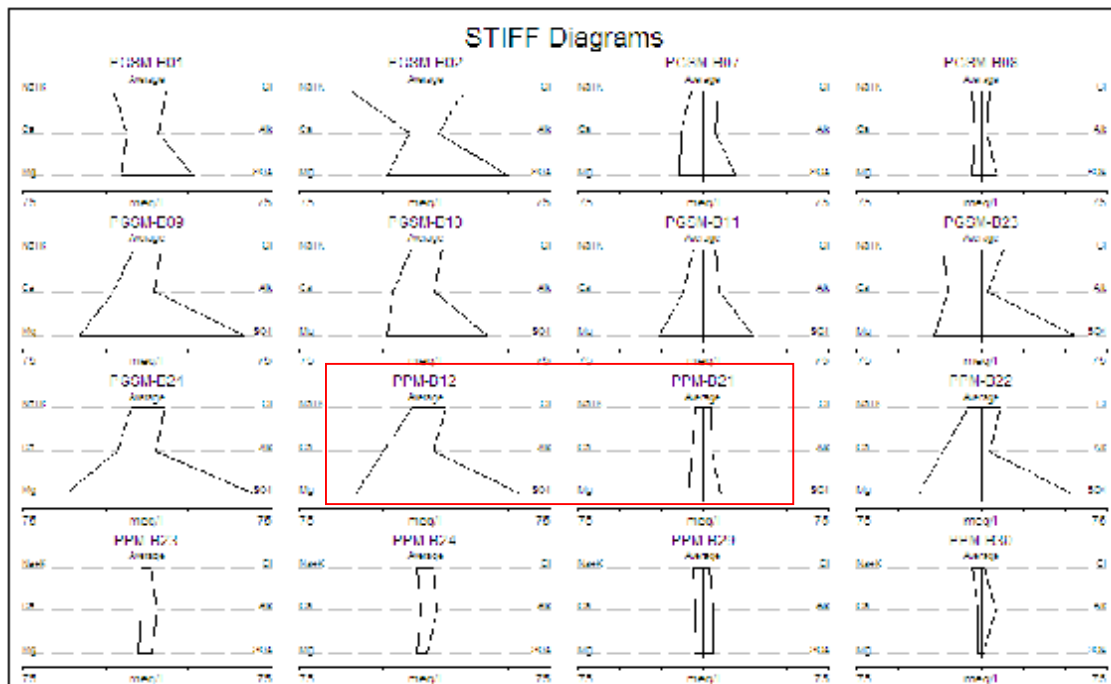


Figure 6-69: Stiff Diagram of some CS-related groundwater (2000-2008).

Furthermore, the presence of high sulphate might also be attributed to the reactions that occur within the tailings dams themselves depending on the waste being dumped.

In other words, it is probable that the high sulphate concentration present in the groundwater could be derived from the following overall neutralization reactions involving Covellite ( $\text{CuS}$ ) and Chalcocite ( $\text{Cu}_2\text{S}$ ), two of the copper sulphides minerals that are being mined at PMC:

This assumption is based upon the fact that WR used to contain the marginal ore, whereas CS is known as being the copper sulphide waste dump. The marginal ore is predominantly composed of foskorite with copper content of about 0.1 to 0.15%, (PMC, 2007). This material likely has low sulphide content because it was removed in the process. Moreover, it is also likely that the material has a higher carbonate content, (PMC, 2007).

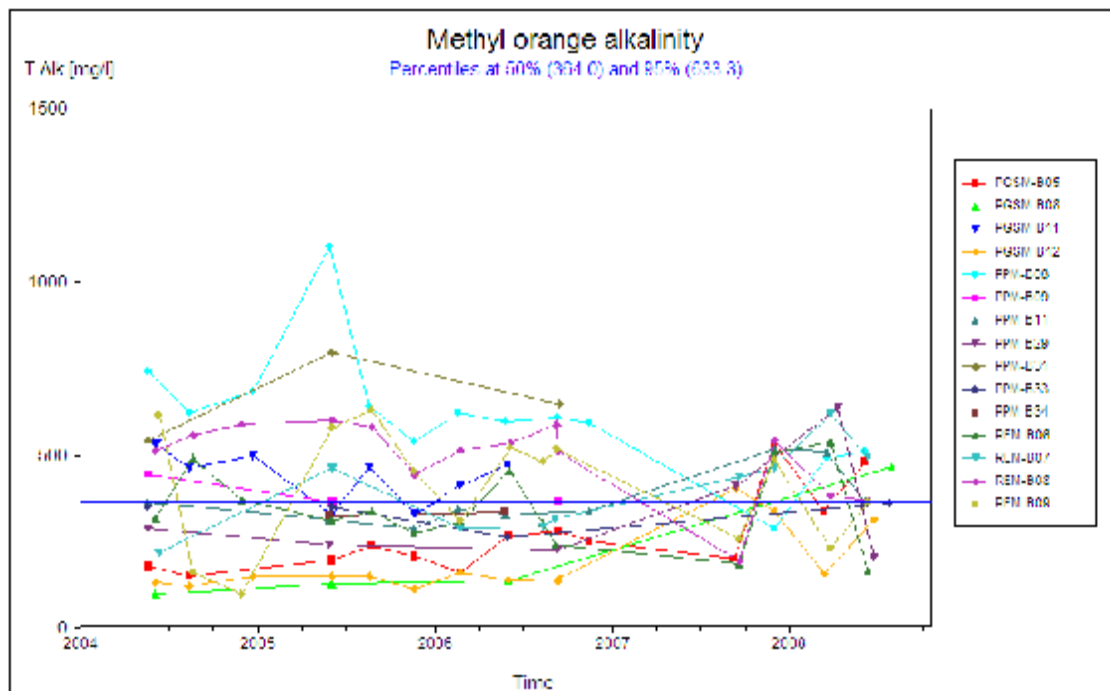


Figure 6-70: Total alkalinity graph for CS-related boreholes.

Calcite is not the only carbonate imbedded in the carbonatite ore from where the Copper Tailings are predominantly derived. Analysis has also shown a high presence of magnesium in the groundwater, (Figure 6-71 below), and this is either related to magnesium carbonates, i.e.  $\text{MgCO}_3$  or a compound that contains both magnesium and calcium carbonates: Dolomite. This can also come from the dissolved minerals in the groundwater (Chapter 7).

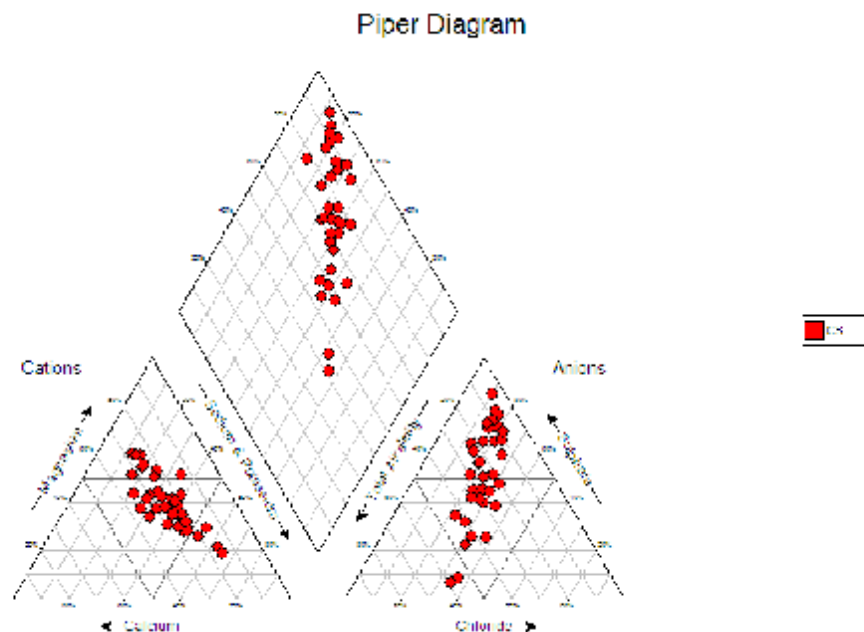


Figure 6-71: Groundwater facies of CS (average values).

The groundwater facies (Figure 6-71) of CS clearly show that it is a (Calcium, magnesium) sulphate kind of water. It is assumed, that the presence of dolomite in CS waste samples and not in WR might be due to the fact that the processed marginal ore from WR, which is then dumped at CS, is present as copper sulphides waste ( $\text{CuS}$  and or  $\text{Cu}_2\text{S}$ ), and then react with the carbonates possibly present from rainwater among others in an auto-neutralization process.

Sources of magnesium include vermiculite  $(\text{MgFe,Al})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  , though not present as the dominant mineral in CS, appears greatly in CS than in WR. Another source include clinocllore  $(\text{Mg}_5\text{Al})(\text{AlSi}_3)\text{O}_{10}(\text{OH})_8$  ,as well as dolomite  $(\text{CaMg}(\text{CO}_3)_2)$ .

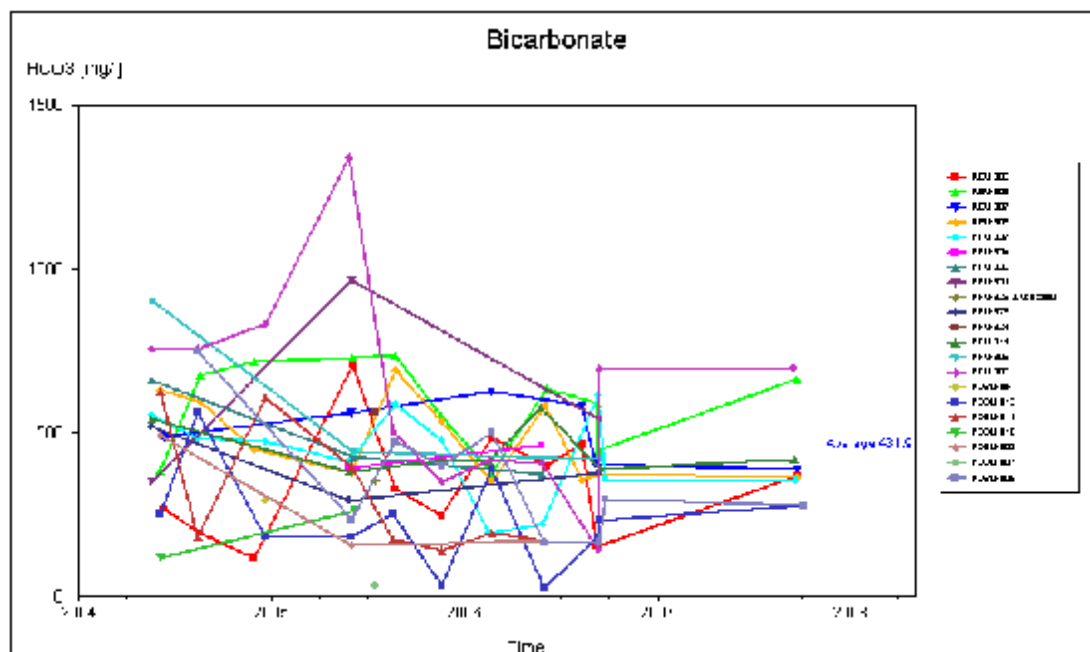


Figure 6-72: Bicarbonate concentration at CS-related boreholes. Note the average value.

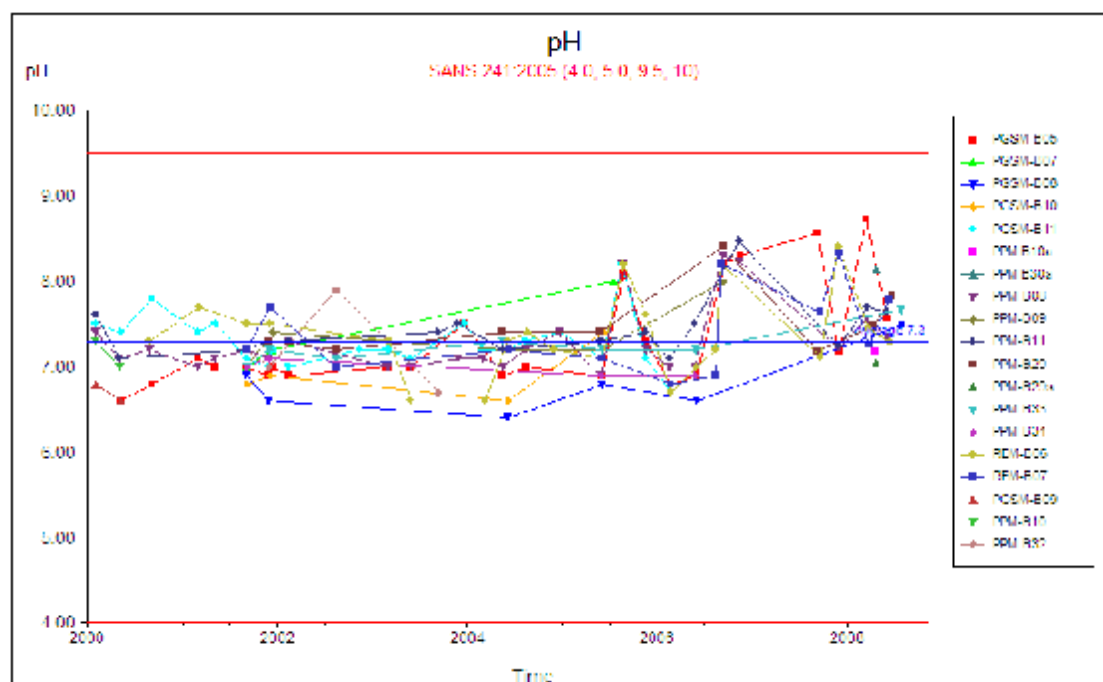


Figure 6-73: pH values of CS-related boreholes, (2000-2008).

pH values had slightly increased over the last nine years as well in CS, but remain within the pH 7.5 to 8 range with the average value of the groundwater at

pH 7.4. This can be attributed to the carbonate contents in the Copper Tailings waste deposits, which saturated between pH 7.5 and 9.5, but also from the water used to solidify the Copper Tailings as the majority of the leachate emanating from this dump come from that water as it is used, (see section 6.4 on chemical analysis of the water).

### 6.3.3 The Magnetite tailings, (2000-2008)

Both tailings are very small in size compare to the WR and CS. For that reason, a combined analysis was performed.

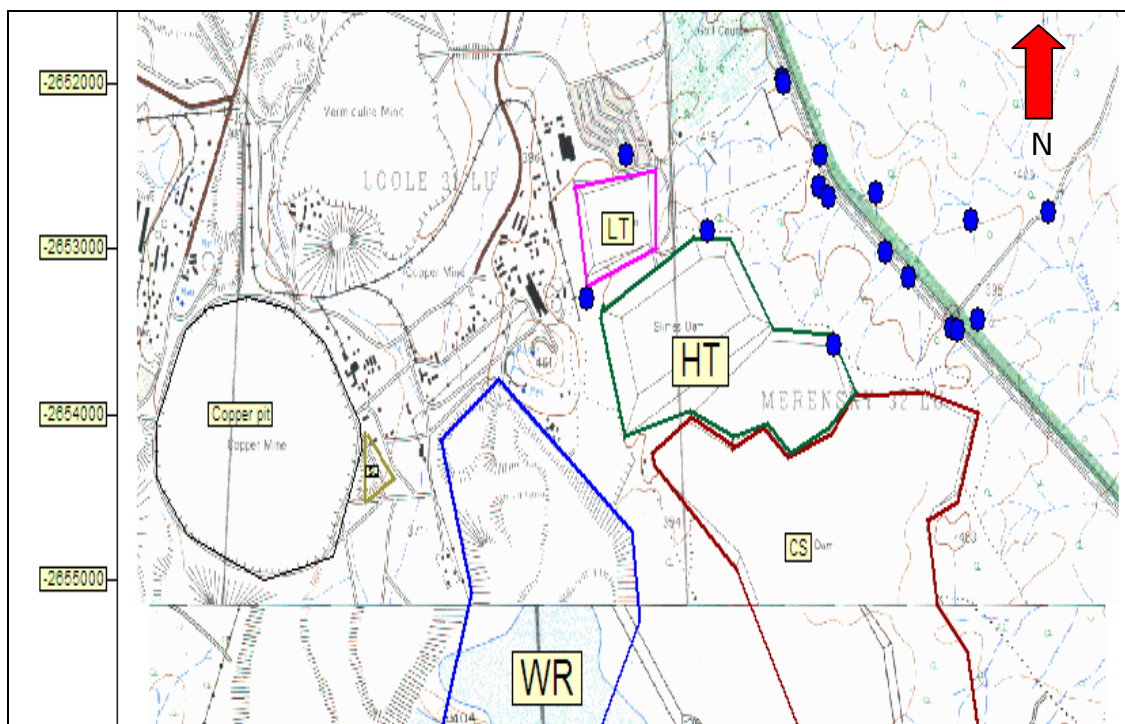


Figure 6-74: Sampling boreholes at the magnetite tailings.

At HT and LT, it has also been noticed that though magnetite is undoubtedly dominant, plagioclase appears at a lesser extent, but the concentrations of bicarbonates are quite high in the groundwater. The Acid-Base Accounting (ABA) indicates no acidity.



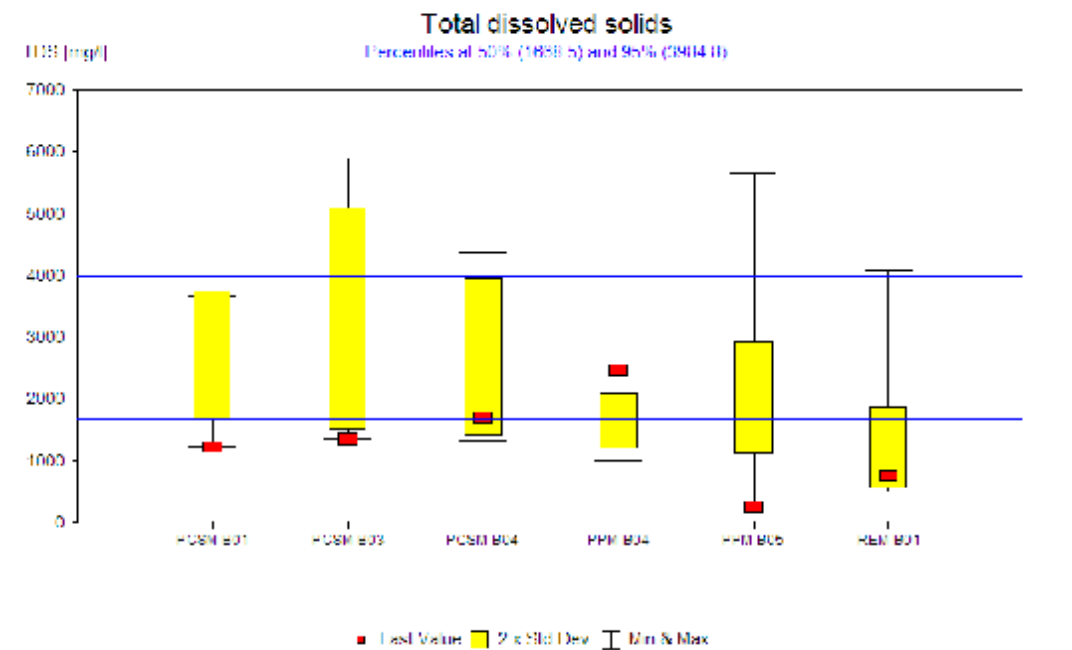


Figure 6-75: TDS values for Magnetite tailings-related boreholes.

No acidity, but some total dissolved solids (TDS) values that are above standards groundwater values, the 50<sup>th</sup> centile is above the threshold values of 950mg/l standard.

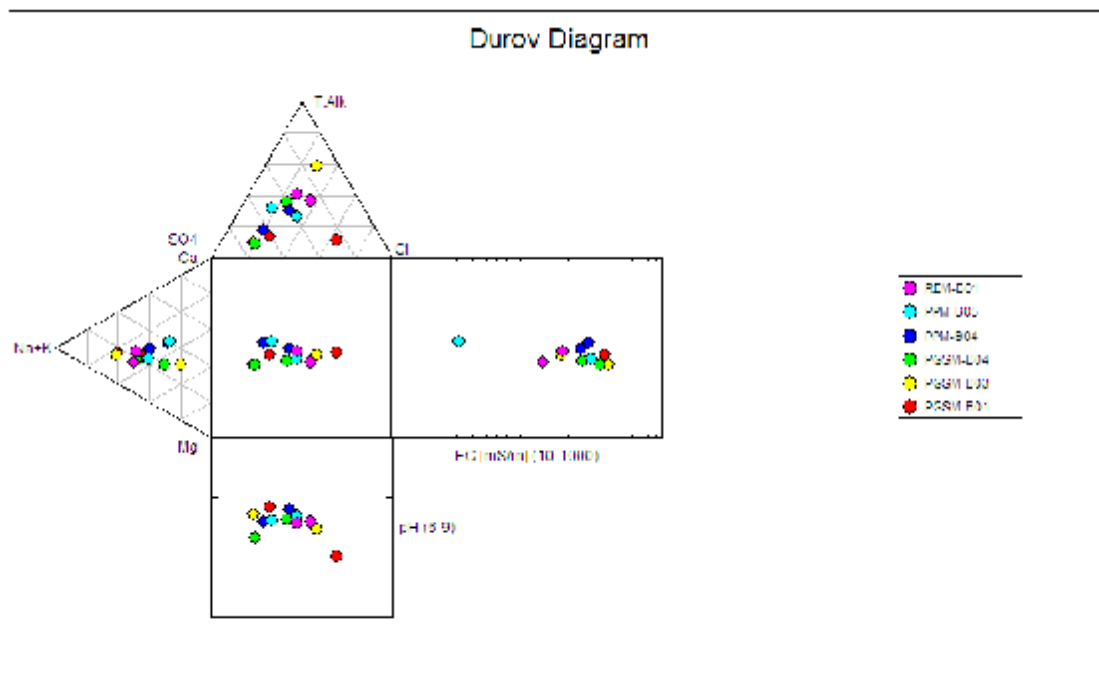


Figure 6-76: Durov diagram in HT and LT-related boreholes.

The waters from the HT and the LT some fairly elevated sulphate values, as well as fairly elevated EC values. However, the pH range is in an acceptable range. By the end of the sampling in 2008, removal of magnetite from the tailings had already begun as it was being sold to overseas buyers.

#### 6.4 Salinity generated within the mining area, (surface water)

The first consideration in terms of the salinity on site is to consider the amount of waste on site. According to the PMC data, as recorded in the waste data for the mine there are very large quantities of different waste types on site. This can be seen in the following table:

Table 6-22: Tonnages of different waste types on site (PMC, 2007).

Waste Type	tons on site	Mt
Tailings	379317022	379.3
Waste Rock	1084668018	1084.7
Vermiculite	9553142	9.6

In terms of aerial coverage the waste also covers a significant proportion of waste on site. The implication of this is that, even if the waste is only very slightly reactive, a large salt loading can be expected per facility.

Moreover, the tailings dams are solidified using water pumped from the Return Water Dam, through huge pipes and out to the tailings, and back to the return water dam. On a random sampling, it was found that the water pumped to the tailings from the Return Dam (RWD) had a pH of 7.80, and an EC of 6200  $\mu\text{S}/\text{cm}$ , and the water returning from the tailings, (RWT) and back to the Return Dam right at the source had a pH of 7.77 and a corresponding EC of 7000  $\mu\text{S}/\text{cm}$ .

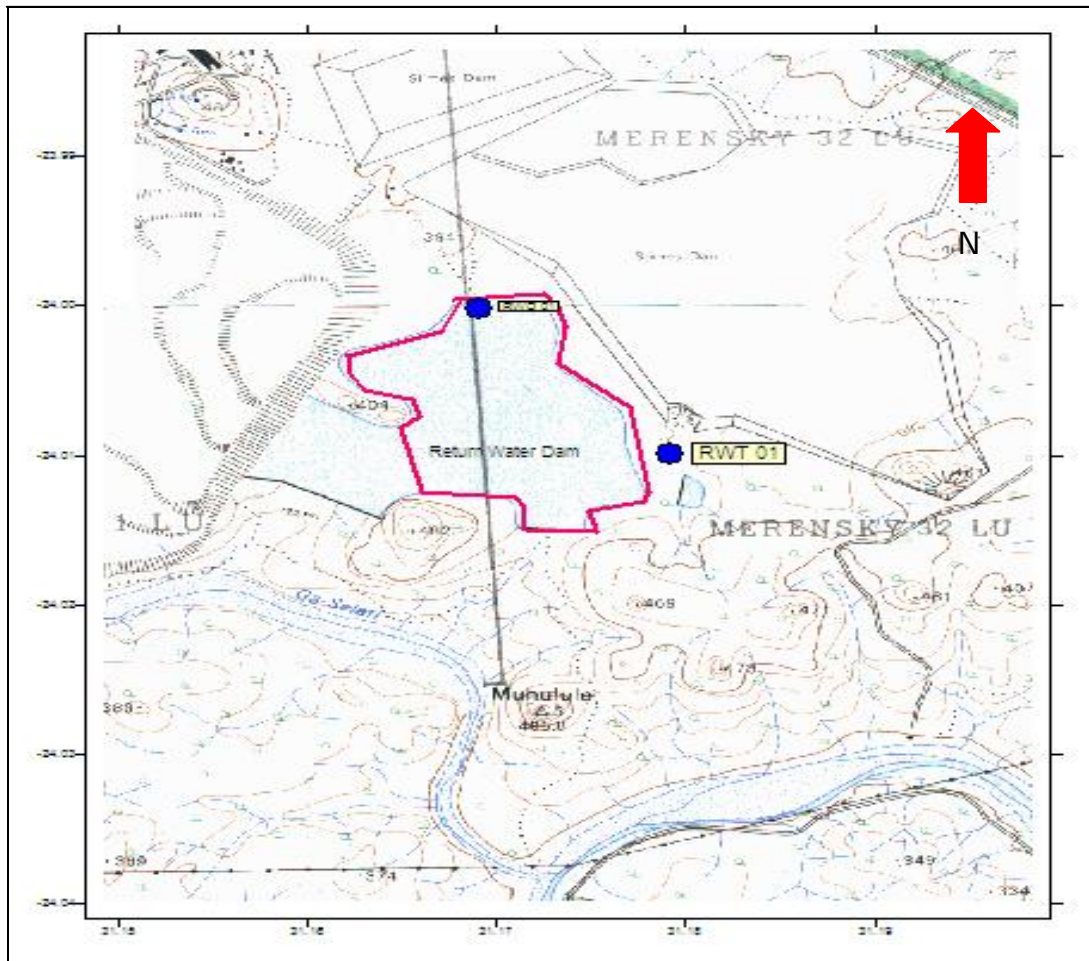


Figure 6-77: Positions of RWD and RWT on the Return Water Dam.

While the pH remains within a near-neutral range, (pH 7-pH 8), the EC is quite high, so are the sulphate concentrations. Furthermore, one needs to point out the fact that in this case, the water was coming exclusively from the Copper Tailings dam. This is also a good indicator of the salinity generated by the Copper tailings alone, and this is a good indicator of the quality of the leachate that can be generated from the Copper Tailings alone. Other filter drains were located around the Copper Tailings, but were closed by the time of the investigation.



Figure 6-78: Return water from the Copper Tailings dam: EC is of the range of 7000  $\mu\text{S}/\text{cm}$ .

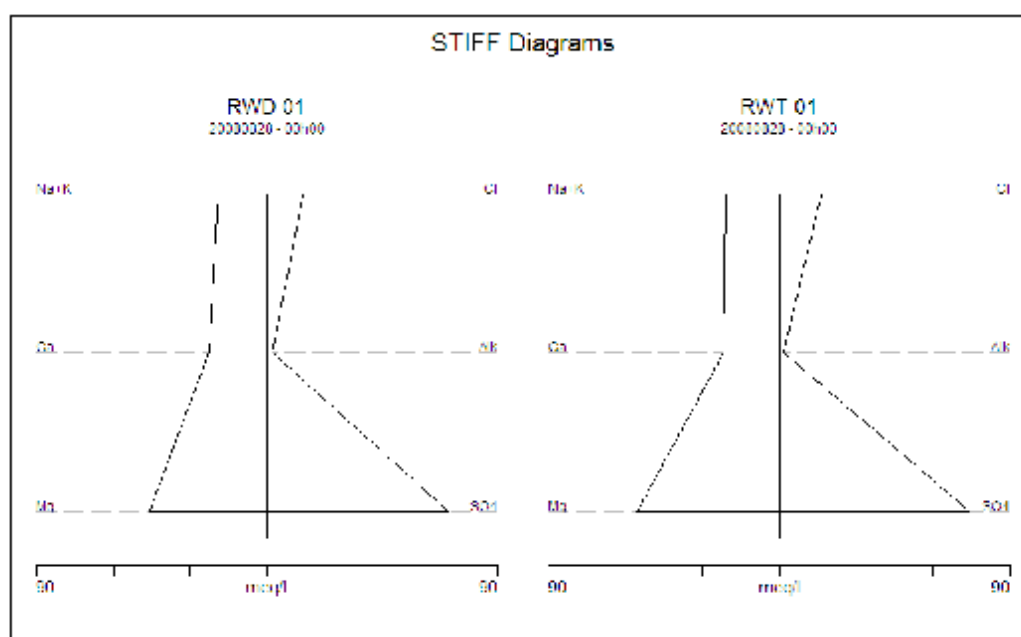


Figure 6-79: Stiff Diagrams of RWT and RWD.

The water used to deposit the Copper Tailings is very high in sulphate, and very low in alkalinity. Moreover, it gets higher in sulphate and other elements as it

returns to the Return Water Dam, as an indication of the current reactivity of the Copper Tailings.



Figure 6-80: EC, sulphate concentrations and pH of the return water. (Standard values in red lines).

The quality of the water is very important parameter as it gives an indication of the leachate from the Copper Tailings to the groundwater.

## 6.5 Salinity generated within the mining area, (groundwater)

During the course of the investigation, new boreholes and replacement boreholes were still being drilled around the waste facilities and a very recent sampling was done on all boreholes to monitor the continuous impact of the waste facilities on the groundwater mostly for the replacement boreholes. These latter boreholes were drilled almost at the exact positions as the previous boreholes from which their nomenclature is derived. Using the FC program (van Tonder *et al*, 2001), aquifer parameters of the newly-drilled boreholes (hydraulic conductivity and transmissivity values) were determined with the Cooper-Jacob method. The

results are presented in the Table 6-23 below. These parameters are very important for contaminant transport modelling.

Table 6-23: Aquifer parameters of the new boreholes.

Borehole name	Transmissivity (m <sup>2</sup> /d)	Depth of pump (m)	Hydraulic conductivity (m/d)
NE 12	83.3	35.82	2.33
NE 13	16.6	35	0.47
NE 14	17.4	33.42	0.52
PGSM-B32	5.9	22.32	0.26
PGSM-B30	0.5	30.95	0.02
PGSM-B31	103.2	22.16	4.66
PGSM-B33	265.6	14.58	18.22
PGSM-B34	12.1	22.55	0.54
PGSM-B35	123.8	19.11	6.48
PGSM-B36	555.9	14.71	37.79
PGSM-B36s	643.6	2.46	261.63
PGSM-B38s	52.5	4.91	10.69
PPM-25a	21.6	17.49	1.23
PPM-56s	4.7	8.31	0.57
PPM-60	2.9	23.82	0.12

Further analysis were performed on these replacement boreholes recently so as to confirm the impacts of the waste facilities on the groundwater. Figure 6-81 below shows the boreholes.

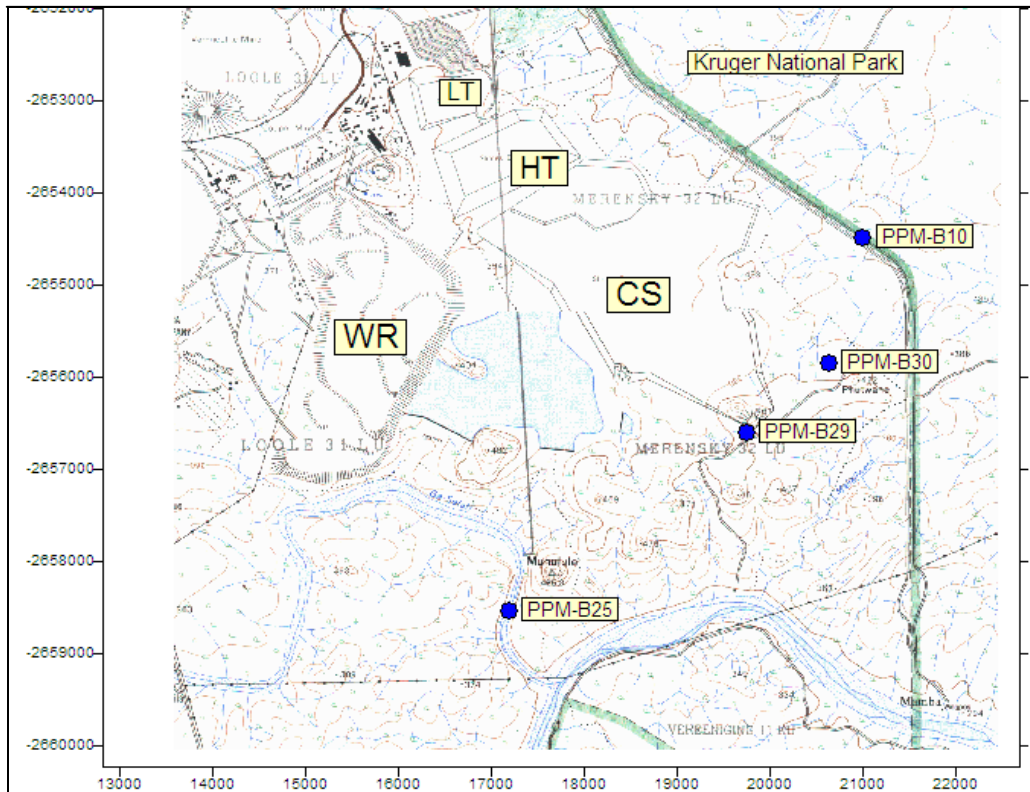


Figure 6-81: Selected boreholes for sampling.

### PPM-B10 and PPM-B10-N

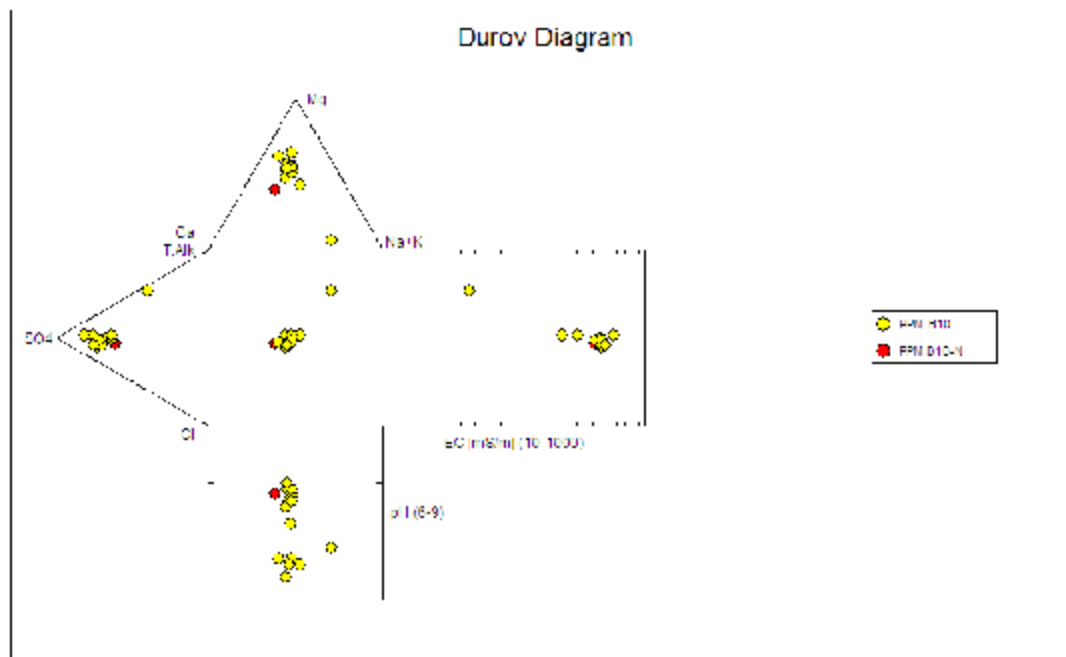


Figure 6-82: Durov diagram of PPM-B10 and PPM-B10-N.



PPM-B10-N is the latest and newest chemical analyses of the borehole PPM-B-10. The latest monitoring data available for this borehole was performed back in April 2000. PPM-B10-N is a sampling data of April 2008, (8 years later), and from the Durov diagram, these latest analyses are very similar to the one dating from eight years back, and thus confirm that the chemistry of the water has been constant.

#### PPM-B25 and PPM-B25-N

This borehole was drilled at the bank of the Selati River. Previous monitoring have shown a high sulphate concentrations, but overall, the chemistry of PPM-B25-N is very similar to the chemistry of the monitoring of PPM-B25 from 1996 to 2008, (Figure 6-83 and Figure 6-84 below). These high concentrations could be suspected to emanate from the infiltration to the ground of water from the Return Water Dam as its chemical compositions are very similar to borehole PPM-B25.

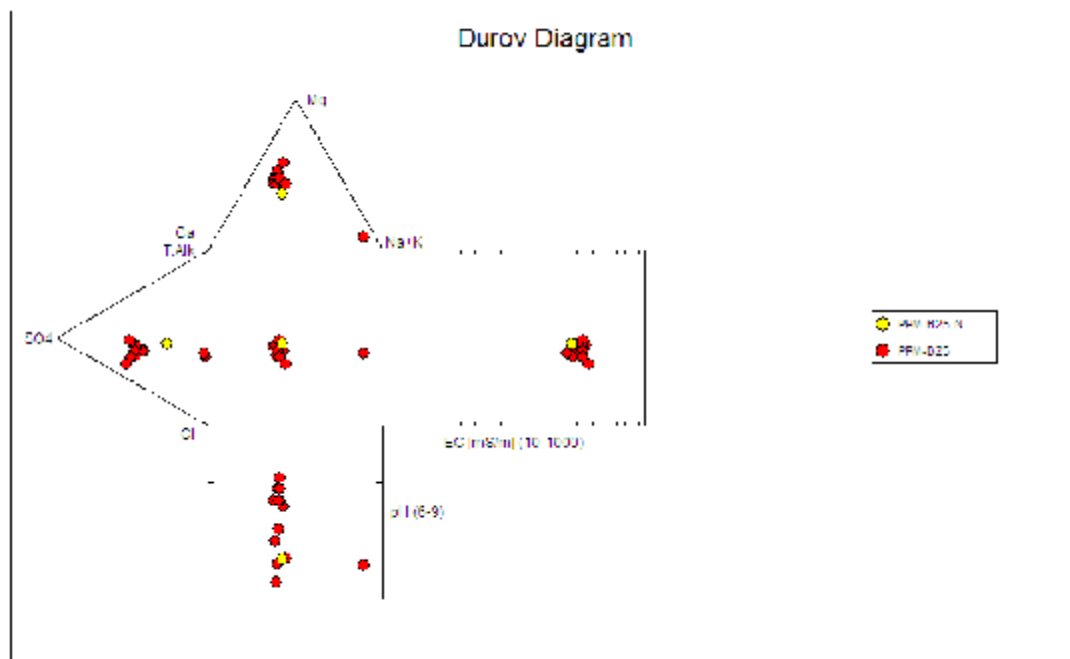


Figure 6-83: Durov diagram of PPM-B25 and PPM-B25-N.

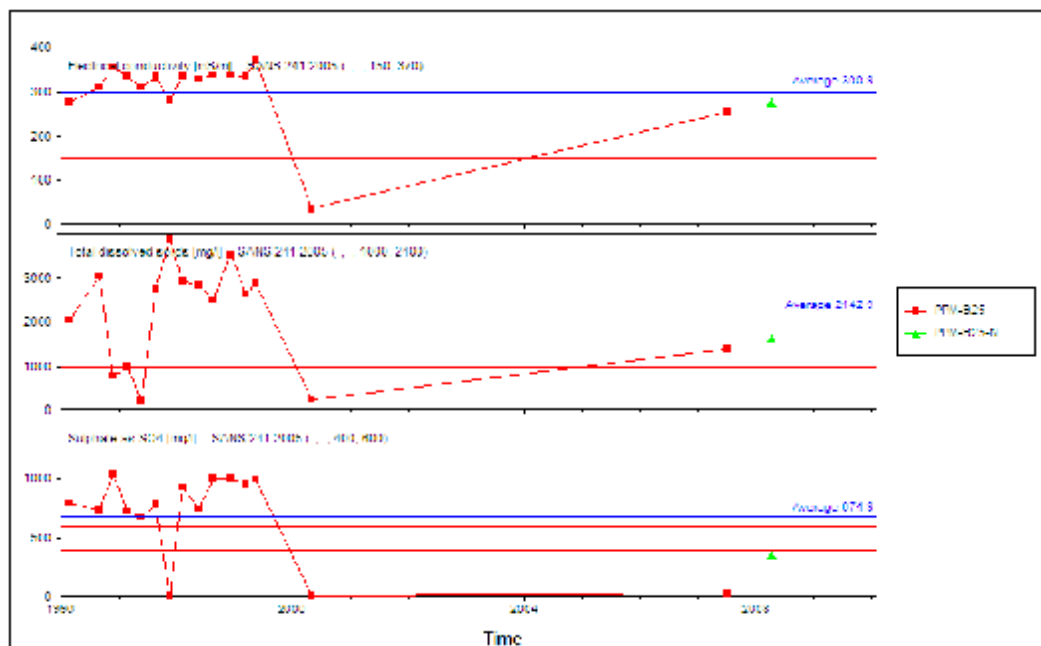


Figure 6-84: Average values of samples PPM-B25 and PPM-B-25-N.

### PPM-B29s and PPM-B29-N

On average, the latest sampling (PPM-B29-N) from this borehole has not been consistent with the previous monitoring, (Figure 6-85 and Figure 6-86).

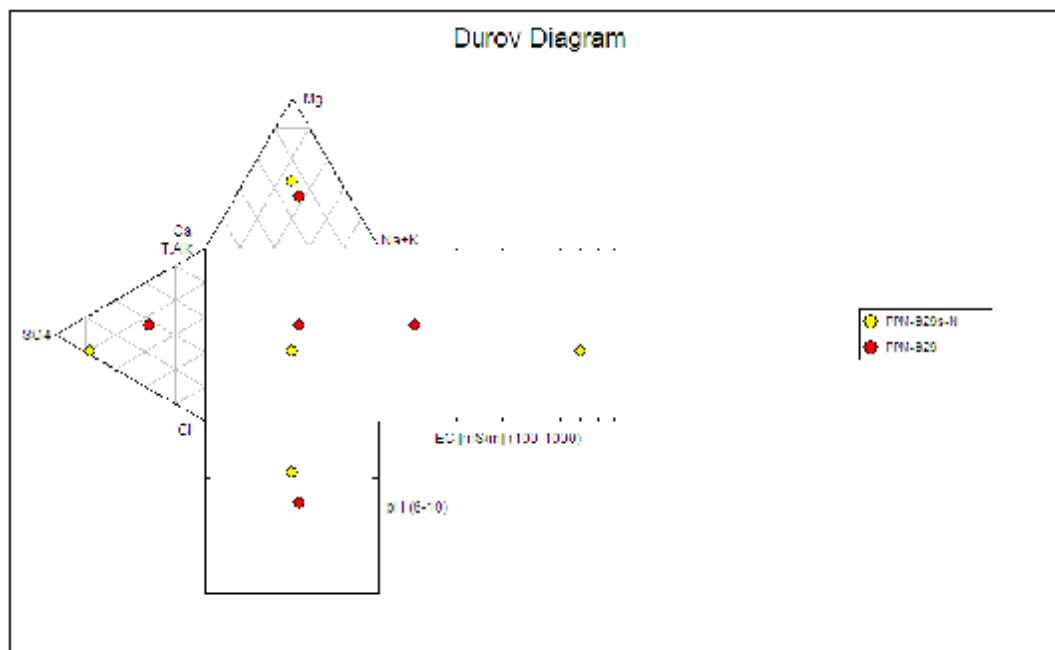


Figure 6-85: Average values of PPM-B29s.

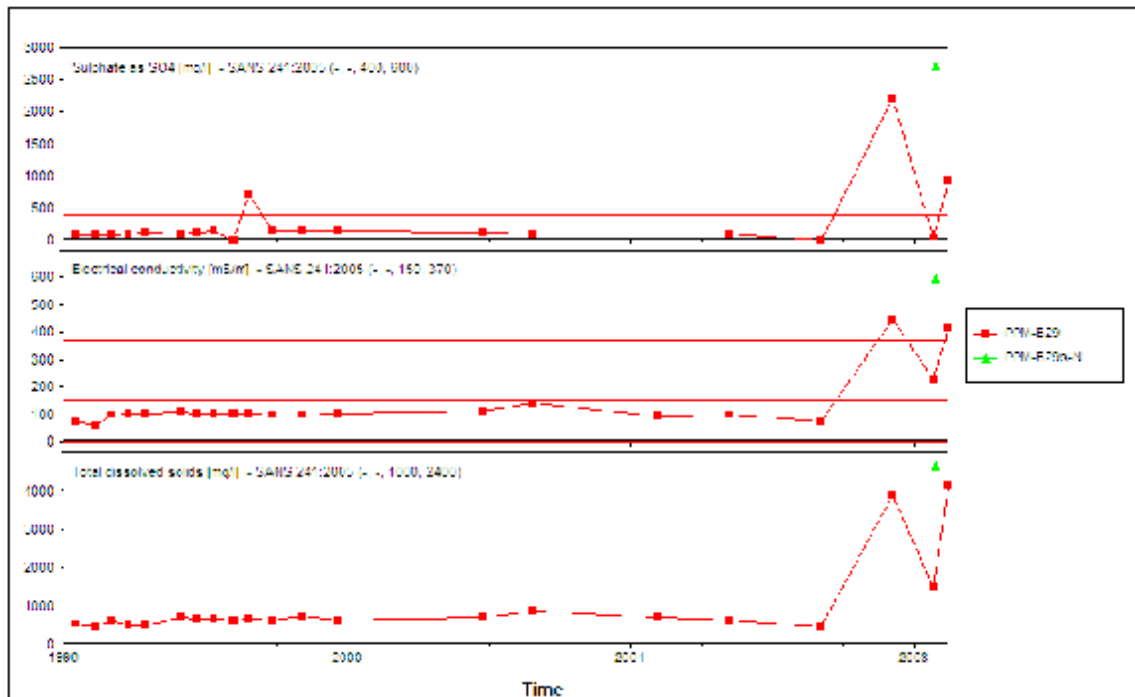


Figure 6-86: Monitoring of PPM-B29s from 1996 to 2008.

From 1999, the monitoring of this borehole stopped being regular (quarterly per annum). This borehole is located right at the foot of the Copper Tailings Dam and the topography onsite in southwards. Moreover, the Copper Tailings is solidify using the high-sulphate water from the Return Water Dam. Since the monitoring was no longer regular, it was not possible to observe the gradual increase in sulphate and other variables during the monitoring. The sharp sudden increase observed can be speculated to happen when the seepage from the Copper Tailings reached the water table.

## PPM-B30 and PPM-B30a-N

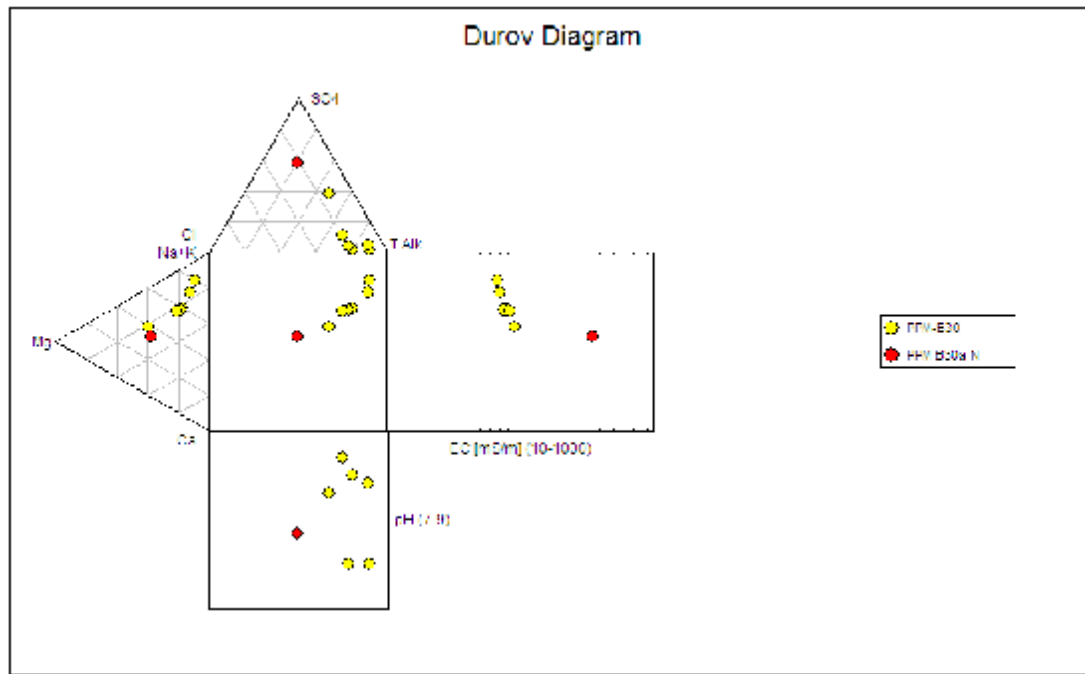


Figure 6-87: Durov diagram of boreholes PPM-B30 and PPM-B30a-N.

This is definitely two sets of analyses, however one can argue that monitoring of PPM-30 had stopped in 1998, and thus that an increase in chemical parameters would have been observed, had the monitoring been regular.

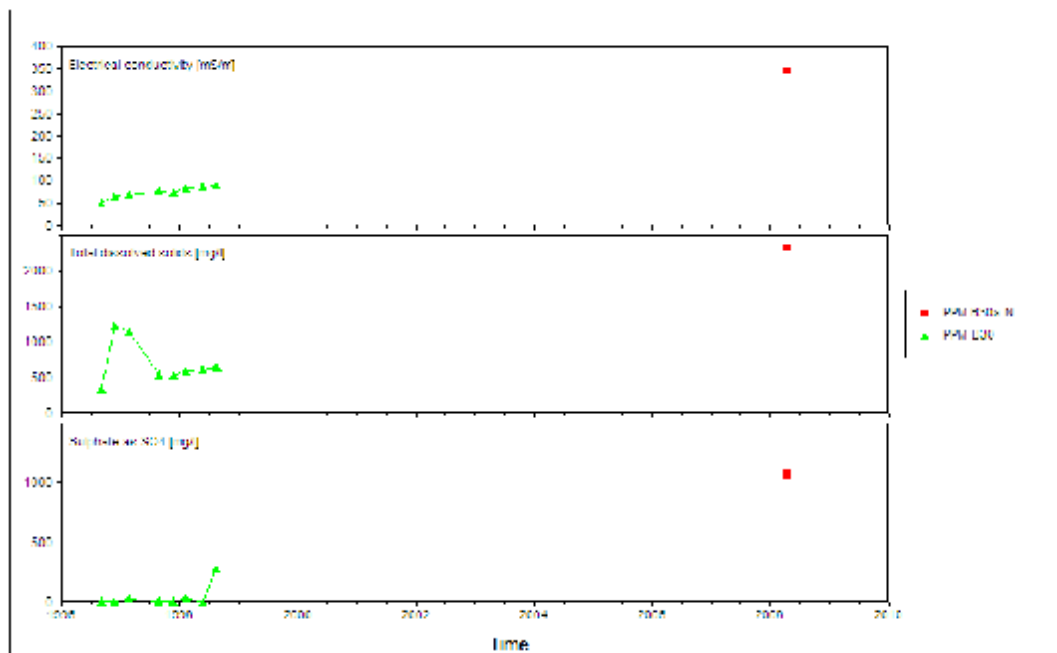


Figure 6-88: Chemical analysis of boreholes PPM-B30 and PPM-B30a-N.

Figure 6-88 actually shows that there was already an upward trend in terms in the chemistries of the groundwater. This tells us that over the years, the quality of the groundwater has been deteriorating, and that the waste facilities are more and more reactive as new waste is being added on them.

## 6.6 Salinity generated beyond the mining area

The Palabora Mining Company (PMC) is not only a mine, but also a wildlife sanctuary. It is thus very important to put a strong accent on environmental issues. This exercise will help in understanding with more certainty where the observed salinity in the mine comes from, where it goes, and more importantly the extent at which it can spread. In this exercise, three separate sites were chosen, where some observations were made, and a sought explanation is provided.

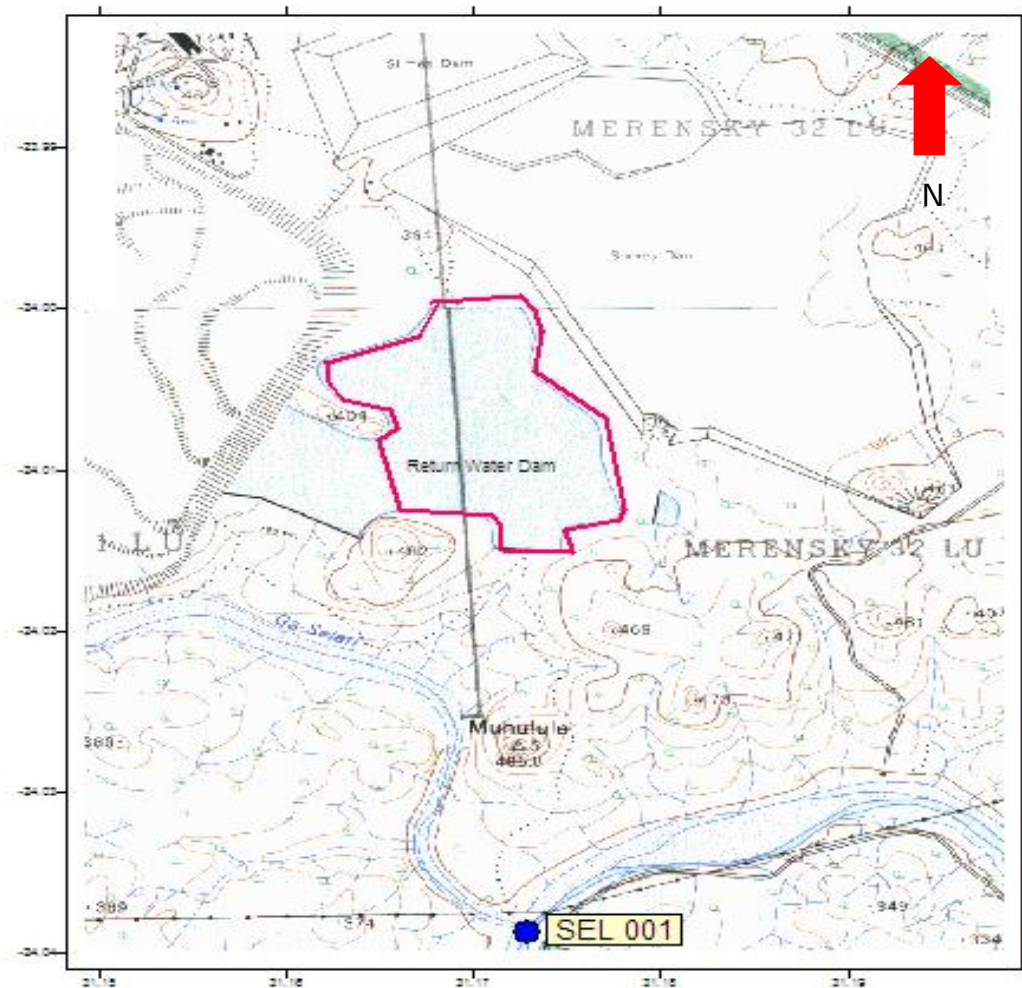


Figure 6-89: Position of SEL001, at the Selati River.

A water sample was collected in the Selati River, just to have an idea of the influence from the tailings. Unfortunately, a single sample is not representative enough. Analysis of that sample however show that the water is within acceptable range, Figure 6-90 below.

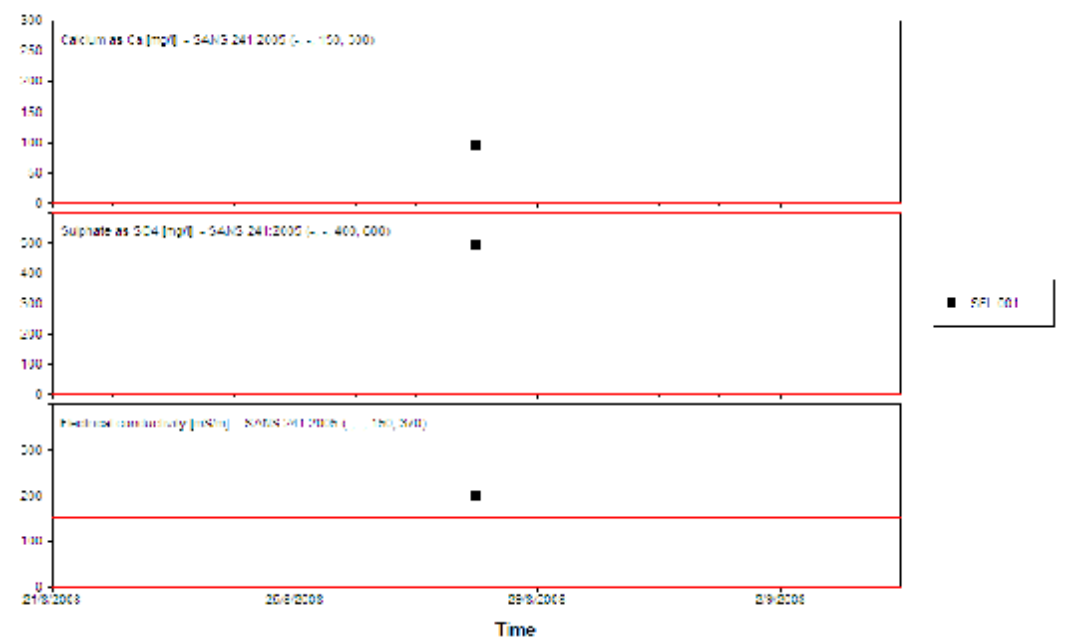


Figure 6-90: Analysis of Selati River water.

## 6.7 Radioactivity

It is also vital to specify that the analysis do not mention all types of plausible contaminants present in the tailings.

In effect, dams' details provided by the mine for as late as August 2007 mention some presence of hazardous substances contained in the stored materials like Uranium and Thorium. The Main copper tailings dam for instance contains Uranium 238 (0.47Bq/g), Uranium 235 (0.02 Bq/g) and Thorium 232 (0.44 Bq/g).

Note:  $39.55 \mu\text{g}/\text{m}^3 = 25280 \text{ Bq/g}$  of Uranium

Table 6-24: Inhalation of Uranium (ATSDR, 1999).

Inhalation of uranium (based on chemical toxicity)	
	TAC ( $\mu\text{g}/\text{m}^3$ )
[ATSDR1999] intermediate duration, soluble	0.4
[ATSDR1999] intermediate duration, insoluble	8
[ATSDR1999] chronic, soluble	0.3
[Jacob1997]	0.07

TAC = Tolerable Air Concentration

Those same concentrations were observed in the Return Water Dam as well, and more recent soil samples (August 2008) were collected in the Magnetite Tailings and the Waste Rock that all yielded some radioactivity, ( $\alpha+\beta = 0.46 \text{ Bq}/\text{cm}^2$  and  $0.49 \text{ Bq}/\text{cm}^2$ ) Eventhough the uranium concentration is still within the limits in certain areas of the mine, in others it is nevertheless a little bit above the acceptable range ( $\alpha+\beta= 0.40 \text{ Bq}/\text{cm}^2$ ); thus its presence should be acknowledged.

However, this discussion is beyond the scope of this dissertation.



## 7 GEOCHEMICAL MODELLING USING PHREEQC

This section of the dissertation involves the use of the geochemical software PHREEQC (Parkhurst and Appelo, 1999) to determine the saturation indexes of the groundwater.

The saturation indices were calculated using the equation:

$$SI = \log(IAP/K_{sp}),$$

Where IAP is the ion activity product observed in solution, and  $K_{sp}$  the theoretical solubility constant. The results indicate that a positive SI is an over-saturation with respect to the given solid phase, while a negative SI is an under-saturation of the given solid phase. At  $SI=0$ , the solution and the solid phase are at equilibrium. The output from these PHREEQC simulations is given on the figures below. A complete list of table is available as an appendix.

The figure plots the saturation state of the expected controlling mineral phases as a function of pH for over 1700 groundwater samples.

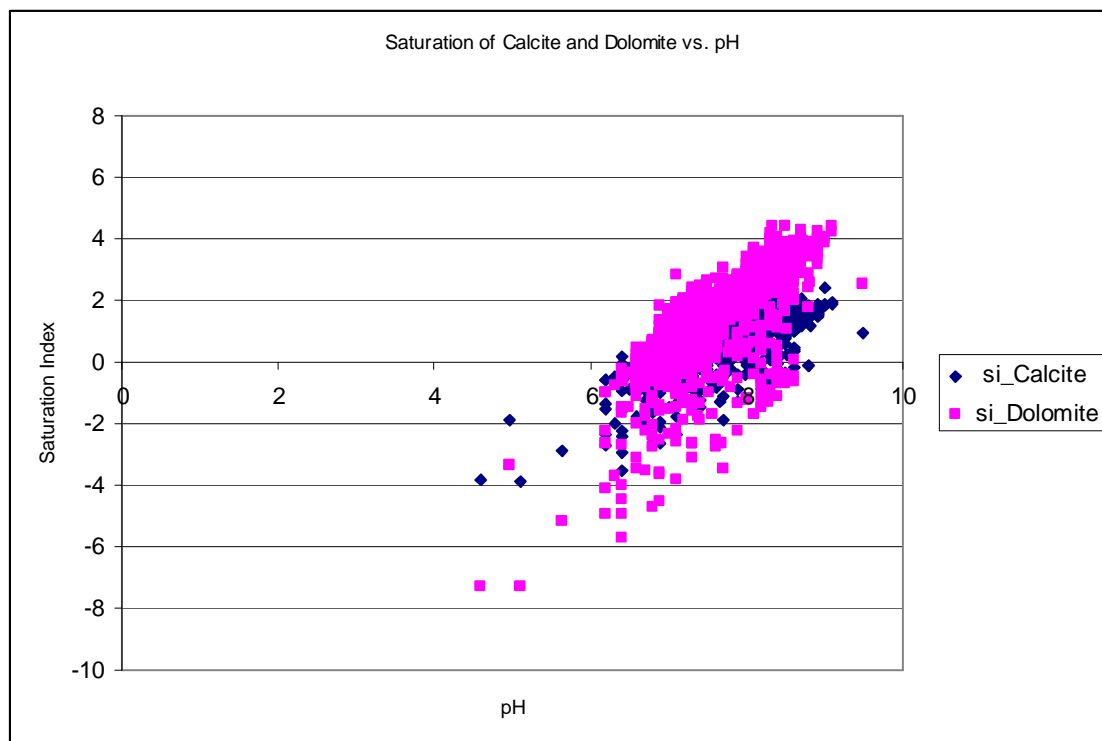


Figure 7-1: Calcite and Dolomite saturation with respect to pH.

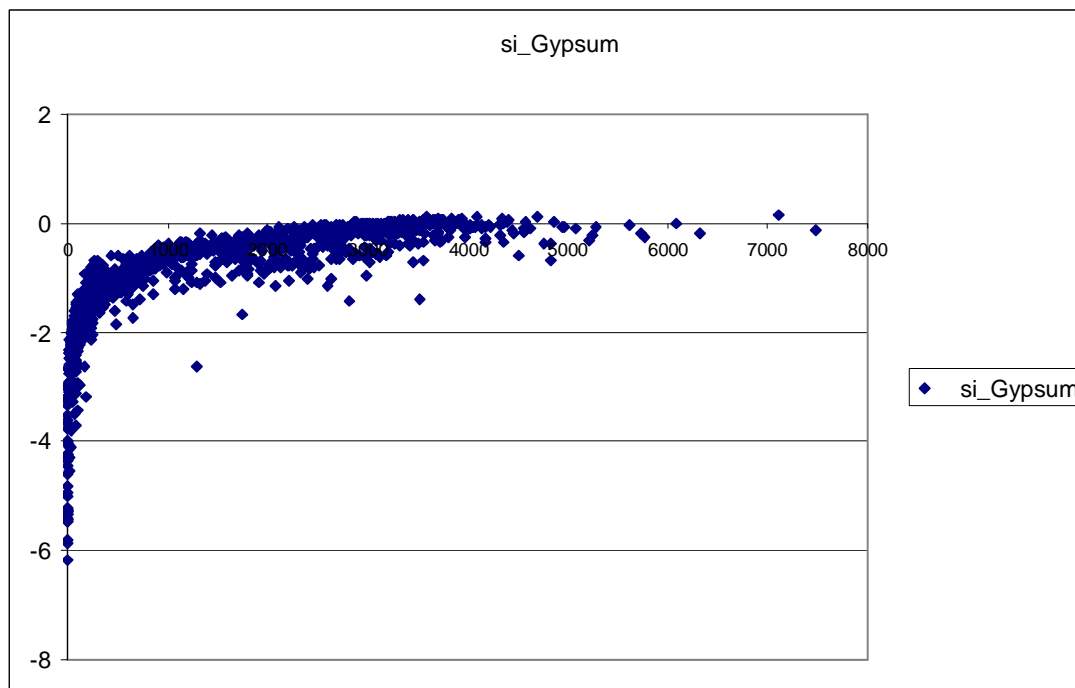


Figure 7-2: Saturation of gypsum as a function of sulphate concentration.

It is interesting to note that calcite and dolomite are consistently oversaturated at pH-values above 6.3, (Figure 7-1). This is a very important observation, and following this is that, as the pH increases, the relative degree of apparent supersaturation also increases. For sulphate concentration well beyond 2000 mg/l, the water would be oversaturated with calcium and sulphate, thus would be precipitating gypsum, which will limit sulphate concentrations due to the high Ca content in the water, (Figure 7-2).

The abundance in carbonates plays a very important in the sense that there is more than sufficient neutralizing potential for one reason, and another reason being that very little pyrite and other acid-forming sulphides present. Thus the overall result is that it is very unlikely that acid generation will be a significant issue from the samples collected. A complete table of the results is available as an appendix.

Moreover, the neutralization reactions contribute to the release of aqueous sulphate and calcium in groundwater, as can be seen on the figure below for the same set of boreholes.

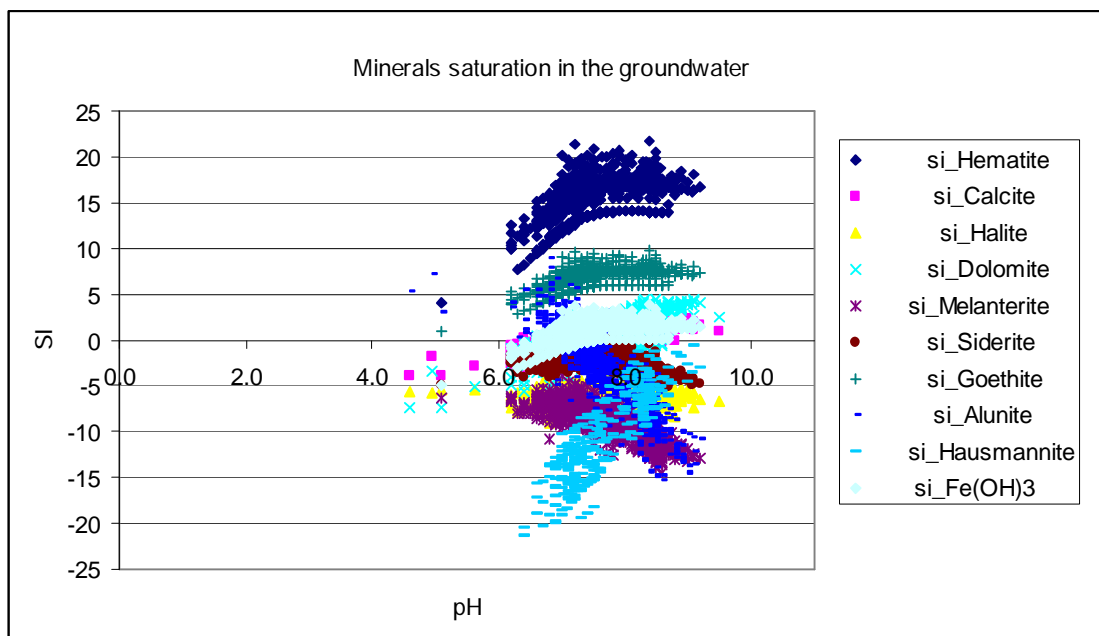


Figure 7-3: Saturation Indices of minerals vs. pH (1).

While some minerals get to be under-saturated, others super-saturate from a pH to between 6.2 to 9.5, with iron oxides Goethite ( $\text{FeO}(\text{OH})$ ) and Hematite ( $\text{Fe}_2\text{O}_3$ ) dominating the non-carbonated super-saturated minerals. It is understood as a reminder that if the pH of AMD is increased, as would happen in contact with basic minerals such as calcite ( $\text{CaCO}_3$ ) or dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) or entry into a water system of higher pH, then metallic ions such as  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{As}^{3+}$  will react to eventually form hydroxides as precipitates by the general reaction:



where:  $\text{OH}^-$  = hydroxyl ion;  $\text{M}(\text{OH})_n$  = metal hydroxide.

As hematite is the more thermodynamically stable solid form of iron (III), it would not dissolve to a lower concentration than ferrihydrite ( $\text{Fe}(\text{OH})_3$ ). However, oxidizing groundwaters are generally in equilibrium with ferrihydrite, ( $\text{SI} \approx 0$ ), not hematite. In fact, the saturation indices for are often greater than 10, which

represents oversaturation by a factor of  $10^{10}$ , (Deutsch, 1997). Moreover, hematite does not precipitate fast enough to control the dissolved iron concentration; thus it is not reactive enough to limit the dissolved concentration. Ferrihydrite may convert to the more stable hematite form of iron given sufficient time, but this process occurs by a mechanism that does not limit dissolved iron concentration to the hematite saturation value. The attenuation of heavy metals concentrations is possible as the result of adsorption and co-precipitation with goethite and other iron oxides, (Herbert, 1994). For instance, investigations have indicated that iron (Fe) solubility can be controlled by siderite ( $\text{FeCO}_3$ ) at high pH,  $\text{Fe}(\text{OH})_3$  at moderate to slightly acid pH values, (Dubrovsky *et al*, 1985), (Levy *et al*, 1996). In general, as metals are transported away from their source, their concentrations in groundwater may be controlled by precipitation-dissolution and co-precipitation reactions, adsorption-desorption reaction and solid-solution substitutions, (Blowes and Jambor, 1990, Anderson *et al*, 1991).

In natural aqueous environments, the redox system may not always be in equilibrium. In a system that has many redox couples, if the redox potential (pe) of all the couples is the same, then the redox system can be considered in equilibrium and the measured pe would be the system pe as was the case in this study, (Chapelle, 2004; Herbert, 1994). Many groundwater systems however are not well balanced, (Lindberg and Runnels, 1984).

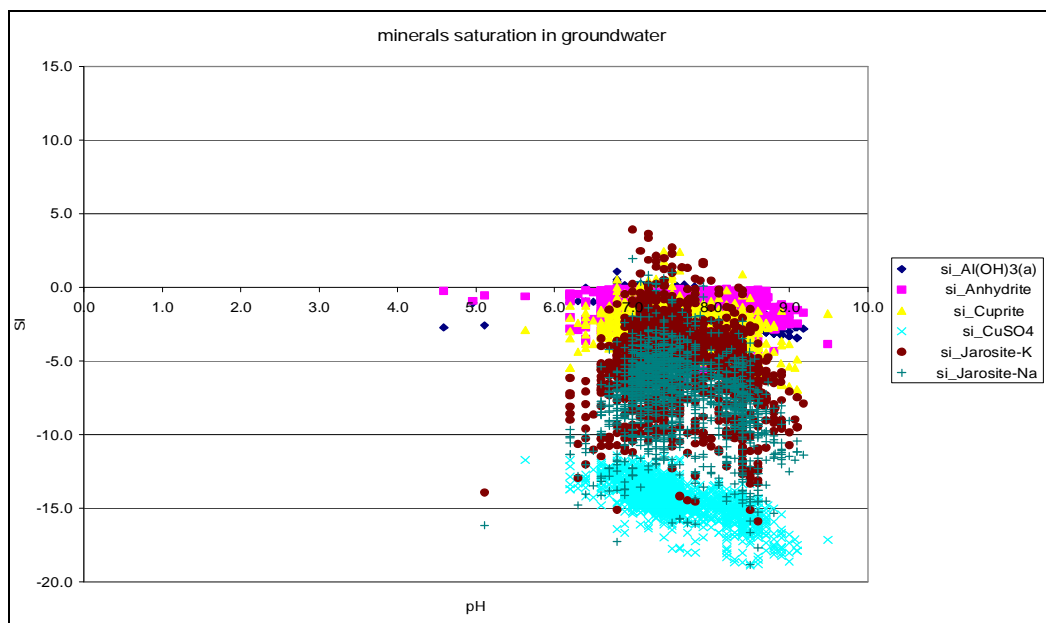


Figure 7-4: Saturation indices of minerals vs. pH (2).

This graph, (Figure 7-4) shows some other minerals present in the groundwater. Anhydrite ( $\text{CaSO}_4$ ) and copper (II) sulphate can form from the overall net reaction of Chalcocite and/or Covellite neutralisation. Continuous exposure of hydrated iron sulphate minerals such as melanterite, ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) to oxidizing conditions, can lead to less stable hydroxides such as jarosite  $[(\text{K}, \text{Na}), (\text{Fe}, \text{Al})_3(\text{SO}_4)_2(\text{OH})_6]$ , ferrihydrite ( $\text{Fe}(\text{OH})_3$ ) or even goethite ( $\alpha\text{-FeOOH}$ ), (Schwertmann and Taylor, 1989; Bigham, 1994).

Attention should be brought to using saturation indices to identify reactive minerals. It is often possible that by some fortuitous circumstances that the concentrations in groundwater of the components of a mineral will just happen to be at the right combination of values to calculate a saturation index close to zero even though the mineral is not forming in the aquifer environment: this could simply be occurring because the concentrations might be in the correct ratios in the groundwater, due to control of solution concentrations by other minerals, thus it is said that the minerals appear as XRD-transparent phases.

However, though precipitation of iron was not experimentally tested, neither was it observed. Moreover, the neutralization of acidic drainage is not hindered. The neutralization would be impeded if there were not sufficient carbonates present.

Net neutralization potential driven by the weathering of carbonates, aluminosilicates and hydrous oxides buffers any possible acid production from sulphide oxidation and hydrolysis reactions on site.

## 8 SALT LOADS ESTIMATIONS

The salt loads estimations are a useful tool to quantify the long-term salinity from the mine wastes and unto the environment.

The usual way to get these estimates is by obtaining the individual quantities of the elements released per each facility times the total volume of the corresponding waste facility. However this method is not the best as it does not provide with the long-term release of the elements, see Table 8-1.

Table 8-1: Elements released (tons) per facility using the ABA.

mass released	WR average (estimated)	CS (average)	HT (average)	LT (average)
per element(tons)				
Ca	2.37E+12	7.43E+05	1.95E+05	1.82E+04
Cu	6.95E+09	1.56E+03	5.76E+02	8.69E+00
Fe	7.10E+09	3.04E+03	1.17E+02	7.66E+01
K	8.30E+11	3.39E+04	1.25E+04	1.92E+02
Mg	1.37E+12	2.80E+05	2.12E+05	1.75E+04
Mn	5.23E+09	5.44E+02	4.26E+02	5.58E+01
Na	3.12E+11	4.90E+04	2.81E+04	1.07E+03
Ti	4.36E+08	2.15E+02	4.73E+01	3.66E+00
Pb	8.28E+08	3.32E+01	1.04E+01	1.63E+00
Zn	4.71E+08	5.94E+01	4.37E+01	4.21E+00
SO <sub>4</sub> <sup>2-</sup>	4.91E+12	5.04E+05	1.77E+05	1.63E+04

Another method widely used is the humidity cells method. It consists of incubating a 1:1 weight for volume (w/v) of crushed and dry waste samples into distilled water weekly for at least twenty (20) consecutive weeks in a container. After wetting the samples, they are allowed to precipitate and an hour later, each water from containers was extracted and analyzed once a week for its chemical compositions. Samples should be kept wet at least for four (4) days in a week to simulate field situations. After analysis, a graph of the results is drawn, in which constant reactivity of elements can be observed.

A third method, in addition to humidity cells methods would be to use a geochemical reactions modelling software, in which many scenarios can be predicted, i.e. different kinds of water as input, different kinetic rates, etc... In the case on this discussion, the *Geochemist's Workbench* software was used and selected results appear in the Figure 8-1 to Figure 8-3 below.

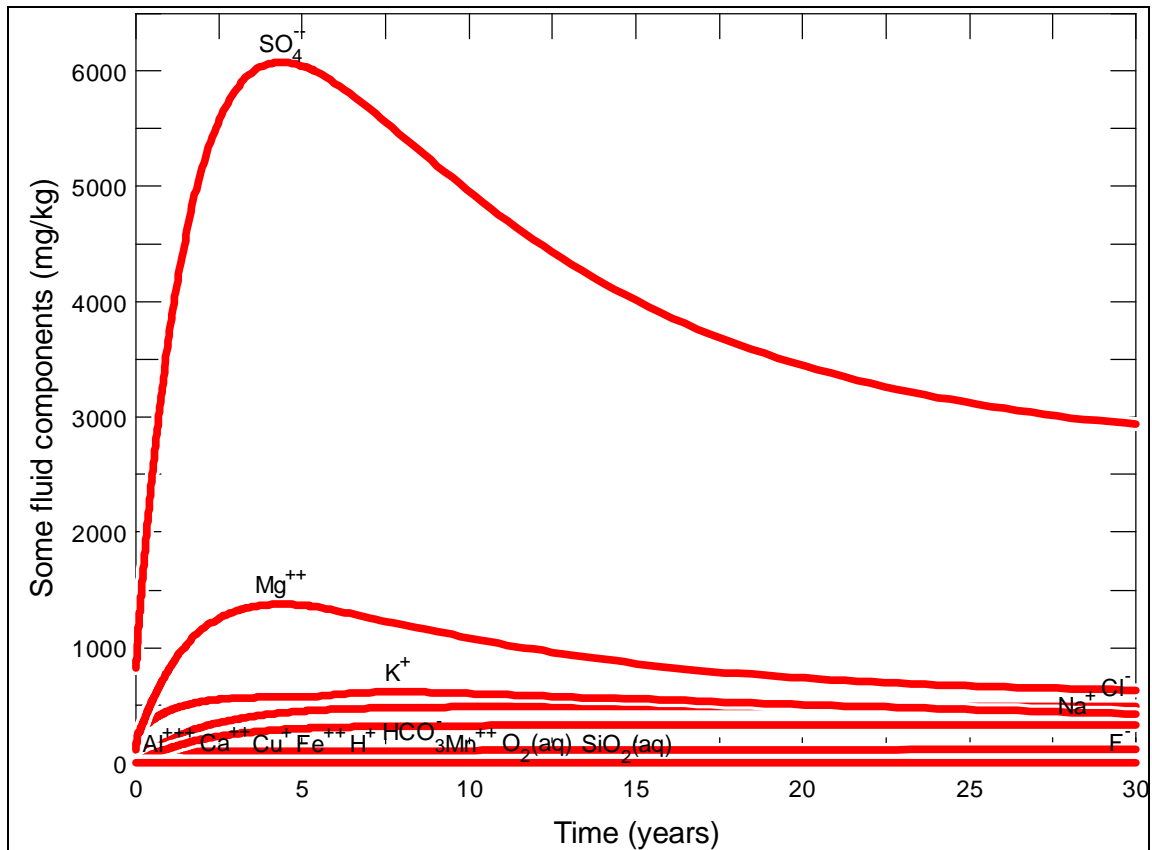


Figure 8-1: Expected water quality profile at the Copper Tailings with return water used as input (very high waste: water ratios), (Usher and Moukodi, 2008).



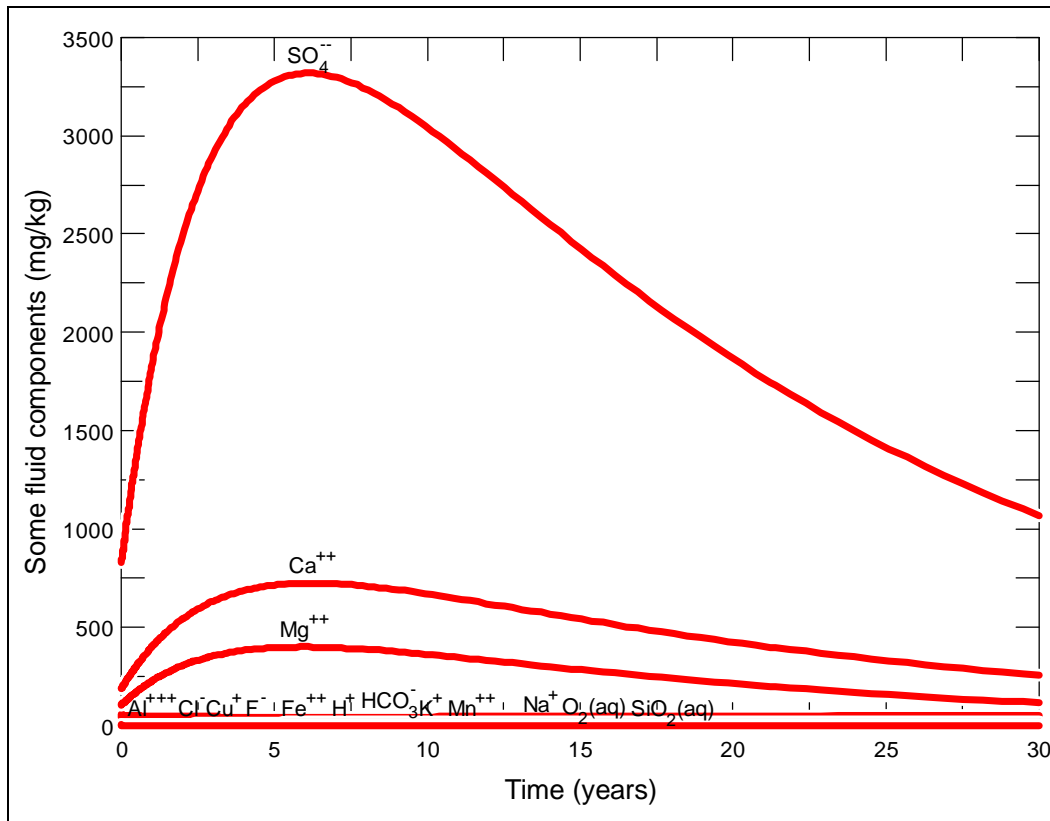


Figure 8-2: Expected water quality profile at the Copper Tailings with rain water used as input (very high waste: water ratios), (Usher and Moukodi, 2008).

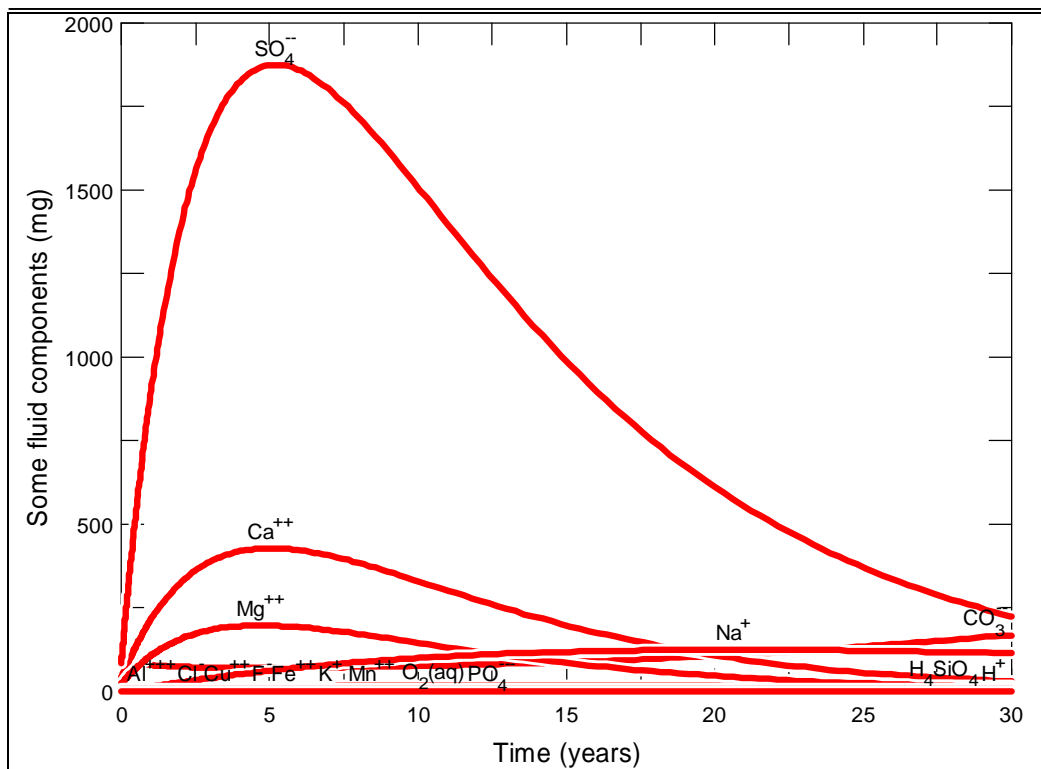


Figure 8-3: Dissolved ion profile from the waste rock over time (reactive case), (Usher and Moukodi, 2008).

Using this latter approach above it is therefore possible to project expected salt loads from each facility over time.

These can be calculated as follows:

Table 8-2: Expected loads from each facility (t/year), (Usher and Moukodi, 2008).

	Load			
	Lowest	Expected Range		Highest
Copper Tailings	217	347	277	722
High Ti	6	13	10	36
Active High Ti	3	7	5	18
Low Ti	1	2	1	6
Waste Rock	68	165	132	419
Vermiculite Tailings	0.29	0.48	0.4	2
Vermiculite Waste Rock	0.09	0.13	0.11	0.55

## 9 CONCLUSIONS

The investigation into the acid mine drainage potential and salt loads at Palabora Mining Company was undertaken. The most important findings from this can be summarised in the following points:

- Over 280 samples of the solid waste were obtained across the mine site.
- Over 1700 water samples were chemically interpreted.
- These samples were taken using a variety of methods most appropriate to waste material sampling.
- A statistical assessment of the samples indicates that a sufficient number of samples were obtained to provide at least an 80% confidence, even though this does not mean that sufficient samples were taken for each type of waste; nonetheless the results can be regarded as statistically representative for the mine waste as a whole. However, at each of the waste sites, samples were distributed spatially as far as it could be possible.
- The samples were obtained from copper tailings, waste rock, magnetite tailings (both high and low titanium), vermiculite tailings, vermiculite waste rock and the spills ponds and slag wastes.
- The determination of initial pH values corresponds very well to paste pH values measured in the field. These are generally at pH values above 8, which correspond very well to the field pH values.
- The pH values of the oxidised samples indicate that very few samples acidify under strong oxidation conditions. This has important implications for the potential generation of acid mine drainage at PMC.
- The acid potentials determined by hydrogen peroxide oxidation and determination of reactive sulphide, indicate that most of the waste contains very low values of sulphide, and from a reactive perspective most of the

waste should be relatively inert. This would suggest that in the majority of cases the amount of sulphate generated per ton of material would be low. However, as with all these results, the sheer volume of waste material means that despite this inert nature, elevated concentrations of dissolved constituents may still be possible.

- The neutralisation potential of the waste material tested is generally very high, and the waste has a significant potential to neutralise acid. The values obtained, suggest that mildly alkaline waters should persist at PMC in the future.
- Oxidation of the samples with hydrogen peroxide allows the analysis of the supernatant to provide the quantities of sulphate and metals released by the waste when fully oxidised. In most mining waste high in reactive sulphides, this would release a significant amount of sulphate and an increase of several orders of magnitude for different metals as pH drops. Due to the relatively inert nature of the waste and the neutral conditions maintained in the overwhelming majority of the waste samples, the increase of salt release under oxidation is not as significant. This is a very important finding as most of the waste exists under potentially oxidising conditions on the site, and suggests that salt loads should not be expected to dramatically increase over time.
- An equally significant finding is that due to the prevention of acidic conditions and the consequent near-neutral conditions that will exist, very few metals are significantly soluble.
- The mineralogy results generally correspond very well to the acid-base accounting and solubilisation results. The most important findings from this include dolomite as the major neutralising/ alkaline mineral, occurring as part of what is characterised as the carbonatite at the mine, the confirmation of high magnetite values in the magnetite tailings dams, the confirmation of significantly higher Ti in the Hi-Ti than Lo-Ti, and the very low Copper (Cu) values found in the Copper Tailings.

- The particle size distribution indicates low particle sizes for the tailings, with the finest material found in the copper tailings. Reactive surface areas were estimated from this data.
- The geochemical modelling using PHREEQC to determine the minerals controlling the observed water quality show that Ca-containing carbonates, dolomite and calcite, are important controls on pH, gypsum solubility constraints limit sulphate concentrations, the important weathering phases may include Illite/montmorillonite with K-feldspar, and alunite possibly being important minerals in the water quality observations.
- The laboratory results suggest that the vermiculite waste should pose a relatively low salinity risk due to the geochemical compositions.
- The results as a whole suggest that the waste is relatively inert. The high concentrations found on site are due to the very large volumes of mining waste, the long reaction time and the very high estimated rock: water ratios projected at the site.
- Because no acidic drainage was found, it could be said that Covellite and Chalcocite were the sulphides of copper involved in the mining, rather than chalcopyrite, which is much more acid-generating. Thus all copper sulphides minerals should not be expected to produce the same results.
- In addition to the carbonates, the silicate minerals also play an interesting role in consuming the acid that could have been generated as they dissolve. The silicates themselves will not play a significant role in the neutralization of acidic drainage over the short term (during the life of the mine) as their slow reaction rates are shadowed by the carbonates' much faster rates, but in the longer run, they help maintain pH values not too high.

## SUMMARY

This dissertation characterised geochemically waste from a copper mine in the Bushveld Igneous Complex, coupled with hydrochemical interpretations. In the first part of the dissertation, the methods involved in the quantification and qualification of mine acidic drainage were discussed. This included paste and rinse pH, Acid and Base potentials, net neutralisation potentials and neutralisation potential ratio. These methods form what is known as Acid-Base Accounting, (ABA). In the second part of this dissertation, the sampling methods and representativeness of the samples were discussed. All these methods are scientifically justifiable as they are in agreement with methods used internationally. In the third and most important part of this dissertation, results were discussed and proven to correlate with visual estimates from the field.

In sulphides-containing waste material, Acid Mine Drainage (AMD) is produced due to the ingress of oxygen and water mainly from rainfall, and thus subsequent oxidation of sulphide-bearing minerals with the help of bacteria. However, in the presence of sufficient neutralisation potential, alkaline drainage is favoured as carbonated minerals (mainly dolomite and calcite) buffer the acidity. For this study, copper sulphide is recovered from foskorite ore imbedded with carbonatite which helped at the non acidification of the mine site.

In the dissertation, the geochemical software PHREEQC was used and it confirmed that many silicates and alumino-silicates minerals are dissolved in the groundwater. This is an important finding as the presence of silica is an indication that substantial amount of acidity could have been released. This also constitutes reasonable evidence for the fact that chalcocite and covellite which are the main sulphides of copper mined on site can be considered as "weak" sulphides unlike pyrite which can be more severe to the environment. The software PHREEQC also confirmed that dolomite and calcite control the pH of the water, thus only fairly alkaline values in the range of pH 8 to pH 9.5 are expected on site.

With visual investigations, it has been noticed that natural vegetation is taking place around the site even on the most hostile tailings like the magnetite. This is a very important aspect as positive outcome is expected for the fauna after mine closure.

The following serve as recommendations:

- The neutralisation processes release sulphate into the groundwater, and it is recommended that tracer tests methods be conducted to estimate the travelling time of the salts.
- It is also recommended that the mine speed up the re-vegetation process as many animals cross the Kruger National Park to feed themselves within the mine.
- It is recommended that more regular monitoring on boreholes be conducted as many dataless. Also it is suggested that anomalous boreholes be investigated, geochemically logged and re-sampled to verify or determine likely origins and interactions.
- For further research, standard values of salt loads should be implemented so as to compare acceptable values with abnormal values.
- The study of ABA using static tests should always be coupled with the humidity cells methods. While the former provides with the probability of acid formation, the latter provides with the reaction rates.
- Additional studies should be conducted exclusively outside the mine to corroborate with the results from inside the mine.

## RESUME

Cette étude géo-chimiquement a examiné les déchets d'une mine de cuivre dans le Complex Igneux du Bushveld (Bushveld Igneous Complex), ainsi qu'interprété les données hydro-chimiques des eaux souterraines. En première partie de cette thèse, les méthodes utilisées dans la quantification et la qualité des écoulements acides en milieu minier y sont discutées. Il s'agit entre autres des pH initiaux et finaux, des potentiels acides et alcalins, des potentiels net de neutralisation, ainsi que le ratio de neutralisation potentiel. Ces méthodes sont connues comme étant des méthodes statiques ou Comptabilité Base-Acide (Acid-Base Accounting). En seconde partie de cette dissertation, les méthodes d'échantillonnage et de représentativité des échantillons y sont discutées. Toutes ces méthodes sont internationalement reconnues et sont donc justifiables et scientifiques. En troisième partie de cette étude, les résultats obtenus corréleront avec la situation observée sur le terrain.

Les écoulements acides en milieux minier sont produits lorsque les roches contenant des sulphides sont exposées aux conditions atmosphériques, l'eau et l'oxygène de l'air, et en présence de quelques bactéries. Toutefois, lorsqu'il y a assez de potentiel tampon, les écoulements alcalins sont favorisés aux dépens des écoulements acides. Pour cette étude, le minerai d'intérêt est entouré de carbonatite qui empêche toute formation acide à cause de son grand potentiel tampon.

Dans cette dissertation, le logiciel de géochimie PHREEQC y est utilisé et il confirme la grande présence des silicates et des aluminosilicates dans les eaux souterraines. Cette découverte est assez importante car elle met en exergue toute présence acide à s'être neutralisée. Ceci constitue une preuve raisonnable que les minerais d'intérêt se trouvent être la covellite et la chalcocite, et que ces dernières sont des sulphides « faibles » par opposition à la pyrite qui est un sulphide beaucoup plus sévère envers l'environnement. Le logiciel PHREEQC démontre également que le carbonate de calcium et la dolomite sont les minerais



qui contrôlent la qualité des eaux. Ceci est important dans la mesure où les valeurs du pH se situeront entre 8 et 9.5.

Il a été observé que la végétation réapparaît tout autour du site. Ceci peut porter à croire qu'une issue positive pour la faune y est à espérer après fermeture de la mine.

Pour cette étude, les recommandations suivantes sont importantes :

- le processus de neutralisation libère les ions sulfatés et il est recommandé que des tests pour déterminer la vélocité du flux des eaux soient conduits.
- Il est recommandé également que la mine accélère le processus naturel de re-végétation pour le bien-être de la faune.
- Il est recommandé un suivi plus régulier des forages qui ont des données incohérentes, ceci dans le but d'y déterminer l'origine et les interactions.
- Des recherches approfondies doivent être faites pour délinéer une marge d'alcalinité à être produite.
- Il est aussi suggéré que les tests statiques soient obligatoirement associés aux méthodes des cellules humides pour pallier au manque du taux de virage des réactions dans le premier cas, et à la prédiction des écoulements acides dans le deuxième cas.
- Des études approfondies doivent exclusivement être conduites à l'extérieur de la mine pour que les résultats observés à l'intérieur puissent corroborer.

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## KEYWORDS

Hydro-geochemistry

Characterisation

Acid Mine Drainage

Salt loads

Sulphides

Tailings dams

Waste rock

Mineral dissociation

Groundwater

Alkalinity

## APPENDIX

Hard copy of all useful data for this dissertation.