Evaluation of Acid-Base Accounting Methods and the Prediction of Acid-Mine Drainage in the Middelburg Area

by

Moipone Precious Mokoena

A dissertation submitted to meet the requirements for the degree of

Magister Scientiae

Faculty of Natural and Agricultural Sciences

Institute for Groundwater Studies

at the

University of the Free State

Supervisor: Mrs. L-M Cruywagen-Deysel

Co-Supervisor: Dr. D Vermeulen

February 2012

Acknowledgments

First and foremost, the Lord God deserves all the honor and praise.

I would hereby wish to express sincere thanks to the following people and personnel without whom this thesis would not be possible:0

- My parents (Nthofela and Sello Mokoena), for their continuous prayer, encouragement and support of my career.

- Lore-Mare Cruywagen-Deysel, for her patient supervision, support and guidance over the duration of this study.

- Dr Danie Vermeulen for his assistance and valuable insight into some aspects of this study.

- Special thanks to the Head of IGS laboratory, Lore-Mare Cruywagen-Deysel, for accepting on behalf of the Institute the financial implications of my studies.

- Prof Gideon Steyl for providing me with substantial comment or review.

- Institute for Groundwater Studies Laboratory personnel for their assistance and continues interest in the progress of my work.

- Hezel Masilela and Moses Njoti for proofreading and IT matters.

Declaration

I, Moipone Precious Mokoena, hereby declare that this submission is my own work and that, to the best of my knowledge and belief it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgement has been made in the text. I furthermore concede copyright of the dissertation/thesis in favor of the University of the Free State.

-------------------------- --------------------------------
Signature Date

Table of contents

CHAPTER 1 1

1. Introduction 1

1.1 Relationship between AMD from open-cast mining activities and groundwater studies 1

1.2 A brief review on the importance of AMD prediction in South Africa 3

1.3 Objectives of study 4

1.4 Methods of investigation 5

1.5 Thesis structure 5

CHAPTER 2 6

2. Literature review on the processes associated with AMD 6

2.1 Definition of ARD and AMD 6

2.2 The Sulphur cycle 9

2.3 Geochemical processes that are related to AMD 10

2.3.1 Oxidation of Sulphide minerals 10

2.3.2 Dissolution of carbonates, oxyhydroxides and silicates 12

2.3.3 Precipitation of oxyhydroxides 13

2.3.4 Dissolution and precipitation of sulphate minerals 14

2. 4 The influences of bacteria in AMD 14

2.4.1 Direct and Indirect mechanism of Microbial Activity 18

2.5 Interrelations and Differences between Sulphur oxidation and Sulphur reduction 20

2.6 Conclusions for chapter 2 22

CHAPTER 3 24

3. Australian versus South African Acid-Base Accounting methods 24

3.1 Sampling 24

3.2 Different Methodologies of ABA 27
3.2.1 Actual acidity of samples 27
3.2.2 Potential acidity method 28
3.2.3 Neutralising potential 29
3.3 Results and Observations of the ABA methods 30
3.3.1 Actual Acidity method 30
3.3.2 Peroxide (Potential Acidity) Methods 38
3.3.3 Neutralising potential method 48
3.4 Conclusion and Recommendations on Chapter 3 51
Chapter 4 54
4. Case study: Prediction of AMD in the Middelburg area 54
4.1 Locality of the Study Area 54
4.2 Objectives 62
4.3 Methodology 62
4.3.1 Sampling 62
4.3.2 Static tests 63
4.3.3 Kinetic tests 68
4.3.4 The importance of pH in the prediction of AMD 70
4.4 Overall climate 71
4.4.1 Temperature 71
4.4. 2 Precipitation 72
4.4.3 Evaporation 73
4.5 Geology and Mining 73
4.5.1 Basin shape and tectonic setting of the Karoo Supergroup 73
4.5.2 Geology 75
4.5.3 Mining operations at the Study area 77
4.6 Surface hydrology and Geohydrology of the investigated area 77
4.6.1 Surface hydrology 77

4.6.2 Geohydrology 84
4.6.3 Decant 89
4.7 Sites investigated, results and interpretation 90
4.7.2 Hartebeesfontien 97
4.7.3 Discards 108
4.8 Summary of all sites, results and interpretation 114
4.8.1 Static results versus Humidity cell pH 116
4.9 Conclusion and Recommendations on chapter 4 123
CHAPTER 5 126
5. Overall conclusions and recommendations 126
6. References 134
7. Abstract 141
8. Opsomming 143
9. Keywords 145

List of figures

Figure 1-1 South African Coalfields. 2
Figure 1-2 Diagrammatic sketch showing the relationship between AMD and groundwater. 2
Figure 1-3 Prediction chart for mine drainage chemistry. 3
Figure 2-1 A basic conceptual model of the oxidation of minerals and the decay of sulphuric heavy metal minerals. 7
Figure 2-2 The simplified Sulphur Cycle. 10
Figure 2-3 Pathway illustration of sedimentary pyrite formation. 12
Figure 2-4 The presence and absence of pH in mine waste. 16
Figure 2-5 Phylogeny of prokaryotic 16S rRNA genes from acid mine drainage and bioleaching sites (in bold) with reference lineages. 17
Figure 2-6 Direct mechanism of sulphuric heavy metals. 18
Figure 2-7 Direct mechanism of pyrite or maroasite. 19
Figure 2-8 Indirect mechanism of metals. 19
Figure 2-9 Potential iron, sulphur, and carbon cycling based on known metabolic capabilities (1, 2, 3, and 4) associated with AMD members. 21
Figure 2-10 Interrelations between oxidation and reduction of Sulphur in AMD. 22
Figure 3-1 pH precision/accuracy of the Actual Acidity methods (2010). 31
Figure 3-2 Comparison of pH results, Actual Acidity methods (2010). 32
Figure 3-3 Titratable Actual Acidity (TAA) 2010. 32
Figure 3-4 %Ca precision/accuracy of the Actual Acidity methods (2010). 33
Figure 3-5 %Cation comparisons, Actual Acidity methods (2010). 34
Figure 3-6 pH precision/accuracy of the Actual Acidity methods (2011). 35
Figure 3-7 Comparison of pH results, Actual Acidity methods (2011). 35
Figure 3-8 Titratable Actual Acidity (TAA) values in 2011. 36
Figure 3-9 %Ca precision/accuracy of the Actual Acidity Methods (2011). 37
Figure 3-10 %Cation comparisons, Actual Acidity methods (2011). 37
Figure 3-11 pH precision/accuracy of the peroxide methods (2010). 39
Figure 3-12 Comparison of pH results, peroxide methods (2010). 40
Figure 3-13 Titratable Potential Acidity versus Acid Potential 2010. 41
Figure 3-14 %SO_4 precision/accuracy of the peroxide methods (2010). 42
Figure 3-15 %Mg precision/accuracy of the peroxide methods (2010). 43

Figure 3-16 %Cation comparisons, peroxide methods (2010). 44
Figure 3-17 pH precision/accuracy of the peroxide methods (2011). 44
Figure 3-18 Comparison of pH results, peroxide methods (2011). 45
Figure 3-19 Titratable Potential Acidity versus Acid Potential 2011. 46
Figure 3-20 %Mg precision/accuracy of the peroxide method (2011). 46
Figure 3-21 %SO4 precision/accuracy of the peroxide method (2011). 47
Figure 3-22 %Cation comparisons, peroxide method (2011). 47
Figure 3-23 %CaCO3 precision/accuracy of the Neutralising potential methods (2010). 49
Figure 3-24 Comparison of %$CaCO_3$, Neutralising potential methods (2010). 50
Figure 3-25 CaCO3 precision/accuracy of the Neutralising potential methods (2011). 51
Figure 3-26 Comparison of %$CaCO_3$, Neutralising potential methods (2011). 51
Figure 4-1 Locality of the study area (Mpumalanga province: Middelburg). 60
Figure 4-2 Catchment map showing that the study area falls under the B100. 61
Figure 4-3 Open cast mining at the Middelburg North mines. 61
Figure 4-4 Sampling points of the Middelburg AMD Case Study. 63
Figure 4-5 A graph example defining NNP. 66
Figure 4-6 An example of a graph showing the categories of NPR. 67
Figure 4-7 A graphical example of the NPR vs. % S. 68
Figure 4-8 Components used in Kinetic testing for this case study. 70
Figure 4-9 Correlation of pH with $CaCO_3$. 70
Figure 4-10 Mean Annual precipitation. 72
Figure 4-11 Potential evaporation in the Olifants catchment. 73
Figure 4-12 Diagrammatic illustration of the Ecca formation. 74
Figure 4-13 Lithostratiographic map of the Karoo Supergroup. 75
Figure 4-14 Geological time table with emphasis on the Highveld Coalfield. 76
Figure 4-15 Cross sectional view of the Karoo and Cape Supergroup. 76
Figure 4-16 Typical stratigraphy map of the Middelburg mines. 77
Figure 4-17 Olifants catchment showing the main tributaries and urban centres. ... 78
Figure 4-18 Surface hydrology with the current open cast operation (pink). 78
Figure 4-19 Dam and pit points of the analysed water chemistry for surface hydrology. 79
Figure 4-20 Stiff diagrams for the surface hydrology. 80

Figure 4-21 Piper diagrams for the surface hydrology. 81
Figure 4-22 EC measurements of the surface hydrology. 82
Figure 4-23 EC distribution of the surface hydrology. 82
Figure 4-24 Time graph of SO_4. 83
Figure 4-25 SO_4 proportional distribution for Surface hydrology. 83
Figure 4-26 Correlation between surface topography and groundwater level 84
Figure 4-27 Groundwater flow direction with the water levels. 85
Figure 4-28 Sampling points for groundwater assessment. 86
Figure 4-29 Time graph of Geohydrology of the investigated area. 86
Figure 4-30 Stiff diagrams for the groundwater. 87
Figure 4-31 Piper diagrams for the groundwater. 88
Figure 4-32 Time graph of EC values of groundwater. 88
Figure 4-33 EC proportional distribution of the geohydrology. 89
Figure 4-34 Decant point at the investigated area. 89
Figure 4-35 Sampling point of Goedehoop Ramp 4 90
Figure 4-36 Initial pH of Goedehoop Ramp 4 samples. 92
Figure 4-37 Final pH showing Goedehoop Ramp 4 samples. 92
Figure 4-38 NNP Goedehoop Ramp 4. 93
Figure 4-39 Graphical presentation of NPR results for Goedehoop Ramp 4. 94
Figure 4-40 % S vs NPR for the Goedehoop Ramp 4 sample 95
Figure 4-41 Kinetic cell pH value for Goedehoop Ramp 4. 96
Figure 4-42 Cumulative SO_4 of Goedehoop Ramp 4 sample. 96
Figure 4-43 Sampling points of Hartebeesfontein area. 97
Figure 4-44 Initial pH showing Hartebeesfontein samples. 100
Figure 4-45 Final pH showing Hartebeesfontein samples 101
Figure 4-46 NNP Hartebeesfontein results. 101
Figure 4-47 Graphical presentation of NPR results for Hartebeesfontein. 105
Figure 4-48 % S vs NPR for the Hartebeesfontein samples. 106
Figure 4-49 Kinetic cell pH value for the Hartebeesfontein. 107
Figure 4-50 Cumulative SO_4 of the Hartebeesfontein samples. 107
Figure 4-51 Sampling point of Discard samples. 108
Figure 4-52 NNP results for Discard samples 110
Figure 4-53 Proportional Initial pH showing discard samples. 110
Figure 4-54 Proportional final pH showing discard samples. 111

Figure 4-55 Graphical presentation of NPR results for Discards. 112
Figure 4-56 %S vs NPR for the Discard samples. 113
Figure 4-57 Kinetic c ell pH values of the Discard samples. 114
Figure 4-58 Cumulative SO_4 of Discard sample. 114
Figure 4-59 NNP results of all the investigated sites. 115
Figure 4-60 NPR results for all the investigated sites. 115
Figure 4-61 pH value over 20 weeks for each cell 118
Figure 4-62 Cumulative sulphate production for each cell. 119
Figure 4-63 Cumulative Ca, Fe and Al. 120

List of Tables

Table 2-1 Bacteria found in AMD environment (Cowan *et al.,* 2007). 15
Table 2-2 Differences between reduction and oxidation... 20
Table 3-1 The list of samples names used in 2010. 25
Table 3-2 The list of samples used in 2011. 26
Table 3-3 Actual acidity, Australian vs. South African methodology. 28
Table 3-4 Potential Acidity, Australian vs. South African methodology. 29
Table 3-5 Neutralising potential, Australian vs. South African methodology. 30
Table 4-1 Rough guidelines for categorizing samples (Price *et al.,* 1997)............... 65
Table 4-2 Guidelines for ABA screening criteria (Price *et al.*, 1997). 67
Table 4-3 Values used to verify that the pH is related to the buffering capacity of the sample.. 71
Table 4-4 Temperature over the Middelburg area (Steve Tshwete Municipal, 2005). 71
Table 4-5 Classification table for mineralogical results... 90
Table 4-6 Mineralogical analysis of Goedehoop Ramp 4. 91
Table 4-7 Interpretation of ABA pH and NAG results Goedehoop Ramp 4. 91
Table 4-8 Interpretation of ABA Net Neutralising Potential results. 93
Table 4-9 Interpretation and NP/AP ratios for the Goedehoop Ramp 4 samples. ... 94
Table 4-10 Mineralogical analysis of Hartebeesfontein 97
Table 4-11 Interpretation of ABA pH and NAG results for Hartebeesfontein. 99
Table 4-12 Interpretation of ABA Net Neutralising Potential results. 102
Table 4-13 Interpretation and NP/AP ratios for Hartebeesfontein. 103
Table 4-14 Mineralogical analysis of Discard samples. 108
Table 4-15 Interpretation of ABA pH and NAG results for Discard samples.......... 109
Table 4-16 Interpretation of ABA Net Neutralising Potential results for Discard samples. 111
Table 4-17 Interpretation and NP/AP ratios for the Discard samples. 112
Table 4-18 Initial pH's of humidity cell samples vs paste pH (static ABA). 116
Table 4-19 Cumulative values of the major ions from the humidity cells after 20 weeks (mg/kg). 121
Table 5-1 Static pH values, XRF and NNP results. 130

List of Formulas

Equation 2-1 Oxidation of polysulfide to sulphate by $O_{2.}$ 7
Equation 2-2 Oxidation of ferrous iron to ferric iron by $O_{2.}$ 8
Equation 2-3 Hydrolysis of Ferric ion.......... 8
Equation 2-4 Ferric iron released into a solution. 8
Equation 2-5 Oxidation of polysulfide to sulphate by Fe^{3+} at a low pH. 8
Equation 4-1 Acid potential. 64
Equation 4-2 Base potential. 65
Equation 4-3 Net Neutralising Potential open (NNP). 65
Equation 4-4 Net Neutralising Potential closed (NNP). 65

List of acronyms and abbreviations

%Ca:	Percentage of Ca
%Mg:	Percentage of Mg
%SO_4:	Percentage of SO_4
ABA:	Acid- Base Accounting
ABACUS:	Acid Base Accounting Cumulative Screening Tool
ABATE:	Acid-Base Accounting Techniques and Evaluation
AMD:	Acid Mine Drainage
ANC:	Acid Neutralising Capacity
AP:	Acid-generating Potential
APP:	Acid Producing Potential
ARD:	Acid Rock Drainage
ASS:	Acid Sulphate Soil
ASTM:	American Society of Testing and Materials
Ca:	Calcium
Cum:	Cumulative
Dol:	Dolomite
Gyp:	Gypsum
H_2SO_4:	Sulphuric acid
HCl:	Hydrochloric acid
Hem:	Hematite
IGS:	Institute for Groundwater Studies
K:	Potassium

Kaol:	Kaolinite
Kg/t:	Kilogram per tonne
Kvsp:	Potassium Feldspar
mg/l:	Millgram per litre
Mg:	Magnesium
Montm:	Montmorillonite
Na:	Sodium
NAG:	Net Acid Generation
NAPP:	Net Acid Producing Potential
NNP:	Net Neutralizing Potential
NP:	Neutralisation Potential
NPR:	Neutralisng Potential Ratio
NPR:	Neutralizing Potential Ratio
pH:	Hydrogen Potential
Pyrr:	Pyrrhotite
Q:	Quartz
Sid:	Siderite
SO_4:	Sulphate
TAA:	Total Titratable Acidity
TDS:	Total Dissolved Solids
TPA:	Total Peroxide Acidity
XRD:	X-ray Diffraction
XRF:	X-ray Fluorescence

CHAPTER 1

1. Introduction

In 2009 South Africa was ranked sixth in the world for the total coal output of 247 million tons (Mt) with China, USA, India, Australia and Indonesia in the lead. More than 500 000 employees are dependent on coal production as South Africa is largely dependent on this energy-economy sector (Eberhard, 2011). Figure 1-1 shows the majority of coal reserves and mines in South Africa including the Central Basin's Witbank, Highveld and Ermelo coalfields.

Mining operations are a source of Acid Mine Drainage (AMD) in South Africa that renders water useless for consumption, industrial and agricultural purpose if not treated (Steyl, 2012). Coal and other sulphide-bearing mining operations expose sulphide to air and water, thereby increasing the surface area, the rate of acid generation and then possibly the salt load. The metal toxicity, acidity of the water and salinization from these mines is known as AMD (Mey & Van Niekerk, 2009). 40% of coal mining in South Africa is operated as open-cast mining because coal occurs as thick shallow seams (Usher, 2003). Open-cast mining is more viable compared to the board-pillar underground techniques used primarily in coal mining operations therefore open-cast mining activities are practiced at the featured case study in this thesis.

1.1 Relationship between AMD from open-cast mining activities and groundwater studies

Coal opencast-mining activities poses a big threat to the groundwater resources from varies processes as shown in Figure 1-2. Fundamentally collection dams that are located upslope and cut-off trenches are used to minimise the volume of water that comes in contact with the coal seams, waste rock and spoils, However recharge from rainfall onto Ramps, voids runoff, seepage from spoils and groundwater seepage are hard to manage (Mey & Van Niekerk, 2009). When the pathways created by the capillary forces in the geology (soils, spoils etc.), fracturing in coal seams and/or waste rock comes in contact with the water (i.e. precipitation), AMD processes are motivated.

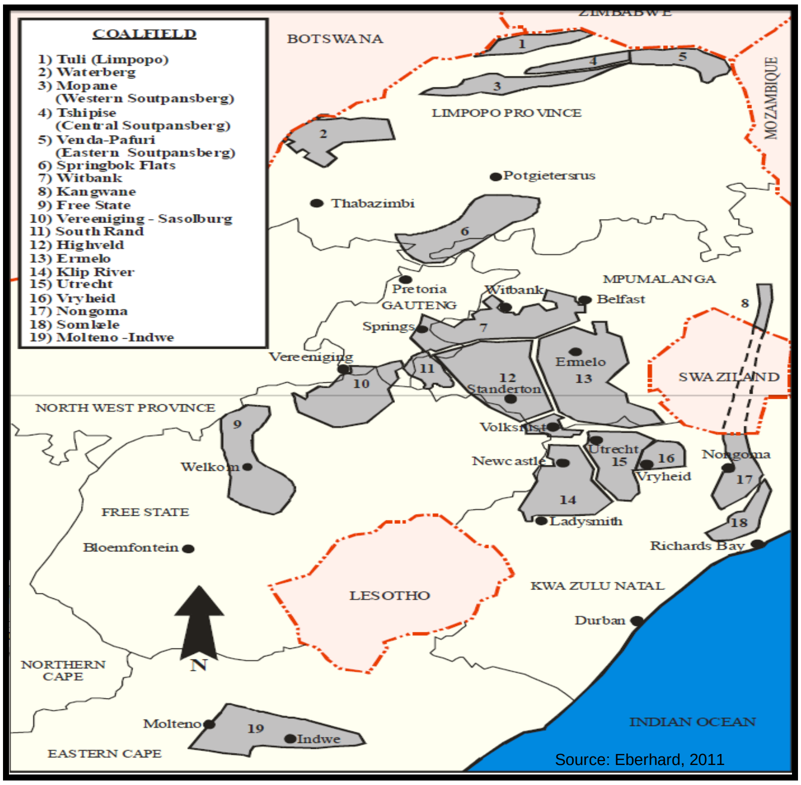

COALFIELD
1) Tuli (Limpopo)
2) Waterberg
3) Mopane (Western Soutpansberg)
4) Tshipise (Central Soutpansberg)
5) Venda-Pafuri (Eastern Soutpansberg)
6) Springbok Flats
7) Witbank
8) Kangwane
9) Free State
10) Vereeniging - Sasolburg
11) South Rand
12) Highveld
13) Ermelo
14) Klip River
15) Utrecht
16) Vryheid
17) Nongoma
18) Somkele
19) Molteno -Indwe
ZIMBABWE
BOTSWANA
MOZAMBIQUE
LIMPOPO PROVINCE
Potgietersrus
Thabazimbi
Pretoria
GAUTENG
Witbank
MPUMALANGA
Belfast
Springs
Vereeniging
Ermelo
SWAZILAND
Standerton
NORTH WEST PROVINCE
Volksrust
Newcastle
Utrecht
Vryheid
Nongoma
Welkom
FREE STATE
Ladysmith
Richards Bay
Bloemfontein
LESOTHO
KWA ZULU NATAL
Durban
N
NORTHERN CAPE
Molteno
Indwe
EASTERN CAPE
INDIAN OCEAN
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
Source: Eberhard, 2011

Figure 1-1 South African Coalfields.

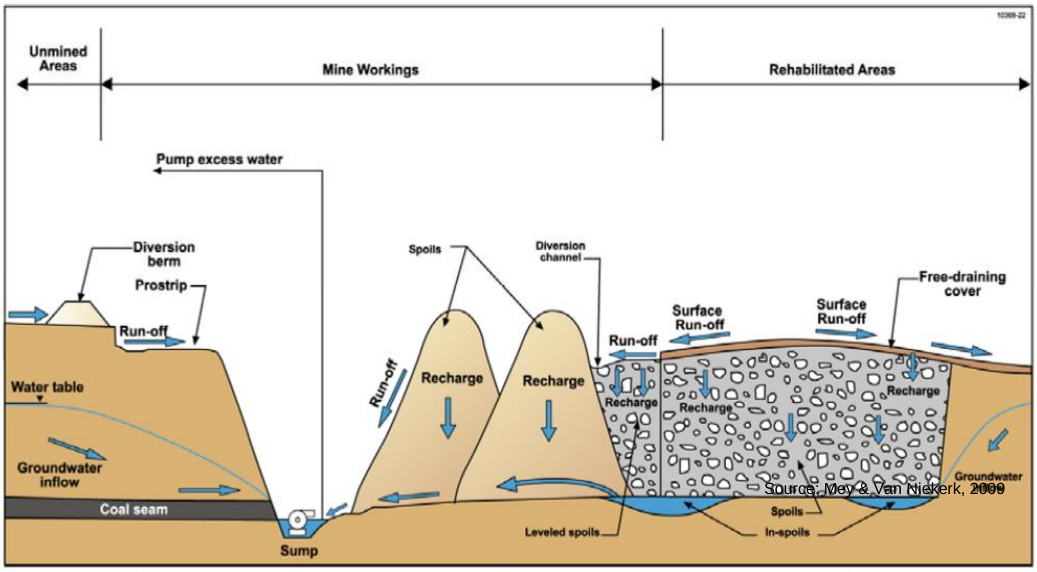
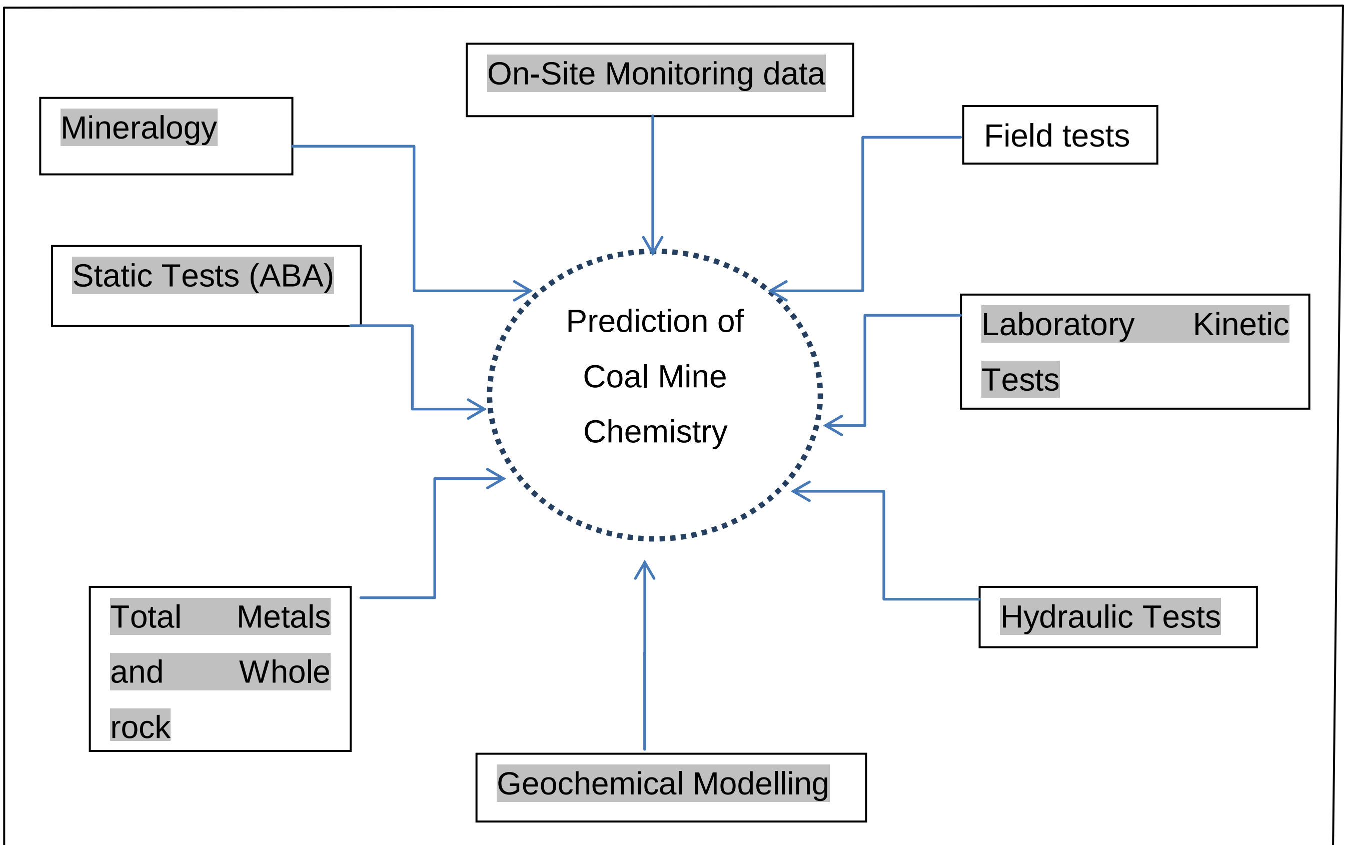

10368-22
Unmined Areas
Mine Workings
Rehabilitated Areas
Pump excess water
Diversion berm
Prostrip
Run-off
Water table
Groundwater inflow
Coal seam
Sump
Spoils
Diversion channel
Run-off
Recharge
Recharge
Run-off
Recharge
Surface Run-off
Recharge
Surface Run-off
Free-draining cover
Recharge
Groundwater
Leveled spoils
Spoils
In-spoils
Source: Mey & Van Niekerk, 2009

Figure 1-2 Diagrammatic sketch showing the relationship between AMD and groundwater.

Prediction of AMD is done by lab methods such as Acid-Base Accounting (ABA); however it is still difficult to predict the rate and quantity of AMD. ABA is a procedure performed in the laboratory to determine the potential of AMD generation, confirm if there will be potential for acid generation and salt load.

Researches such as Morin and Hunt, 1999 defined the Acid-Base Accounting Techniques and Evaluation (ABATE) strategy (Figure 1-3) which assists in giving meaningful assessment in the prediction of AMD. Seven (highlighted in grey) out of eight methods are used in this thesis to predict the AMD at the case study.


On-Site Monitoring data
Mineralogy
Field tests
Static Tests (ABA)
Prediction of Coal Mine Chemistry
Laboratory Kinetic Tests
Total Metals and Whole rock
Hydraulic Tests
Geochemical Modelling

Source: Adapted from Morin and Hutt, 1999

Figure 1-3 Prediction chart for mine drainage chemistry.

1.2 A brief review on the importance of AMD prediction in South Africa

Comparing South Africa to the rest of the world in terms of water resources, South Africa has an average rainfall of 450 mm per annum while the global average is 860 mm per annum (Claassen, 2011). Attention to groundwater is therefore important as South Africa is a semi-arid country with limited water resources. Groundwater relies primarily on rainfall as recharge but it is also a “hidden” alternative source of water for a country that is faced with water pollution and international obligations.

According to the definition of the water cycle, water resources are interconnected (Claassen, 2011) therefore contamination of any water resources needs to be prevented, treated and sustainably utilised. Unfortunately, some outbreaks of pollution to our groundwater resource are often difficult to manage due to socio-economic reasons, negligence and lack of monitoring (Fourie, 2007, Hobbs, *et al.,*2008, Hobbs and Kennedy, 2011*).*

AMD is one of the great threats to the water resource in South Africa therefore it is important that the mining industries are able to predict and evaluate the environmental consequences (Usher, 2003). Management of AMD in practice could be enhanced by understanding geochemistry and hydro-chemistry of a system. To a certain degree, the prediction of AMD will assist the mining project from preparation of environmental impact assessments to get mine permits, mine layout, pollution control management and planning, financial planning of the remediation plan and closure of the mine (Fourie, 2007). AMD if not predicted, prevented and managed could cost more than the “bottom line” of the operating mines (Eberhard, 2011).

1.3 Objectives of study

Part of this thesis is conducted to note the difference between South African and Australian Laboratory methods in determining the potential acidity and the existing acidity in the soil. This is done because South Africa and Australia have the same geology but different methodologies. The aim of this comparison was to determine why Australia uses different methodologies compared to the world, is there similarities in the results yielded by Australia’s methodology compared to South Africa’s and to answer whether it would be applicable, less expensive or logical to use Australia’s methodology. Furthermore, AMD is predicted using South African ABA methods for the Middelburg area.

Therefore the aim of this thesis is to:

- Compare the South African and Australian ABA methodologies;
- Evaluate the results of the South African and Australian samples;
- Geochemical investigation of the Middelburg North Mines;
- Predict Acid Mine Drainage in the Middelburg North Mines.

1.4 Methods of investigation

To achieve the objectives mentioned above the following were done:

- Comprehensive relevant literature review of documents, journals, guidance, website and theses.
- Selection of appropriate testing methods to compare the South African and Australian results.
- Evaluation and comparison of the South African and Australian results.
- The use of South African Static methods to predict AMD in the Middelburg North Mines.
- Extensive long-term Kinetic testing methodology to verify the Static tests.
- Evaluation of the samples mineralogy using XRF and XRD to assist in understanding the process of AMD in the Middelburg North Mines.

1.5 Thesis structure

This thesis is outlined in the following sequence:

- **Chapter 1** is the introduction of the thesis.
- **Chapter 2** details the factors that are involved in the process of AMD. It gives a literature background on the definition of AMD, bacterial and chemical influences on AMD.
- **Chapter 3** discusses and concludes on the methods and results used to compare the South African and Australian ABA testing.
- **Chapter 4** provides details and results of the case study: Middelburg North Mines.
- **Chapter 5** gives an overall conclusion of the thesis and recommendations.
- The appendix is provided on a CD-ROM accompanied by this thesis.

What is discussed in this chapter only constitutes a basic overview of the thesis. AMD plays a vital role in water pollution and has a negative impact on the environment. It is therefore important to understand what AMD is, where it comes from and the processes directly/indirectly involved in AMD generation. Chapter 2 defines AMD and discusses the physic-chemical and biological reactions that are associated with AMD.

CHAPTER 2

Rates of acid generation are increased by mining activities, microbial activity, temperature, mineralogy and fluid chemistry (Bosch, 1990). Combinations of chemical, physical, physic-chemical and biological reactions can either intensify (i.e. oxidation) or attenuate (i.e. reduction, neutralisation) the level of contamination (AMD).

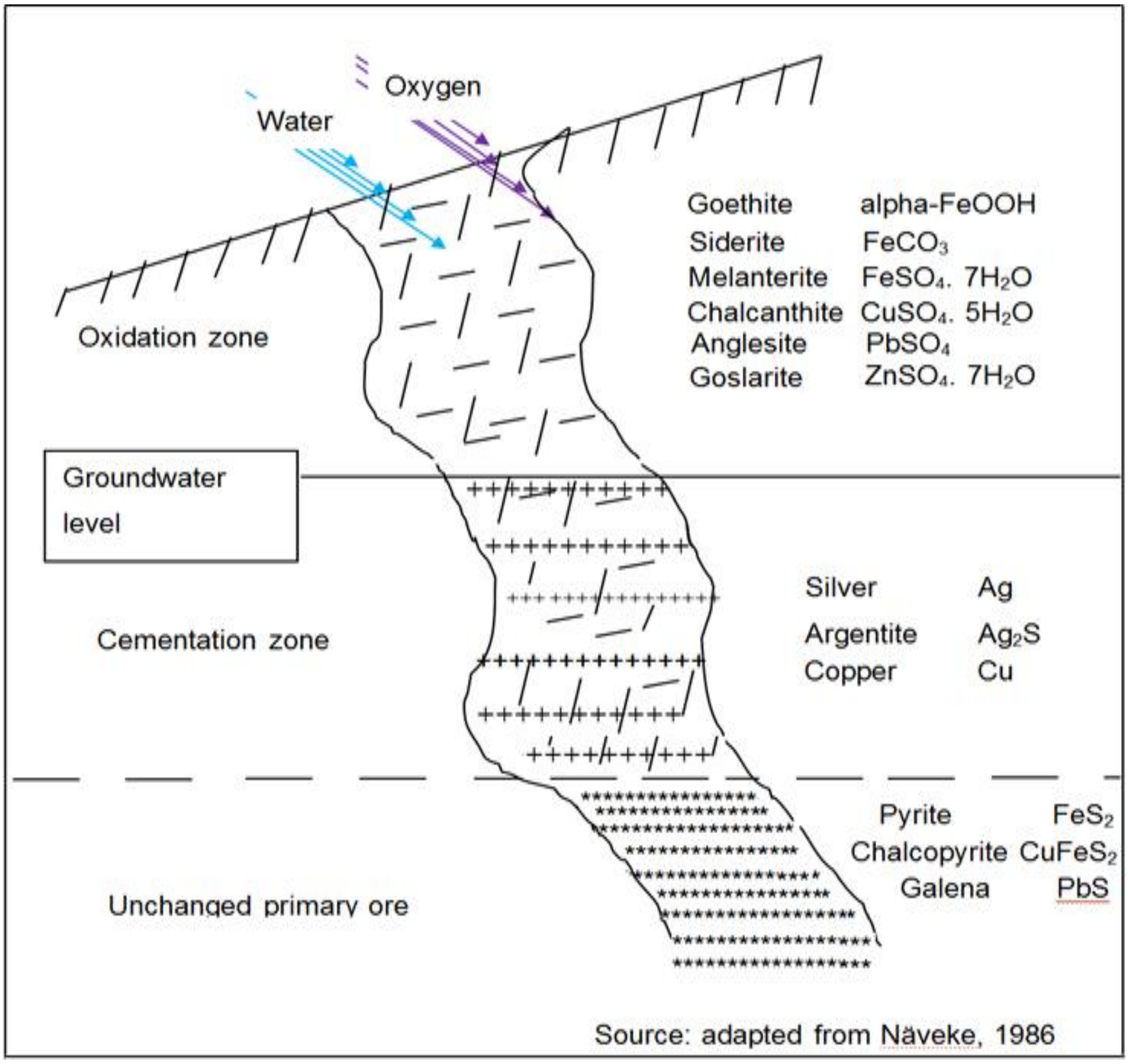
2. Literature review on the processes associated with AMD

2.1 Definition of ARD and AMD

The oxidation zone in Figure 2-1 shows the surface being in contact with atmospheric oxygen and rain water, resulting in oxidisation of minerals and an enrichment of ferric iron. This process is known as Acid Rock Drainage (ARD) or Acid Mine Drainage (AMD). AMD occurs when the sulphide-bearing minerals are exposed by mining operations/constructions to oxygen and water whereas ARD is when a rock that contains sulphide-bearing minerals is exposed or comes in contact with oxygen and water. Leaching solution is accumulated from the oxidation zone into the cementation zone just below the groundwater level. This affects the groundwater quality. A common tell-tale sign of AMD occurrence is a discharge of bright orange colored (yellowboy) water or stained rock due to the precipitation of ($Fe(OH)_3$) ferric hydroxide (Usher, 2003; Lawrence and Day 1997).

This simple definition of AMD belies the complexity of reactions that give rise to the contaminated water.

AMD is a severe environmental pollutant that faces coal and other sulphide-containing ore mining operations because it generates a high salt load and acidity of the water that can have environmental consequences.


Oxygen
Water
Oxidation zone
Goethite alpha-FeOOH
Siderite $FeCO_3$
Melanterite $FeSO_4 \cdot 7H_2O$
Chalcanthite $CuSO_4 \cdot 5H_2O$
Anglesite $PbSO_4$
Goslarite $ZnSO_4 \cdot 7H_2O$
Groundwater level
Cementation zone
Silver Ag
Argentite Ag_2S
Copper Cu
Pyrite FeS_2
Chalcopyrite $CuFeS_2$
Galena PbS
Unchanged primary ore

Source: adapted from Näveke, 1986

Figure 2-1 A basic conceptual model of the oxidation of minerals and the decay of sulphuric heavy metal minerals.

From the following reactions, one can see the interaction of chemical and bacterial interaction. The complex reactions also show an indirect mechanism of microbial activity in AMD generation. Equation 2-1 to Equation 2-3 can have a high pH values that are greater than 4.5 and/or Equation 2-2 to Equation 2-4 can have an intermediate pH with values between 4.5 and 2.5. Equation 2-5 has a low pH which can be any value below the 2.5. Equation 2-2 to Equation 2-5 are self-propagating reactions until ferric ion or pyrite is depleted.

$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4$…………………………….(1)

Equation 2-1 Oxidation of polysulfide to sulphate by O_2.

- Ferrous sulphate and sulphuric acid is caused by an initial abiotic and biotic oxidation of pyrite.
- A favourable condition for *T. ferrooxidans* is created with a decrease in pH.

$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$……………………….(2)

Equation 2-2 Oxidation of ferrous iron to ferric iron by O_2.

- Ferrous sulphate is oxidised to ferric sulphate.
- Abiotic reaction slows down, biotic takes over.
- pH decreases further.

$Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 2H_2SO_4$………………………………………….(3)

Equation 2-3 Hydrolysis of Ferric ion.

- Ferric hydroxide and acid is formed by abiotic hydrolysis mechanism.
- Yellow boy is visible.
- pH drops.

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

Equation 2-4 Ferric iron released into a solution.

- Biotic oxidation of ferric iron.
- *T. ferrooxidans* is a catalyst, increased the rate of oxidation.

$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^-$………………..(5)

Equation 2-5 Oxidation of polysulfide to sulphate by Fe^{3+} at a low pH.

- Ferric ion oxidises pyrite.
- Abiotic reaction; T. ferrooxidans.
- Sulphate and ferrous iron is produced.

To summarise the equations: ferric iron is produced biotically and oxidises pyrite abiotically (Bosch, 1990).

2.2 The Sulphur cycle

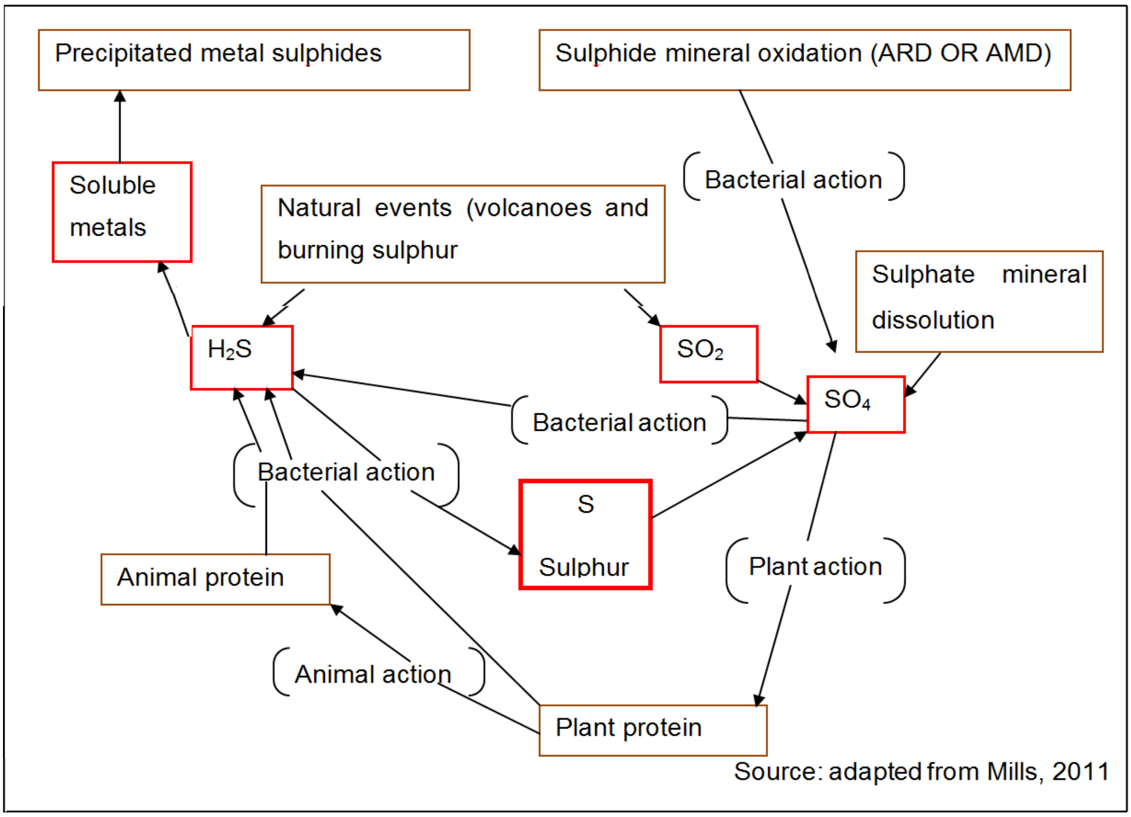
AMD occurs when the sulphide-bearing minerals are exposed to oxygen; therefore the discussion of the sulphur cycle is relevant in this chapter. The sulphur cycle shows how physical, chemical and biological reactions have a relationship with H_2S, S, SO_4 and SO_2. Sulphur in a mineral form can move around in the cycle (Figure 2-2) from oxidation to dissolution of sulphur (Mills, 2011; Hines et al., 2002). The sulphur cycle shown in Figure 2-2 is simplified because the reactivity of sulphide with metals and oxidation of metal sulphides by bacteria is complex, this figure will only assist in understanding the basics of the processes that take place in sulphide-bearing deposits.

The following brief discussion of reactions in the sulphur cycle shows chemical, biological and physical reactions with different sulphur mineral forms.

Oxidation in the sulphur cycle
Sulphide mineral oxidation produces SO_4 by bacterial action.

Reduction in the sulphur cycle
Sulphate Mineral dissolution results in SO_4.

Other reactions in the sulphur cycle
The sulphur ion is taken up by soil and plants and incorporated into protein.
Plant protein is taken in by animals
Animal action gets to produce animal protein.
The death of plants and animals results into bacterial decomposition of protein.
H_2S is produced, Natural events such as volcanic eruptions produces H_2S.
H_2S is oxidised to sulphur.
Through bacterial action sulphur is reacted to form SO_4 (Mills, 2011).


Precipitated metal sulphides
Sulphide mineral oxidation (ARD OR AMD)
Soluble metals
Natural events (volcanoes and burning sulphur
Bacterial action
Sulphate mineral dissolution
H_2S
SO_2
SO_4
Bacterial action
Bacterial action
S
Sulphur
Animal protein
Plant action
Animal action
Plant protein

Source: adapted from Mills, 2011

Figure 2-2 The simplified Sulphur Cycle.

2.3 Geochemical processes that are related to AMD

Oxidation is a major part in the generation of AMD but the processes involved are not as simple as the definition implies. Geochemical reactions give rise to constituents with a number of adverse effects on the surrounding environment

There are four classes of geochemical processes that are related to AMD (Lawrence and Day, 1997).

- Oxidation of sulphide minerals.
- Dissolution of carbonates, oxyhydroxides and silicates.
- Precipitation of oxyhydroxides.
- Dissolution and precipitation of sulphate minerals.

2.3.1 Oxidation of Sulphide minerals

This class of geochemical reactions releases major and trace metals including sulphate. About 28 sulphide minerals are listed as acid generating minerals around the world (Lawrence and Day, 1997) but iron sulphides are the commonly mentioned mineral in the South African literature (i.e. pyrite, pyrhotite, marcasite and arsenopyrite). The major sulphide forms may either be pyritic, organic or sulphate.

Pyritic and sulphates are inorganic sulphurs that are dependent on each other whereas organic sulphur is chemically bound to carbon molecules in the form of (-SH) (Fourie, 2007).

This chapter will emphases more on pyrite (FeS_2) which may form as results of microbial reduction of aqueous sulphate, reaction of monosulphide, iron minerals and elemental sulphur or a reaction between reduced sulphur and sedimentary iron minerals Figure 2-3.

The four different oxidation mechanics of sulphide minerals

1. Abiotic oxidation by O2.

The pH is usually more than 4.
Ferrous sulphate and Sulphuric acid is caused by an initial abiotic and biotic oxidation of pyrite.

2. Abiotic oxidation by Fe(III)

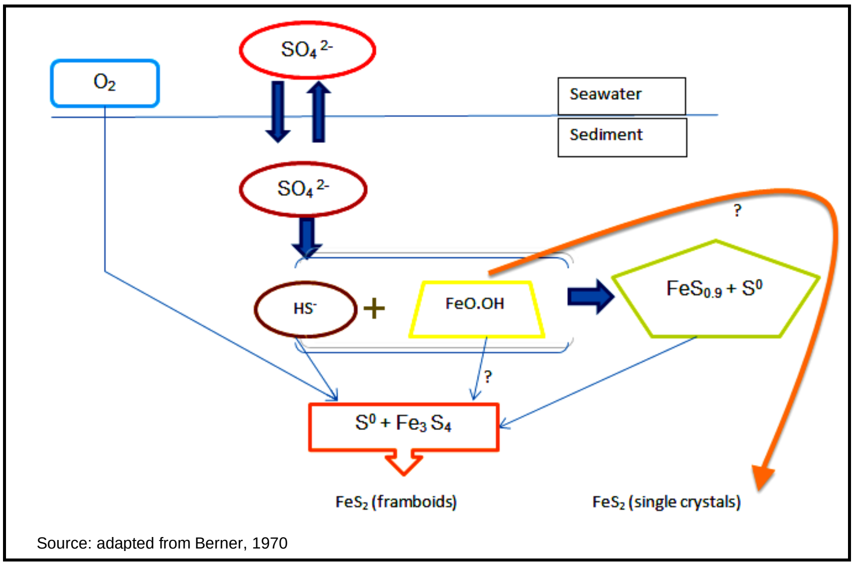
The pH is less than 4.
Ferrous sulphate is then oxidised to ferric sulphate and the abiotic reaction slowed down.
$FeS_2 + 14Fe^{3+}\ 8H_2O \sim\sim> 15\ Fe^{2+} + 2SO_4^{2-} + 16H^+$.

3. Biologically catalysed oxidation

The pH lies between 2 and 4.
Moderate-warmer temperature.
Thiobacillus ferrooxidans accelerate the oxidation of Fe^{2+} to Fe^{3+} therefore the overall rate of pyrite oxidation (Refer to the influence of bacteria section below).

4. Galvanic oxidation

Two sulphide minerals of different electrical potentials come into electrical contact with each other. The mineral with a higher potential acts as a cathode and an anode position is taken up by the mineral with a lower electrical potential. This oxidation mechanism can be seen in thin sections both at acidic or neutral pH. The metal sulphide anode is oxidised to release metal ions and sulphur cathode is not affected (Lawrence and Day, 1997).



Source: adapted from Berner, 1970

Figure 2-3 Pathway illustration of sedimentary pyrite formation.

2.3.2 Dissolution of carbonates, oxyhydroxides and silicates

This class of geochemical reactions consumes acid generally produced by sulphide oxidation. However these reactions depend on whether the system is open or closed, the overall chemistry and the contact time of the solution with the minerals. If the equilibrium conditions did not develop and the natural neutralising capacity of the environment is exhausted by acidic leachate attacking the minerals that buffer the pH, AMD might be produced (Lawrence and Day, 1997). The following brief discussions of the pH buffering minerals are based on the assumption that the equilibrium conditions occur.

Carbonates

Carbonates have a neutralising capacity with the pH near neutral values. Calcium carbonate, dolomite, ankerite, rhodochrorsite are a few minerals that can act as a buffer and attenuate the level of AMD. If the natural neutralising capacity of the environment is not exhausted, AMD might be remediated before the pollution is severe. Depending on the pH, acidity is consumed by a combination of two reactions to produce bicarbonate or carbonic acid.

Although siderite has the chemical formula of $FeCO_{3,}$ its dissolution does not neutralise acid if iron subsequently precipitates as a hydroxide. Siderite constitutes a temporary neutralising agent or it is not effective at all. However it is effective under non-oxidising conditions as a neutralising agent due to ferrous iron that does not oxidise to ferric iron in flooding conditions. Siderite is commonly found in mineralised systems that are associated with coal seams and is frequent in carbonaceous clastic rocks or in non-carbonaceous clastic rock (Lawrence and Day, 1997).

Oxide and Hydroxide minerals

These minerals are dominant in the neutralising reaction with a pH between 4 and 6. First the carbonate buffers, pH shifts to a lower value when carbonate buffering is exhausted then the Iron hydroxides become the principal neutralising mineral. If the iron hydroxides come into contact with a sulphide (Figure 2-3), ferrous sulphate is produced and once it is exposed to oxidation condition AMD is the result (Rose and Ghazi, 1997a).

Silicate minerals

Only at low pH, silicate minerals have an acid neutralising potential. Dissolution of this mineral might trigger the AMD processes further. Phyllosilicate minerals such as clays and mica have been identified as neutralising minerals in the waste rock. However, if the alumina-silicate (kyanite) interacts with acid, aluminum (Al) is released. It also competes with the excess of carbon cation when gypsum is present. If Al succeeds to take up the carbon cation space more Al leachate is produced. Excess Al is a harmful to have in leachate because it can cause multiple problems that can degrade vegetation, soil and groundwater. Such environmental problems include phytotoxicity in plants (García *et al.,* 2007*).* Acidic conditions on the other hand are caused by the hydrolysis of Al and Fe, meaning silicate minerals with Al and Fe in octahedral sites have a lower buffering capacity compared to the other minerals (Fourie, 2007; Lawrence and Day, 1997).

2.3.3 Precipitation of oxyhydroxides

The precipitation of oxyhydroxides releases acid and consumes major elements. This process is prevalent at pH above 5 and is rapid. The precipitation of iron oxyhydroxide associated with AMD has high aluminum and nickel concentration. The formations of aluminum sulphates aqueous complexes are more mobile than nickel that is co-precipitated with iron (Rose and Ghazi, 1997b). Exposure of Al to soil, vegetation and groundwater is toxic, therefore polluting the environment.

2.3.4 Dissolution and precipitation of sulphate minerals

This class concerns secondary minerals; for instance the insoluble sulphate (gypsum) that is formed when sulphide oxidation at or near neutral pH is neutralised by calcium carbonates (Lawrence and Day, 1997). Gypsum is a very soluble mineral which releases calcium and sulphate into the solution as soon as it is undersaturated. A wide variety of Fe-sulphates are formed under humid conditions during the evaporation or oxidation. For every one mole of sulphuric acid formed one mole of pyrite must have been oxidised. Formation of hydrous sulphate can be significant processes as it has the ability to “store acidity” and release it when the minerals are dissolved by recharge or runoff (Fourie, 2007).

2. 4 The influences of bacteria in AMD

Although the case study samples in this thesis were not analysed for microbial activity, it is necessary in this chapter to show the interactions between chemical and biological reactions so that all the processes/stages of AMD are considered in the understanding of AMD generation. Microbial activity has been known as a catalyst in the geochemical reactions involved in AMD since discovered by Colmer and Hinkle in 1947 (Bosch, 1990). Temperature plays a role in the microbial activity and geochemical processes whereas the flow is dependent on the topography, capillary forces and fractures (Baker and Banfield, 2003).

It is believed that bacterial oxygenic photosynthesis reactions did not exist on earth during the Archean age (Baker and Banfield, 2003). The early earth record shows a low abundance of sulphates, hence the early earth environments were anoxic (Bosch, 1990). Only when the oxygen concentration increased, metabolic reactions such as the oxidation of iron and reduction of sulphur were stimulated (Baker and Banfield, 2003).

During the depositional stages of coal, microbes are very active. A small part of the plant residue, that is in great abundance is oxidised by an aerobic bacteria that depletes oxygen. Furthermore the plant residue is degraded by aerobic bacteria. Microbial activity might continue to toxic levels whereby FeS_2 (pyrite) readily precipitate or sulphates reduces.

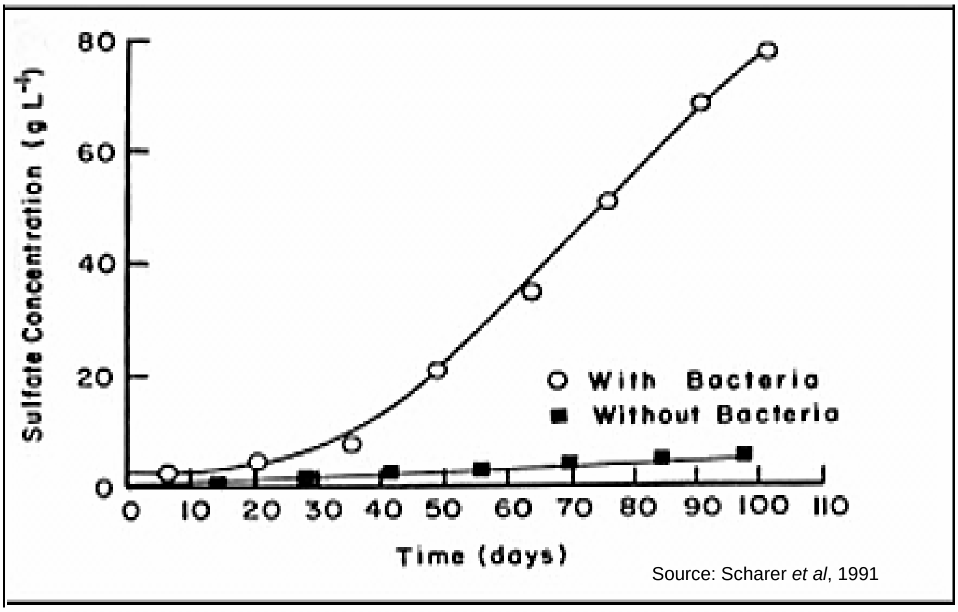
Microbial activity causes natural weathering of sulphuric mineral and converts insoluble metals into water soluble form by oxidation (Rawlings, 1989). Table 2-1 shows some bacteria that occur in the environment. Sulphur can act as both an electron donor and acceptor in microbial activity e.g. elemental sulphur (S^0) and thiosulphate ($S_2O_3^{2-}$). Elemental sulphur and tetrathionate are biologically important sulphurs since bacteria such as *Acidiothiobacillus ferrooxidans* (syn. *T. ferrooxidans*) grows on elemental, tetrathionate and triothionate. *T. ferrooxidans* also increases Fe^{3+} and enhances leaching of a pyrite (Hines *et al*., 2002; Baker *et al*., 2003). *T. ferrooxidans* is a non-filamentous, chemalithotrophic autotroph iron bacterium that is able to grow in an inorganic environment such as that found in mining (Mills, 2011). It is associated with oxidising ferrous iron in acid mine waters and oxidises thiosulphate (pH 4.0), elemental sulphur (pH 5.0), trio/tetrathionate (pH 6.0) chalcopyrite (pH 2.2) and bornite to be at a favorite pH 3. *T. ferrooxidans* uses the oxidation-reduction reactions to biosynthesize instead of sunlight and its energy is released during the oxidation (Table 2-2) of iron or sulphur reduced compounds (Mills, 2011). It can reach 80 % or more of the pyrite from bituminous coals in 3-4 days" (Zajic, 1969).

Table 2-1 Bacteria found in AMD environment (Cowan *et al.,* 2007).

Iron oxidizers	*Leptosprillum ferrooxidans*
	L. ferriphilum
	L. Thermo ferrooxidans
	Ferroplasmaacidiphilum
Sulphur oxidizers	*Acidithiobacillus thiooxidans*
	At. caldus
	Sulphulobus spp.
Iron and Sulphur oxidizers	*Acidithiobacillus ferrooxidans*
	Acidianus spp
	Sulpholusmetallicus
Iron Reducers	*Acidiphilum spp.*
Iron-oxidizers/reducers	*Acidimicrobium ferrooxidans*
Iron oxidizers/reducers and	*Sulphobaccillus spp.*

sulphur oxidizers	

Bacteria play a role in the cumulative production rate of sulphate therefore Figure 2-4 shows the effects of bacteria in a pyritic mine upon the dissolution of sulphate (Scharer *et al*., 1991).

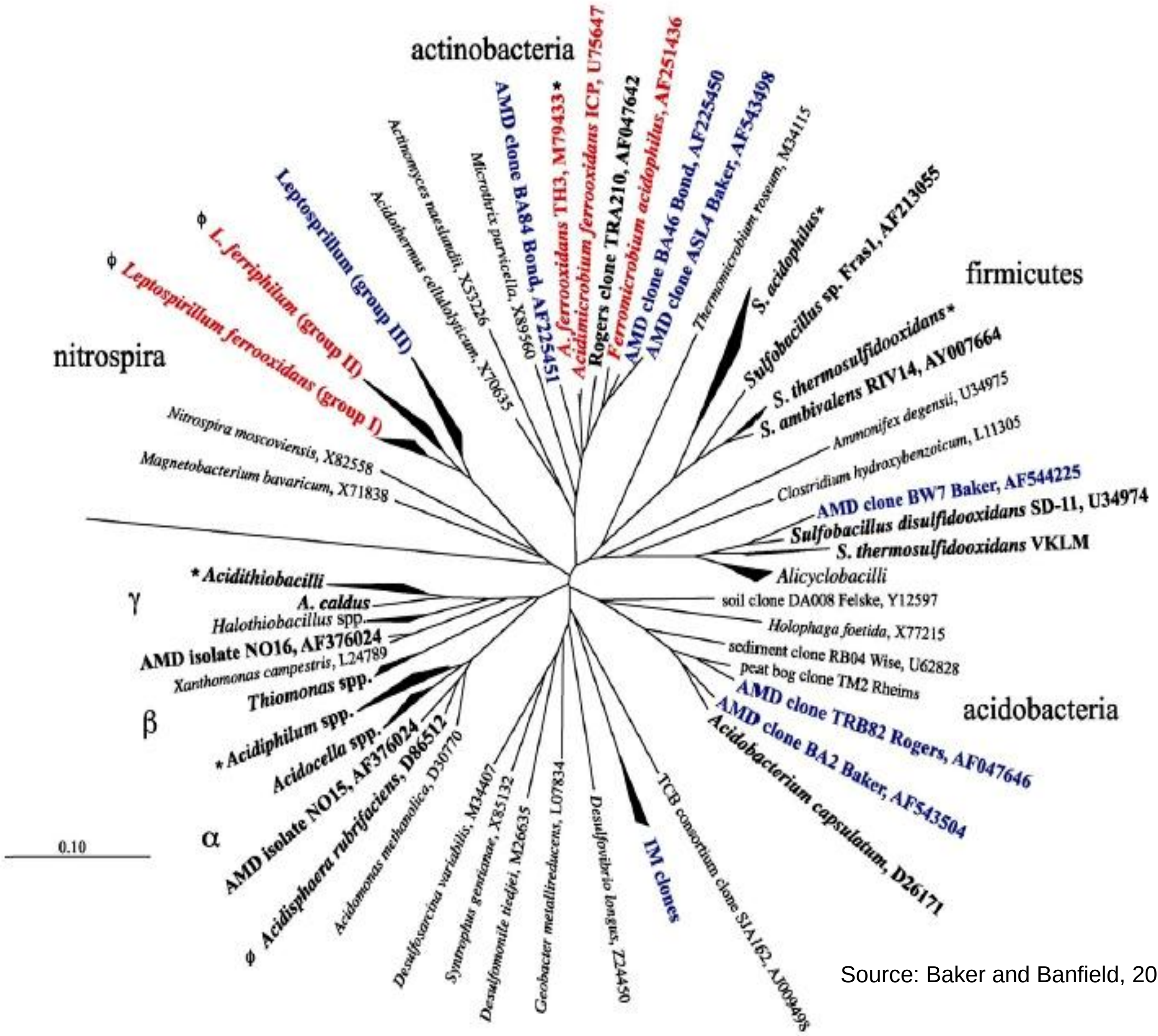


Source: Scharer *et al*, 1991

Figure 2-4 The presence and absence of pH in mine waste.

An AMD system was studied in Richmond Mine, Northern California to evaluate microbial activity and the diversity of bacteria present in AMD (Figure 2-5). Culture-independent molecular methods including 16S rRNA clone library analyses and cell imaging were used in this study. The 16S rRNA sequence is a tool that is used to discovery and evaluating the diversity of soil bacteria. Microbial activity emphasised greatly in this thesis is *Acidiothiobacilli* (syn. *T. ferrooxidans, Thiobacilluscaldus*) which is extensively studied in AMD generating conditions. It is the only organism that has biochemical models illustrating electron transport chain for iron oxidation (Baker and Banfield, 2003). *T. ferrooxidans* and *leptospirillum ferrooxidans* are dominant in pH that is above 1.3 in AMD. This was proved by the phylogenetic analyses based on 16S rRNA gene sequence.

Reference keys for lineages in Fig 2-5:	
* facultative anaerobes	ϕ lineages obligate aerobes
Blue have no cultivated members to date	**Red** are not known to be able to utilize sulphur, only iron oxidizers


actinobacteria
Actinomyces naeslundii, X53226
Acidothermus cellulolyticum, X70635
Microthrix parvicella, X89560
AMD clone BA84 Bond, AF225451
A. ferrooxidans TH3, M79433*
Acidimicrobium ferrooxidans ICP, U75647
Rogers clone TRA210, AF047642
Ferromicrobium acidophilus, AF251436
AMD clone BA46 Bond, AF225450
AMD clone ASLA Baker, AF543498
Thermomicrobium roseum, M34115
S. acidophilus*
Sulfobacillus sp. Frasl, AF213055
firmicutes
S. thermosulfidooxidans*
S. ambivalens RIV14, AY007664
Ammonifex degensii, U34975
Clostridium hydroxybenzoicum, L11305
AMD clone BW7 Baker, AF544225
Sulfobacillus disulfidooxidans SD-11, U34974
S. thermosulfidooxidans VKLM
Alicyclobacilli
soil clone DA008 Felske, Y12597
Holophaga foetida, X77215
sediment clone RB04 Wise, U62828
peat bog clone TM2 Rheims
acidobacteria
AMD clone TRB82 Rogers, AF047646
AMD clone BA2 Baker, AF543504
Acidobacterium capsulatum, D26171
TCB consortium clone SJA162, AJ009498
IM clones
Desulfovibrio longus, Z24450
Geobacter metallireducens, L07834
Desulfomonile tiedjei, M26635
Syntrophus gentianae, X85132
Desulfosarcina variabilis, M34407
Acidomonas methanolica, D30770
ϕ Acidisphaera rubrifaciens, D86512
AMD isolate NO15, AF376024
Acidocella spp.
* Acidiphilum spp.
Thiomonas spp.
Xanthomonas campestris, L24789
AMD isolate NO16, AF376024
Halothiobacillus spp.
A. caldus
* Acidithiobacilli
γ
β
α
0.10
Magnetobacterium bavaricum, X71838
Nitrospira moscoviensis, X82558
nitrospira
ϕ Leptospirillum ferrooxidans (group I)
ϕ L. ferriphilum (group II)
Leptospirillum (group III)

Source: Baker and Banfield, 2003

Figure 2-5 Phylogeny of prokaryotic 16S rRNA genes from acid mine drainage and bioleaching sites (in bold) with reference lineages.

Another oxidizing acidophilic is chemolithoautotrophs is *leptospirillum ferrooxidans*. It uses CO_2 to obtain energy for growth and oxidation of ferrous iron, sulphur and reduced sulphur compounds. To confirm that the most dominant bacteria in AMD is *T. ferrooxidans* and *L. ferrooxidans* a study was done by Cowan, D.A. *et al*. (2007) were they sampled AMD water at the Landau Mine site in Mpumalanga. The Chemical analysis of the water showed sulphate as 4812 mg/l, iron at 4800 mg/l. Phylogenetic analysis concluded that 62% organisms belong to acidithiobacillus sp.

(i.e. *T. ferrooxidans) Acidiphilum sp. Leptospirillum sp* (i.e. *L. ferrooxidans*) *Ferrimicrobium sp. and Schelegella sp*. The dominant community identified was *T. ferrooxidans.*

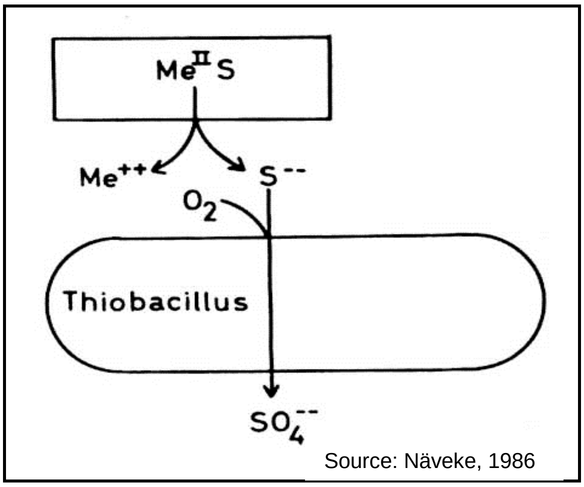
2.4.1 Direct and Indirect mechanism of Microbial Activity

Oxidation of pyrite can be generated by direct bacterial attack or indirect chemical-bacterial mechanism.

Direct bacterial attack

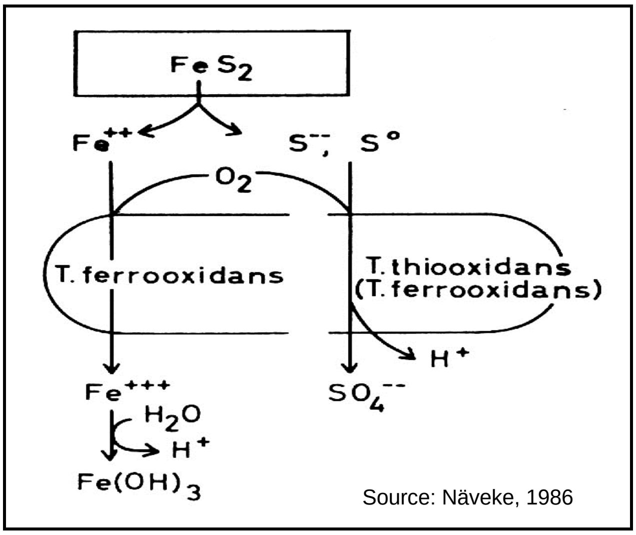
Electron donors or acceptors in oxidation- reduction reactions are characteristics of direct mechanisms (Mills, 2011).

The Direct mechanism is when cells are either close to each other or attached to the solid surface. This speculation was made after the cell-size pits were observed on a pyrite surface after the reaction with *T. ferrooxidans* (Baker and Banfield, 2003). *T. ferrooxidans* in the direct bacterial attack mechanism can grow in neutral pH and then acidify the system to a pH value of 4 in crushed coal (Bosch, 1990). Several reactions involved during the direct mechanism are not fully understood but some are clear. The direct mechanism (Figure 2-6 and Figure 2-7) is disturbed by the oxidation of sulphuric ion and metal ions so that the sulphide mineral may be dissolved slowly. The sulphide mineral is attacked by hydrogen ions and releases metal ions, hydrogen sulphide or elemental sulphur. The Bacteria (*T. ferrooxidans*) oxidises hydrogen sulphide and elemental sulphur to produce sulphuric acid (Rawlings, 1989; Mills, 2011).



Source: Näveke, 1986

Figure 2-6 Direct mechanism of sulphuric heavy metals.

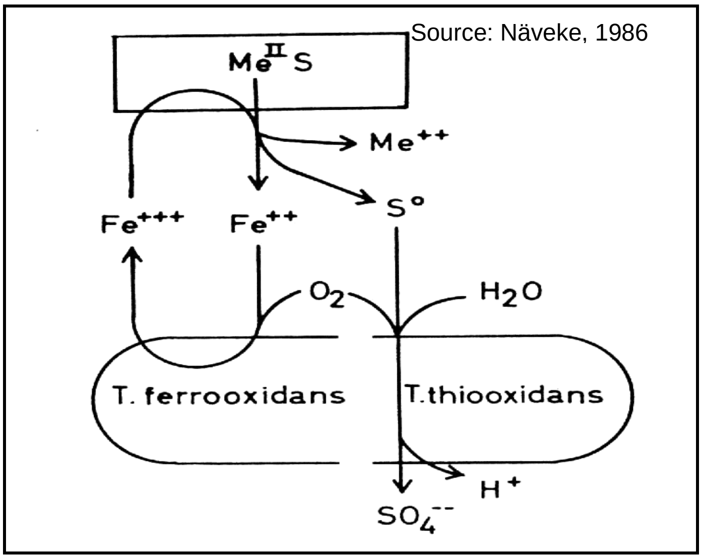

FeS_2
Fe^{++}
S^{--}, S^{o}
O_2
T. ferrooxidans
T. thiooxidans
(T. ferrooxidans)
H^+
Fe^{+++}
SO_4^{--}
H_2O
H^+
$Fe(OH)_3$

Source: Näveke, 1986

Figure 2-7 Direct mechanism of pyrite or maroasite.

Indirect mechanism

Indirect mechanism includes abiotic and biotic *T. ferrooxidans* (Bosch, 1990). During the indirect mechanism there is dissolution of sulphide minerals (acidic conditions), in anaerobic conditions-precipitation of minerals (refer to the processes that are associated with AMD), adsorption of metals (Figure 2-8) by microbial activity (bacteria or algae) and the formation and degradation of organometallic complexes (Mills, 2011).


$Me^{II}S$
Me^{++}
S^{o}
Fe^{+++}
Fe^{++}
O_2
H_2O
T. ferrooxidans
T.thiooxidans
H^+
SO_4^{--}

Source: Näveke, 1986

Figure 2-8 Indirect mechanism of metals.

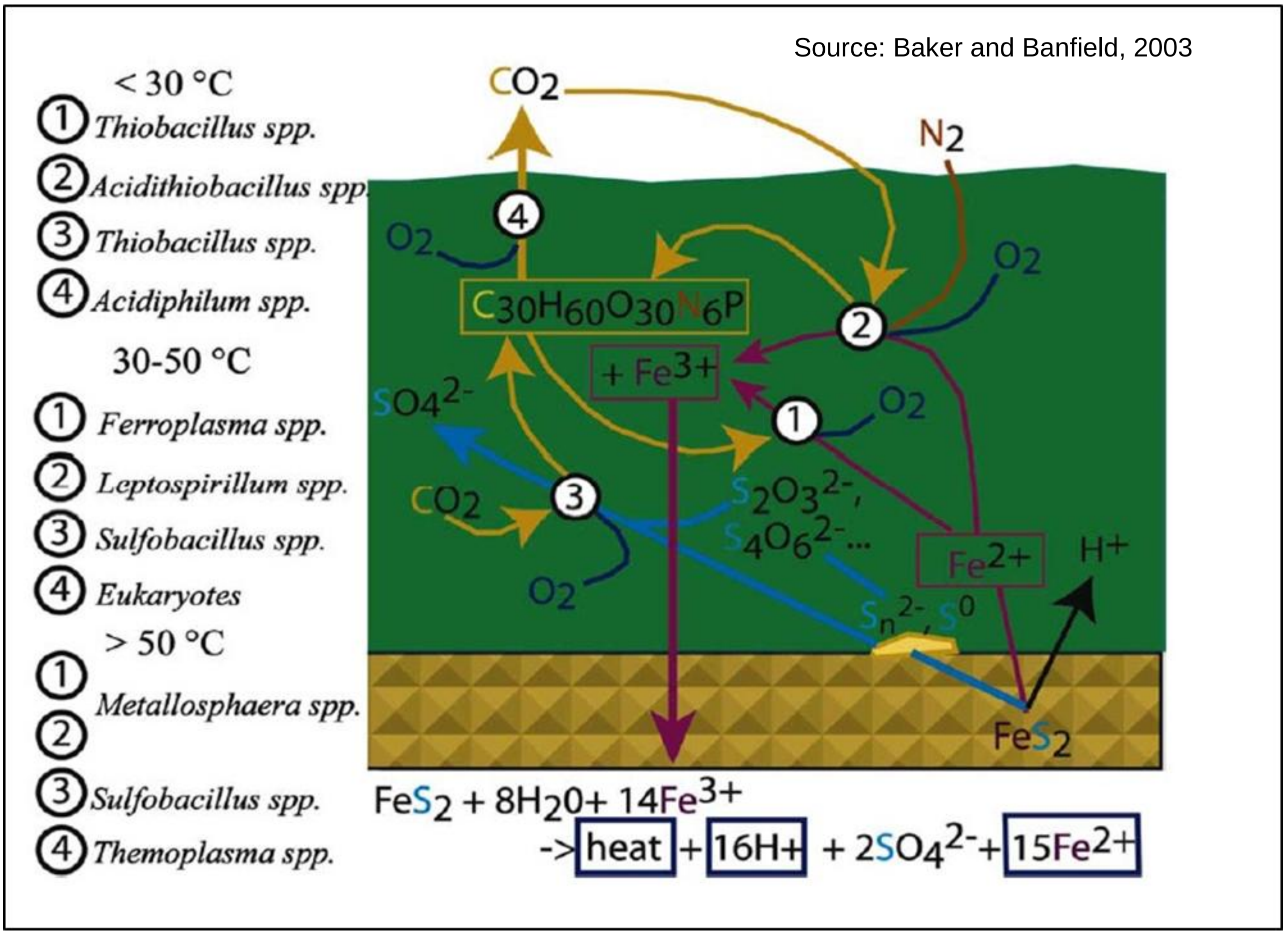
2.5 Interrelations and Differences between Sulphur oxidation and Sulphur reduction

Sulphur oxidation and Sulphur reduction (Table 2-2) are mostly studied separately but both processes must be considered simultaneously because these reactions are coupled during AMD generation (Hines et al., 2002). Tabulated below is the difference between Sulphur oxidation and Sulphur reductions.

Table 2-2 Differences between reduction and oxidation.

Sulphate Reduction	**Sulphate Oxidation**
Anaerobic bacteria	Anaerobic and aerobic bacteria
Highly reduced S (-2 valence)	Highly oxidised SO_4^{2-} (+6 valence)
Major process in marine sediments and decomposition of organic material in anoxic freshwater habitats	Oxic environment
Reduces SO_4^{2-}, metal and O_2 reduction	Degradation of Sulphur containing organic matter
Dissimilatory reduction of SO_4^{2-}	Dissimilatory Sulphate reduction
Utilizes energy to create new cell material from organic matter	Utilizes energy for cell synthesis
Heterotrophic (organic matter utilization)	Autotrophic (Self nourishment using photosynthesis and inorganic matter)
S. Acidophilus	*Acidithiobacillus Ferrooxidans*

AMD conceptual model is illustrated by Figure 2-9 showing the interrelation of bacteria for optimization of AMD. Crystalline pyrite (Fe_2S) is at the bottom in a golden colour, the portion above represents AMD solution (green). Elemental sulphur is shown as a possible inhibitor of surface dissolution and the overall oxidation of pyrite is shown at the bottom, with Fe^{3+} indicated as the primary oxidant. Intermediate sulphur compounds are indicated as follows: $S_2O_3{}^{2-}$(thiosulphate) and $S_4O_6^{2-}$ (tetrationate). $C_{30}H_{60}O_{30}N_6P$ indicates organic carbon compounds (Baker and Banfield, 2003).


< 30 °C
① Thiobacillus spp.
② Acidithiobacillus spp.
③ Thiobacillus spp.
④ Acidiphilum spp.
30-50 °C
① Ferroplasma spp.
② Leptospirillum spp.
③ Sulfobacillus spp.
④ Eukaryotes
> 50 °C
①
Metallosphaera spp.
②
③ Sulfobacillus spp.
④ Themoplasma spp.
CO2
N2
O2
④
O2
C30H60O30N6P
+ Fe3+
②
SO42-
①
O2
CO2
③
S2O32-,
S4O62-...
O2
Fe2+
H+
Sn2-, S0
FeS2
FeS2 + 8H20+ 14Fe3+
-> heat + 16H+ + 2SO42- + 15Fe2+

Source: Baker and Banfield, 2003

Figure 2-9 Potential iron, sulphur, and carbon cycling based on known metabolic capabilities (1, 2, 3, and 4) associated with AMD members.

By donating and accepting electrons, iron can be oxidised or reduced at a rapid rate.

$FeS_2 + 3\frac{1}{2} O_2 + H_2O$ -----------------------------→$FeSO_4 + H_2SO_4$

Pyrite *T.Ferrooxidans* Ferrous Sulphate

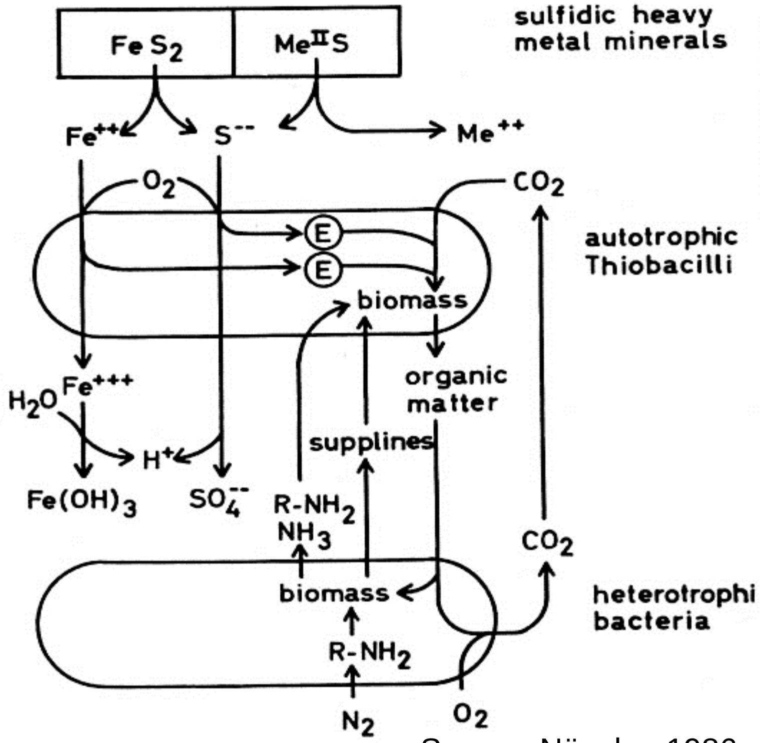
Pyrite is oxidised as soon as ferrous sulphate is formed

$2FeSO_4 + \frac{1}{2} O_2 + H_2SO_4$ -------------------→ $Fe_2 (SO4)_3 + H_2O$

T.Ferrooxidans Ferric sulphate

Depending on the acidity, the presence of oxygen, sulphur and ratio of Fe^{2+} to Fe^{3+} ions the degree hydrolysis will vary. Only a fraction of the sulphur is oxidised (microbial) further to produce sulphuric acid, while the rest of the sulphur is hydrolysed to form basic sulphuric acid and ferric sulphate (Zajic, 1969).

The heterotrophic bacterium active in the reduction process supports metabolic activity and growth of the autotrophic bacterium for the oxidation process (Figure 2-10). The strain of *T. ferrooxidans* cannot grow without an addition of nitrogen compounds so the heterotrophic bacterium reduces molecular nitrogen which is then used by *T. ferrooxidans* for growth and metabolic activity. The interrelations are not all known of and are complex however, the sulphur reduction and sulphur oxidation are definitely interconnected (Näveke, 1986 and Juszczak *et al.,* 1995).


Fe S2
Me II S
sulfidic heavy metal minerals
Fe++
S--
Me++
O2
CO2
E
E
autotrophic Thiobacilli
biomass
organic matter
H2O
Fe+++
H+
Fe(OH)3
SO4--
supplines
R-NH2
NH3
CO2
biomass
heterotrophi bacteria
R-NH2
N2
O2

Source: Näveke, 1986

Figure 2-10 Interrelations between oxidation and reduction of Sulphur in AMD.

2.6 Conclusions for chapter 2

- The processes/stages of AMD are complex and should not be studied separately as they are coupled during the generation of AMD.

- Geochemical reactions associated with AMD may or may not produce an alarming rate of pollution depending on the neutralising capacity of the system at equilibrium conditions. Some reactions may produce other metals (i.e. Al) that are soluble in the event of buffering and cause more damage to the environment.

- A range of species are present in the AMD but Cowan *et al*, 2007 proved that the dominant species found in AMD is *T. ferrooxidans* and *L. Ferrooxidans*.

- Microbiological influence of bacteria has the ability to accelerate the rate of oxidation by converting insoluble metal sulphate to water soluble metal sulphate. In an acid medium, the rate of bioxidation is increased by 30 or more multiples compared to the pure chemical oxidation therefore bacterial analysis in the prediction, management and remediation of AMD should be considered.

- With the understanding of the definition of AMD, the processes and the microbial activity involved, the prediction and evaluation of AMD is discussed in detail in the following chapters.

The methodologies used to predict AMD are laboratory analysis referred to as Acid-Base Accounting (ABA). Since South Africa uses the same ABA guidelines as most countries (USA and Europe) and Australia uses its own guidelines that are modified from time to time, in the next chapter (Chapter 3) more emphasis is on the comparison of the methodologies used in South Africa and Australia. Different samples are subjected to these methodologies and then the results are evaluated. This particular study is conducted to determine whether it is viable to use Australian methods on South African samples.

CHAPTER 3

About 40 000 km^2 of Australian coastal soil has 1 billion tonnes of potential sulphuric acid with a pending legacy of $10 AUD billions of Acid Sulphate Soil (Thomas *et al.,* 2003) while the gold and coal mines in South Africa have the potential to produce an alarming rate of Acid Mine Drainage (Mine water, 2011).

3. Australian versus South African Acid-Base Accounting methods

Acid Sulphate Soil (ASS) occurs mostly at the coastal areas in Australia, mangrove swamps, generally inland 5 m above the mean sea level, higher surfaces, old mines (as Acid mine drainage) and groundwater seepage zones (Thomas *et al.,* 2003). Unique characteristics of ASS are created by evaporation rates that are high, low rainfall, various marine flora and waterlogged environments (McElnea, 2004a).

Acid Mine Drainage (AMD) is associated with sulphide-containing ore mining operations which mainly results in the oxidation of pyrite. AMD is generated when sulphide bearing minerals are exposed to the atmosphere and water (Usher *et al.,* 2003).

Despite the differences in names (AMD and ASS), South Africa and Australia have a predominant sulphuric compound known as pyrite[1] in common that causes acidic conditions and the prediction of these acidic conditions are of great importance.

Laboratory guidelines (i.e. ABA) are set for the standard routine analysis of samples in order to predict the production of AMD or ASS conditions. They provide information for a proper assessment to determine whether the samples are potentially or already acidic. The importance of laboratory analysis is to give the best and worst case scenario of the area that would occur in the field, provided that the samples are representative of the area investigated.

3.1 Sampling

In 2010, Eight South African and Australian soil samples were assigned by the Institute of Groundwater Studies (IGS) laboratory to be analysed for an honours project. The four South African samples were from the Pandora and Tavistock area while the four Australian soil samples were found in the coastal areas and estuaries. The samples were analysed in 2010 and a report was written and submitted (Mokoena, 2010). The report was not as extensive as this chapter and one of the recommendations was that the tests must be repeated again since some results were erratic.

---

[1] Pyrite is not the only sulphide-bearing mineral.

The Table 3-1 shows the pulverised sample names and lab names used in this chapter. All samples were done in duplicate to ensure more accurate results. The Australian sample names are hyphenated by 10 to indicate that they are the samples were received in 2010.

Table 3-1 The list of samples names used in 2010.

Sample name	Lab name	Origin of the sample
Blank 1	Blank 1	Blanks
Blank 2	Blank 2	Blanks
EAS 61-10	EAS 1A	Australian Sample
EAS 61-10	EAS 1B	Australian Sample
EAS 62-10	EAS 2A	Australian Sample
EAS 62-10	EAS 2B	Australian Sample
EAS 63-10	EAS 3A	Australian Sample
EAS 63-10	EAS 3B	Australian Sample
EAS 64-10	EAS 4A	Australian Sample
EAS 64-10	EAS 4B	Australian Sample
T5	SA:T5A	South African Sample (Tavistock)
T5	SA:T5B	South African Sample (Tavistock)
T28	SA:T28A	South African Sample (Tavistock)
T28	SA:T28B	South African Sample (Tavistock)
SB10B	SA:SB10B SAMPLE 1	South African Sample (Pandora)
SB10B	SA:SB10B SAMPLE 2	South African Sample (Pandora)
SB11A	SA:SB11A SAMPLE 1	South African Sample (Pandora)
SB11A	SA:SB11A SAMPLE 2	South African Sample (Pandora)

In 2011, samples were once again received from the Soil and Foliage Lab Check (Australia), only the sample names were similar to the once received the previous year. To be able to compare the Australian and South African methods in 2011, another two South African samples were added.

The Table 3-2 shows the pulverised sample names and lab names received in 2011. All samples were done in duplicate to ensure more accurate results. The Australian sample names are hyphenated by 11 to indicate that they are the samples were received in 2011. Mineralogical analyses were done for the 2011 samples and the results are presented in Appendix 3.

Table 3-2 The list of samples used in 2011.

Sample name	Lab name	Origin of the sample
Blank	Blank	Blanks
Blank 2	Blank 2	Blanks
EAS 61-11	EAS 61-1 AUS	Australian Sample
EAS 61-11	EAS 61-2 AUS	Australian Sample
EAS 62-11	EAS 62-1 AUS	Australian Sample
EAS 62-11	EAS 62-2 AUS	Australian Sample
EAS 63-11	EAS 63-1 AUS	Australian Sample
EAS 63-11	EAS 63-2 AUS	Australian Sample
EAS 64-11	EAS 64-1 AUS	Australian Sample
EAS 64-11	EAS 64-2 AUS	Australian Sample
FKP	FKP 1 GCS	South African Sample
FKP	FKP 2 GCS	South African Sample
FEM	FEM 1 GCS	South African Sample
FEM	FEM 1 GCS	South African Sample

This chapter outlines the research conducted to note the difference between South African and Australian Laboratory methods and results. It will therefore consist of the results from the year 2010 and 2011**.**

3.2 Different Methodologies of ABA

Australian ABA includes the Chromium and SPOCUS suite, depending on the objective of the analysis. The Chromium suite uses only required independent components of the ABA methods whereas the SPOCUS suite is a self-contained ABA with more steps and has measurements such as the residual acid soluble sulphur (S_{RAS}) unlike the Chromium reducible sulphur methods (S_{CR}) in the Chromium Suite (McElnea *et al.,* 2004a). South African ABA includes Static test and Kinetic test. Static tests are the analytical tests used as a screening criterion of the samples; used to determine the difference between the acid-generating capability and the acid-neutralising potential of the samples. The kinetics tests are used to define acid generation characteristics whereby the samples leachate is measured with respect to time (i.e. Humidity cells, field tests, column tests etc.).

In this chapter, Australian SPOCUS suite is used to compare the South African Static ABA methods. The Australian SPOCUS suite methodology is taken from the Acid Sulphate Soils Laboratory Methods Guidelines, Version 2.1 (McElnea *et al.,* 2004b) while the South Africa methodology is adapted from Usher *et al.,* 2003.

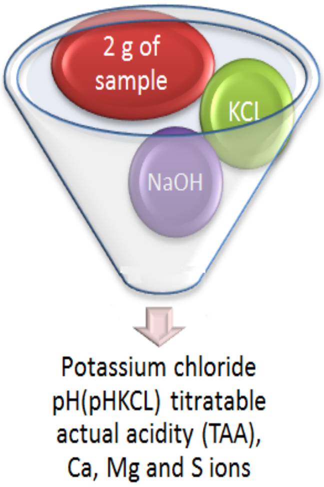
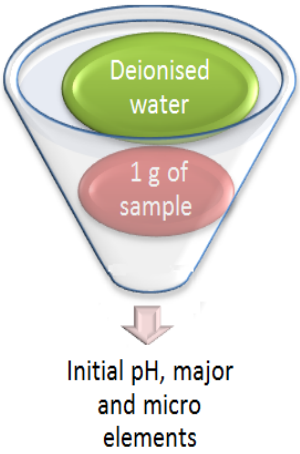
Extensive, step-by-step laboratory methods are found in Appendix 2. To follow the methodologies and understand the components used in this thesis, the section below gives illustrations in a less complex manner. The funnel-like illustrations indicates that the samples were filtered then the filtered sample was analysed by an ICP. For more details on the laboratory equipment please refer to Appendix 1.

3.2.1 Actual acidity of samples

Australian Potassium chloride pH (pH_{KCl}) and Titratable Actual Acidity (TAA) method versus South African Initial pH method

In Table 3-3 the Australian method uses KCl which makes the sample less natural and stabilises the cations. The South African methods uses only deionised water to determine the actual acidity of the sample as accurately as possible. More reagents are used in the Australian methods as compared to the South Africans' therefore the expense of the Australian methodology is higher.

Table 3-3 Actual acidity, Australian vs. South African methodology.

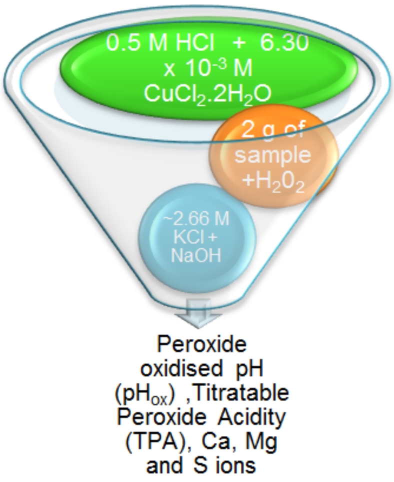
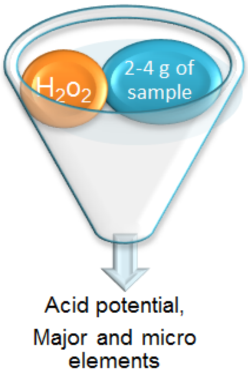
Method and Objective	Australian	South African
Actual Acidity	#KCl and NaOH	----------------
To determine the actual acidity of the sample	*pH, Titratable Actual Acidity (TAA) and S, Ca and Mg ions	*pH, major and minor ions
# Reagents used *Parameters used to evaluate the results	 2 g of sample KCl NaOH Potassium chloride pH(pHKCL) titratable actual acidity (TAA), Ca, Mg and S ions	 Deionised water 1 g of sample Initial pH, major and micro elements

3.2.2 Potential acidity method

Australian Peroxide oxidised pH (pH_{ox}) and Titratable Peroxide Acidity (TPA) vs. South African Acid Potential using Hydrogen Peroxide

In, the Australian method uses a long complex method that includes a total of 20 ml - 45 ml of hydrogen peroxide, hot steam bath, pH control methods such as carbonate modification, addition of other reagents, a longer period of time, and titration using a base (NaOH). However, carbonate modification has an advantage of dissolving excess carbonate using dilute HCL so that the efficiency of peroxide oxidation is not disturbed. South African methods on the other hand are fast, less expensive (less reagents) and a titration using a base is not required.

Table 3-4 Potential Acidity, Australian vs. South African methodology.

Method and Objective	Australian	South African
Potential Acidity **To determine the potential acidity of the sample** # Reagents used *Parameters used to evaluate the results	#10 ml increments of H_2O_2 (20-45 ml) #HCl, $CuCl_2.2H_2O$, KCl and NaOH	#5 ml increments of H_2O_2 (80-120 ml)
	*pH, Titratable Potential Acidity(TPA) and S, Ca and Mg ions	*pH, major and minor ions
	 0.5 M HCl + 6.30 x 10⁻³ M CuCl2.2H2O 2 g of sample +H2O2 ~2.66 M KCl + NaOH Peroxide oxidised pH (pHox) ,Titratable Peroxide Acidity (TPA), Ca, Mg and S ions	 H2O2 2-4 g of sample Acid potential, Major and micro elements

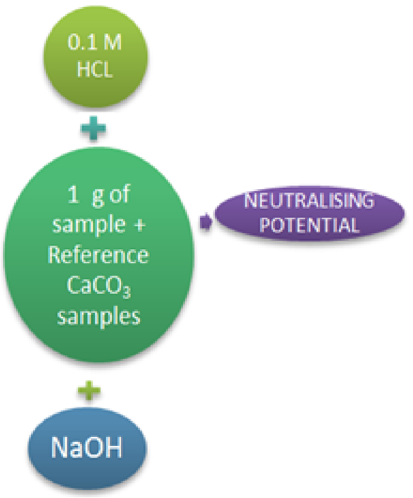
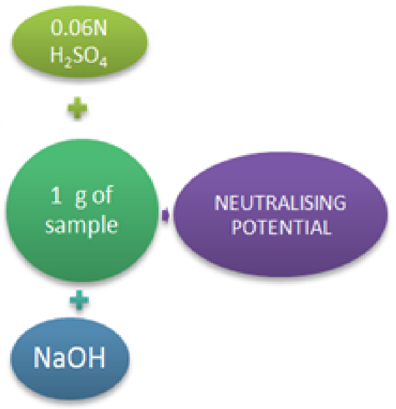
3.2.3 Neutralising potential

Australian Acid neutralising capacity (Back titration) method vs. South African Neutralising Potential Method

The Australian method in

Table 3-5 reference samples of 0.100 AR grade $CaCO_3$, HCL and NaOH are used whereas South Africa uses H_2SO_4, NaOH and assume that all samples have reactive species available but not all samples lacking carbonates or a dunite composition have insufficient neutralising potential (Usher *et al.,* 2003).

Table 3-5 Neutralising potential, Australian vs. South African methodology.

Method and Objective	Australian	South African
Neutralising Potential	#AR $CaCO_3$, HCl and NaOH	#H_2SO_4 and NaOH
To determine the neutralising capacity of the sample	*Amount of the base titrated vs. the amount of acid added	*Amount of the base titrated vs. the amount of acid added
# Reagents used *Parameters used to evaluate the results	 0.1 M HCL + 1 g of sample + Reference CaCO3 samples + NaOH NEUTRALISING POTENTIAL	 0.06N H2SO4 + 1 g of sample + NaOH NEUTRALISING POTENTIAL

3.3 Results and Observations of the ABA methods

3.3.1 Actual Acidity method

It seems fit to compare the KCl method with the initial pH method because the main objectives of the two methods is to record the existing acidity in the samples. Before the comparison of the results, it is imperative to check the consistency of results by checking the dependability of the duplicates. To achieve this, the x-axis (1st duplicate i.e. EAS 4A or EAS 61-1 AUS) is plotted against y-axis (2nd duplicate i.e. EAS 4B or EAS 61-2 AUS). This is done throughout the thesis.

Comparison of the 2010 results

Figure 3-1A and Figure 3-1C represents samples used in the Australian methods while Figure 3-1B and Figure 3-1D represent the samples used in the South African methods. The consistency and linear relationship of the pH in the Australian methods is not the same in South African methods. Australian pH correlation is not as high as the South Africans. This shows that the South African methods have more precise and approximate data.

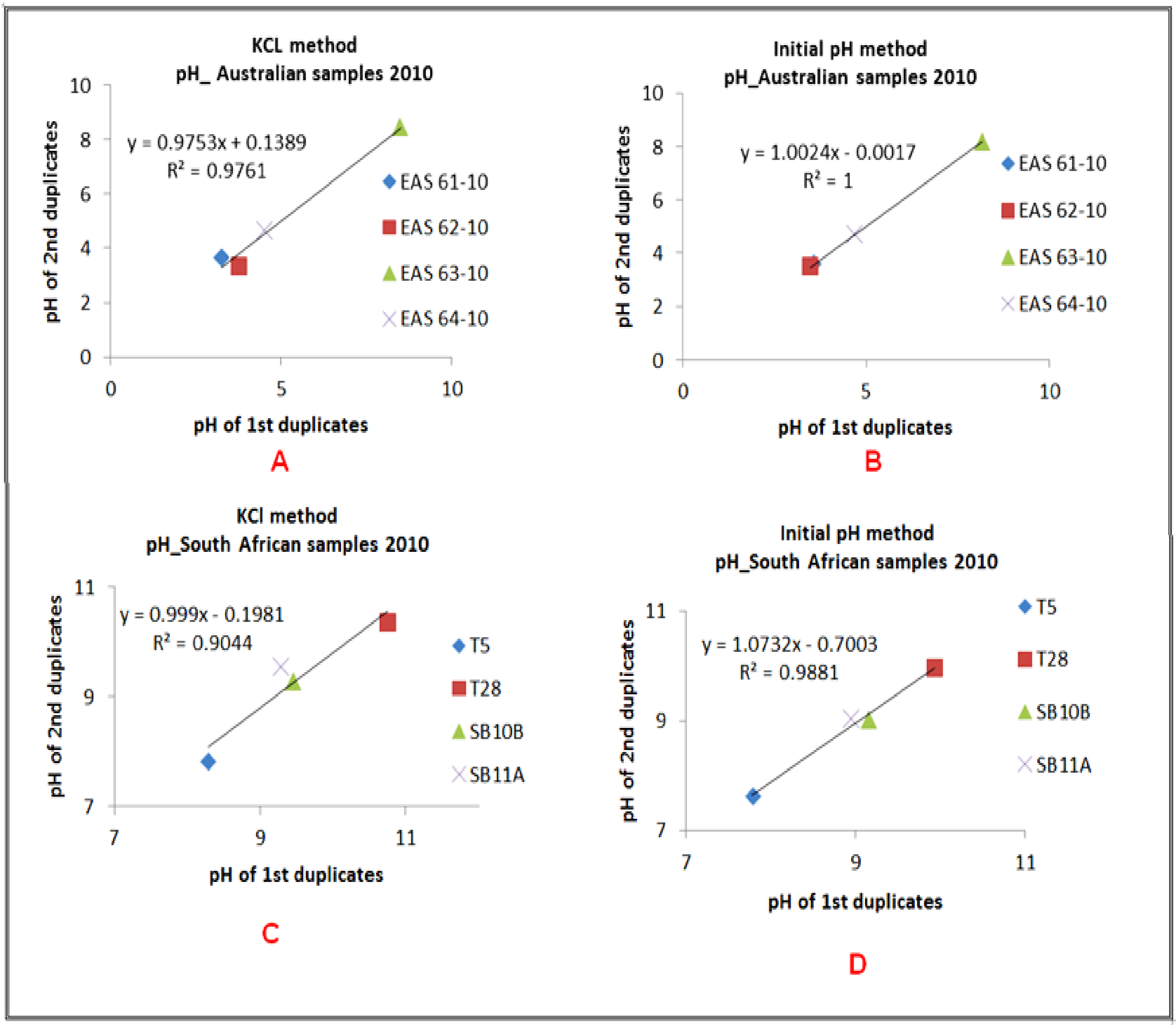


Figure 3-1 pH precision/accuracy of the Actual Acidity methods (2010).

As shown in Figure 3-2, the correlation of pH is high for the method comparison of the Actual Acidity Methods. It has a linear trend and indicates that the pH values of the Australian methods are approximate to the South Africans. Although the methods are different the pH values are similar.

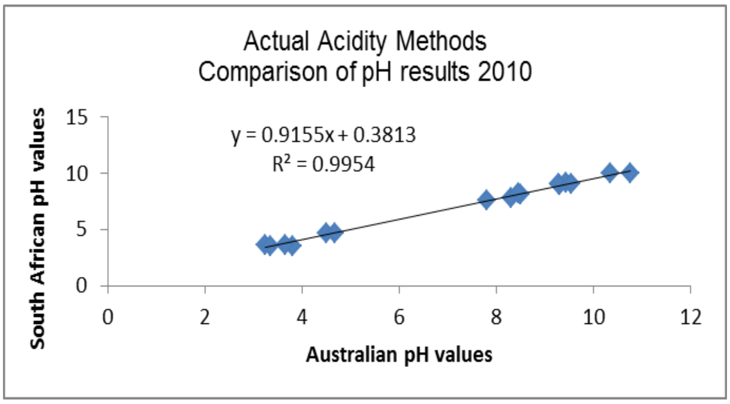


Figure 3-2 Comparison of pH results, Actual Acidity methods (2010).

In the Australian methods a TAA method is done to determine the value of the Titratable Actual Acidity (TAA). This is done by the addition of NaOH to the samples with the rule that If the pH was higher than or equal to 6.5 the TAA is to be recorded as zero (McElnea *et al.,* 2000). The values in Figure 3-3 illustrate that the duplicates are inconsistent with each other with values that are not approximate. This might be due to the different NaOH volume added for each duplicate, please refer to Appendix 3 for the exact values. Samples with a pH of equal/more than 6.5 are deemed to pose lower risk of acidity therefore the “least” acidic the sample is, the lower the TAA value. All South African samples and one Australian sample (EAS 63-10 duplicate) have a TAA value of zero because of the high pH values.

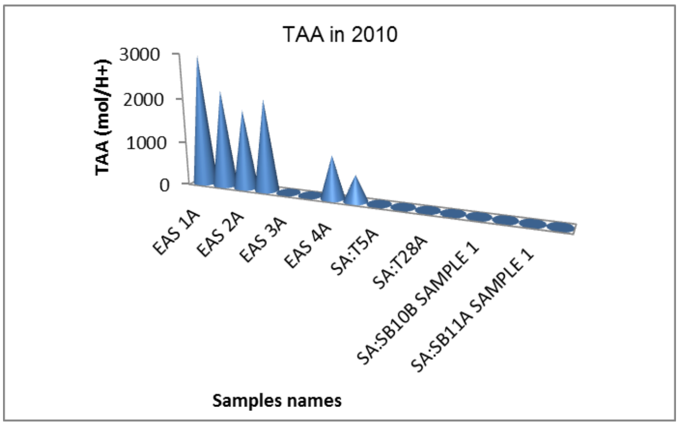


Figure 3-3 Titratable Actual Acidity (TAA) 2010.

The Figure 3-4 only represents the %Ca correlation because it had a low correlation value as shown in Figure 3-5. Only the %cation of the lowest correlation will be discussed in this chapter. The rest of the cation correlation figures are found in Appendix 4.

All the graphs in Figure 3-4 show a correlation greater than 0.90, however the correlation in Figure 3-5 is 0.84. The areas of concern are noted with the red circles in the figure. The left side of the figures will be dedicated to the Australian methods with top left figure showing only the Australian sample, below it will be the South African samples. EAS 64-10 and EAS 63-10 samples (with regards to Figure 3-4A) in the Australian methods showed the lowest TAA value in Figure 3-3, therefore showing that the actual acidity is low in the sample and high Ca values are determined. Figure 3-4A compared to Figure 3-4B show a great difference of values with the EAS 64-10 and EAS 63-10 samples, this might be due to the Australian methods using KCL (stabilising the cations) and NaOH titrated samples with a pH less than 6.5. Figure 3-4C illustrates values that are almost double the values of the samples in Figure 3-4D. This could be explained by the additional reagents used in the Australian methods (i.e. KCL) or it could be either a personal, instrumental or analytical error.

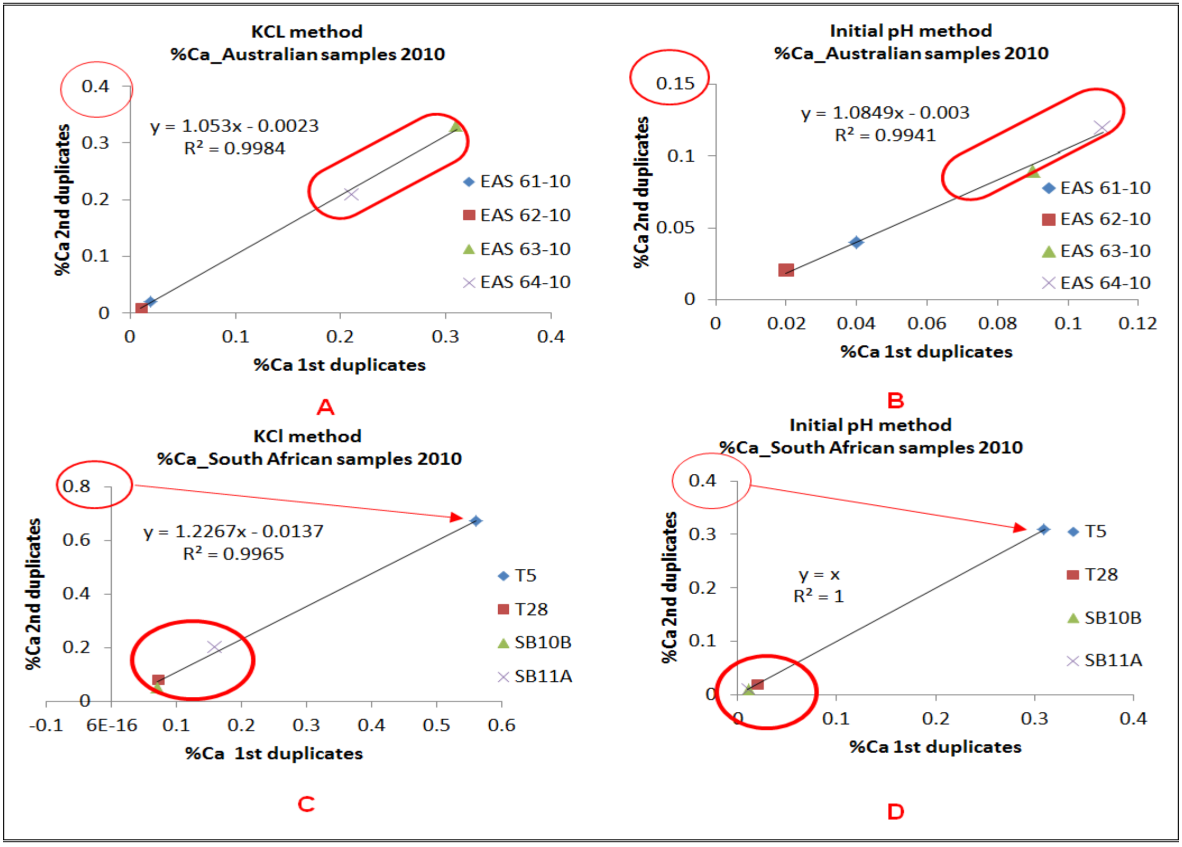


Figure 3-4 %Ca precision/accuracy of the Actual Acidity methods (2010).

Both Actual Acidity methods in question showed T5 duplicates to have high content in Ca whereas EAS 64-10 duplicates have high content of SO_4 and Mg. Since the pH recordings showed that EAS 64-10 duplicates have a TAA value of zero but the sample has high sulphate content it is assumed thus far that the sample will show a high acidic potential in the Potential Acidity method. It is evident that the Australian method yielded similar results to the South African methods (Figure 3-5), suggesting that the methods are comparable.

%SO4 has the highest percentage range and the highest correlation while Mg has the lowest percentages. %Ca has the lowest correlation indicating less approximate values between the South African and Australian methods, the addition of the NaOH in the Australian methods might have interfered with the Ca percentage value.

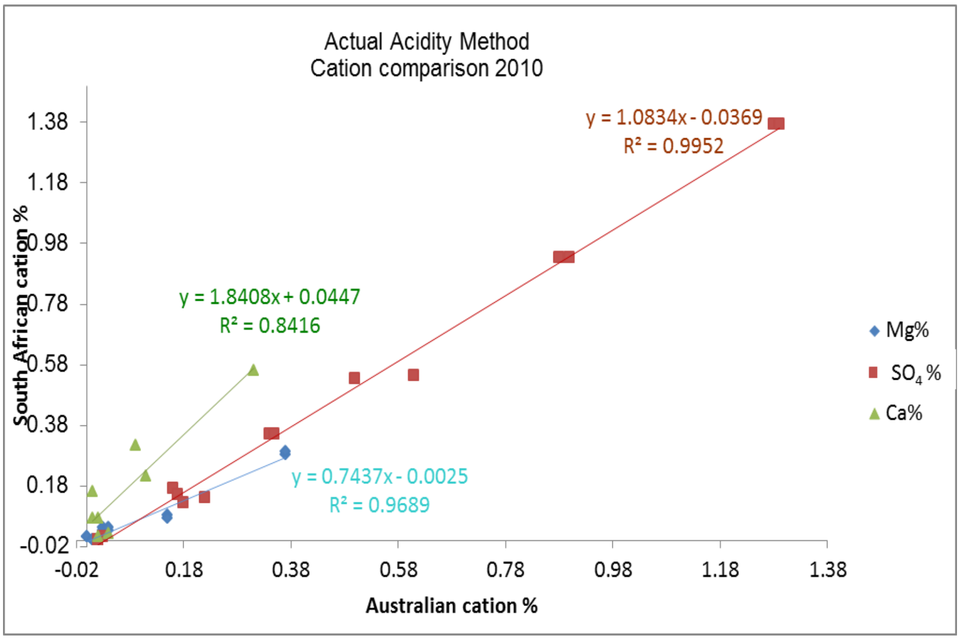


Figure 3-5 %Cation comparisons, Actual Acidity methods (2010).

Comparison of the 2011 results

In 2011, only four Australian samples and two South African samples were used to achieve the main objective of this chapter. It seemed fit to illustrate all the samples on two graphs because the correlation for samples would have yielded R-squared value of 1. South African samples (FEM and FKP) have a slight difference in value (Figure 3-6A and Figure 3-6B) hence the difference in the R-Squared values. The pH precision in both Australian's and South Africa are satisfactory because of the high values. The duplicate values in the Australian methods were not as inconsistent as the 2010 samples values. This could be because of nearly similar quantities of NaOH added to sample and the accuracy of pH recordings.

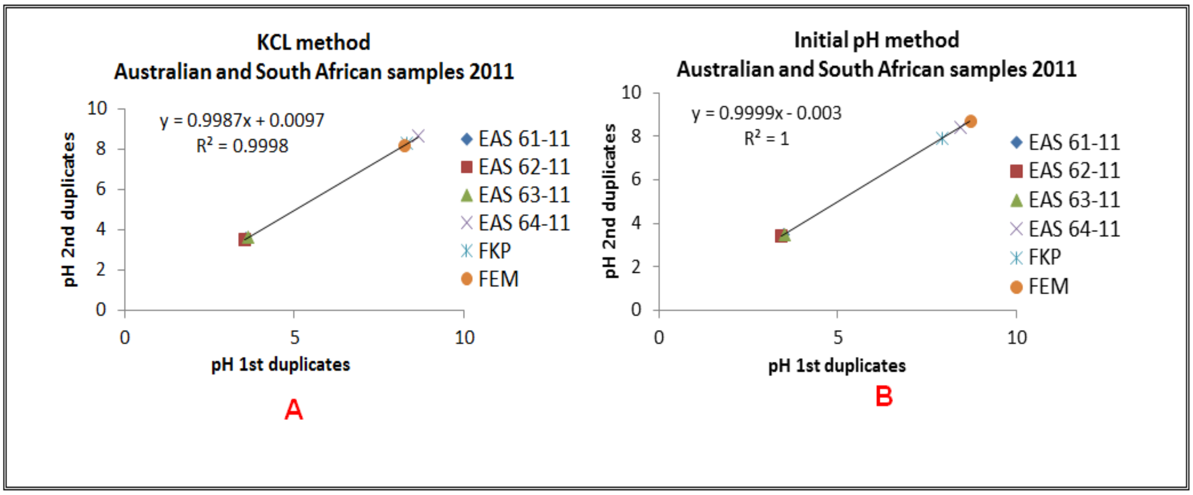


Figure 3-6 pH precision/accuracy of the Actual Acidity methods (2011).

The high correlation of pH in Figure 3-7 indicates that the pH of Australian KCL method and South African Initial pH method are approximate. In 2011 the pH correlation is not as high as the one illustrated for the year 2010 (Figure 3-2). The pH probe used in 2010 is still the same one used in the year 2011 and it was calibrated prior to use. The difference of value might be due to personal, instrumental or analytical error.

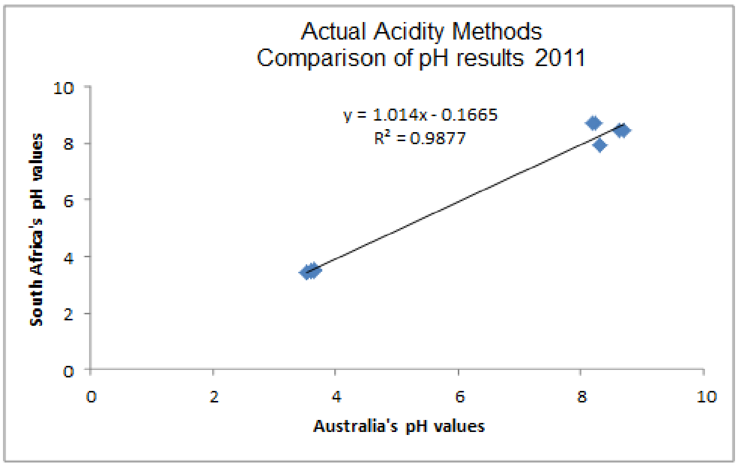


Figure 3-7 Comparison of pH results, Actual Acidity methods (2011).

As already stated, Australian Acidity methods consists of TAA method is done to determine the value of the Titratable Actual Acidity (TAA). The values in

Figure 3-8 illustrates consistent of duplicates, giving more reliable data. Samples with a pH of equal/more than 6.5 are deemed to pose lower risk of acidity therefore the less acidic the sample is, the lower the TAA value. All South African samples and one Australian sample (EAS 64-11 duplicate) have a TAA value of zero because of the high pH values.

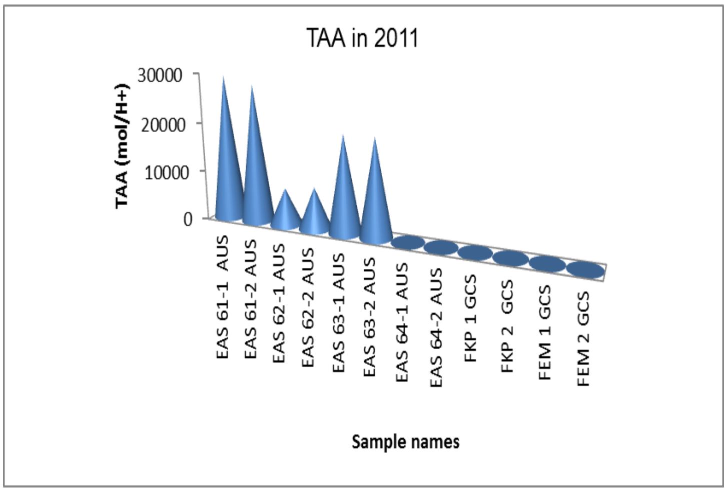


Figure 3-8 Titratable Actual Acidity (TAA) values in 2011.

The Figure 3-9 only represents the Ca cation correlation because it had a low correlation value as shown in Figure 3-10. The rest of the cation correlation figures are found in Appendix 4. The low %Ca correlation shown in Figure 3-10 is due to the difference in the percentages of each method. The areas of concern are noted with the red circles in the Figure 3-9. The left side of the figures is dedicated to the Australian methods whereas the right side illustrates the South African methods. Figure 3-9A compared to Figure 3-9B show a great difference of values, this might be due to the fact that Australian methods used KCL (stabilising the cations) unlike the South African method and the that the samples with a pH less than 6.5 had to be titrated with NaOH or it could be either a personal, instrumental or analytical error.

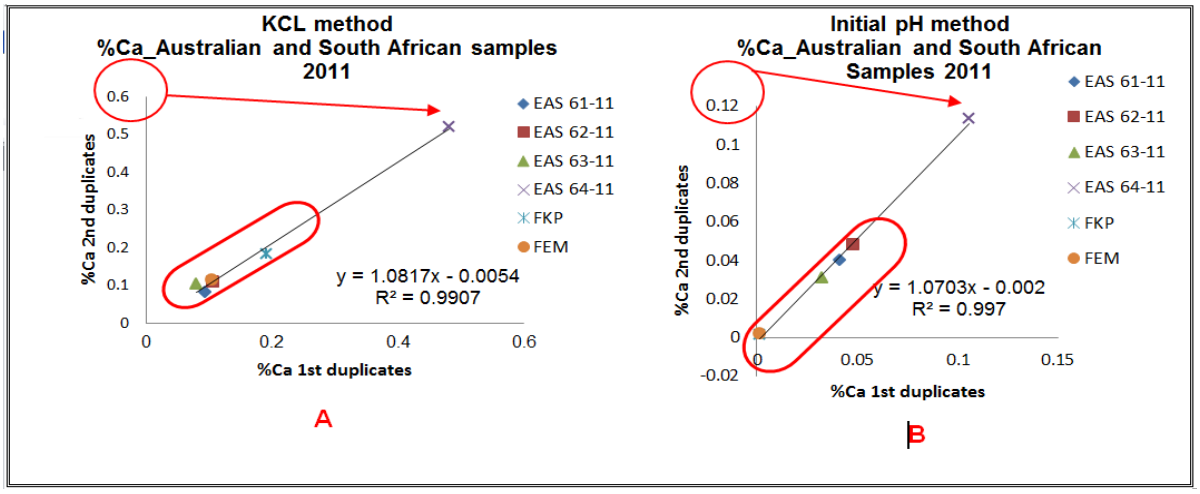


Figure 3-9 %Ca precision/accuracy of the Actual Acidity Methods (2011).

Although the percentages of the correlation is satisfactory (Figure 3-10) and do not show a linear correlation, it is evident that the Australian method yielded similar results to the South African methods. %Mg has the lowest percentage range but the highest correlation values whereas $\%SO_4$ has the highest percentage range. %Ca has the lowest correlation which might be caused by addition of NaOH to samples with acidic pH. The %cation trend is evident also in 2010.

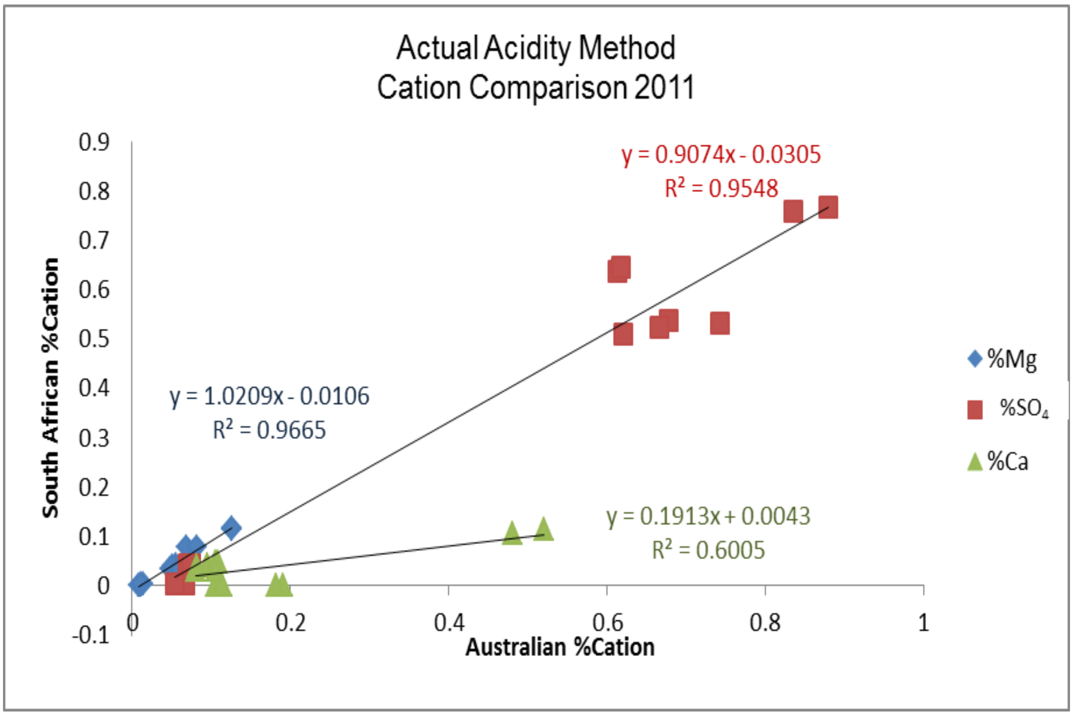


Figure 3-10 %Cation comparisons, Actual Acidity methods (2011).

3.3.2 Peroxide (Potential Acidity) Methods

It is only logical to compare the South African peroxide method with the Australian peroxide method because the main objective of the two methods is to record the potential acidity of the samples. The Australian peroxide method has an additional step to dissolve excess carbon content that could interfere with the efficiency of the peroxide oxidation called carbonate Modification. The carbonate modification step could also be used to determine the Excess Acid Neutralising Capacity of the sample. To ensure there is maximum recovery of the carbonate, a slow titration is necessary however, it became very difficult to standardise and be consistent without the use of an auto-titrator. For detailed data please refer to Appendix 2 and 3. The Australian peroxide method also expresses Titratable Potential Acidity (TPA) and their calculations include volumes of reagents. South African peroxide method uses the SO_4 and peroxide to calculate the Acid Potential (AP) of the sample, expressing it as kg SO4/tonne and categorizes samples into three categories (non-acid-, Low risk- and high risk generating samples) using the pH values.

Comparison of the 2010 results

From both methods in the year 2010, it was suspected that EAS 61-10 and EAS 64-10 duplicates would have high pyrite or manganese content since the sample reacted violently when increments of peroxide were added.

With the Australian peroxide method, 75% of South African samples had to be “treated” to carbonate modification along with one Australian sample (EAS 63-10 duplicates) because of their high pH even after peroxide digestion was done. Comparing the values determined from this method with the South African peroxide method, pH values are recorded. The Australian pH readings are at least 1 unit higher than the South Africans. The highest pH variances are presented by SB10B and T5 samples with about 2-3 units difference (Figure 3-11).

According to the South African peroxide method, all South African samples and EAS 63-10 duplicates have low risk of generating acid. These samples had an alkaline (above 7) pH recorded in the Initial pH method. Australian samples are high risk acid generating samples especially EAS 64-10 duplicates which has the lowest pH value and reacted violently with hydrogen Peroxide (H_2O_2). South African peroxide method has the highest pH correlation values as compared to the Australian method (Figure 3-11).

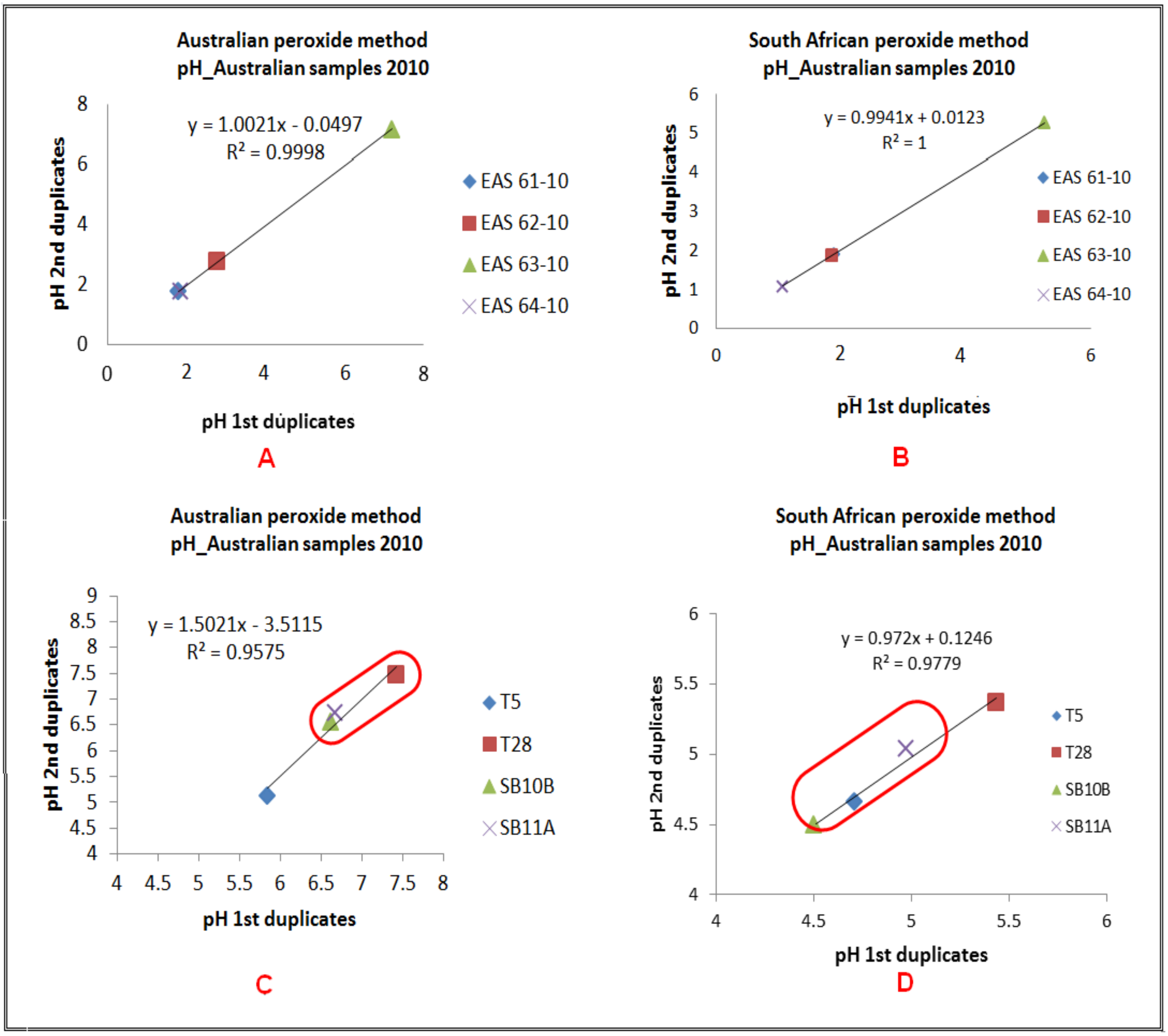


Figure 3-11 pH precision/accuracy of the peroxide methods (2010).

The correlation of pH (Figure 3-12) is high and indicates that the pH values of the Australian methods are approximate to the South Africans. Although the methods are different and more reagents are used, similar pH values are evident.

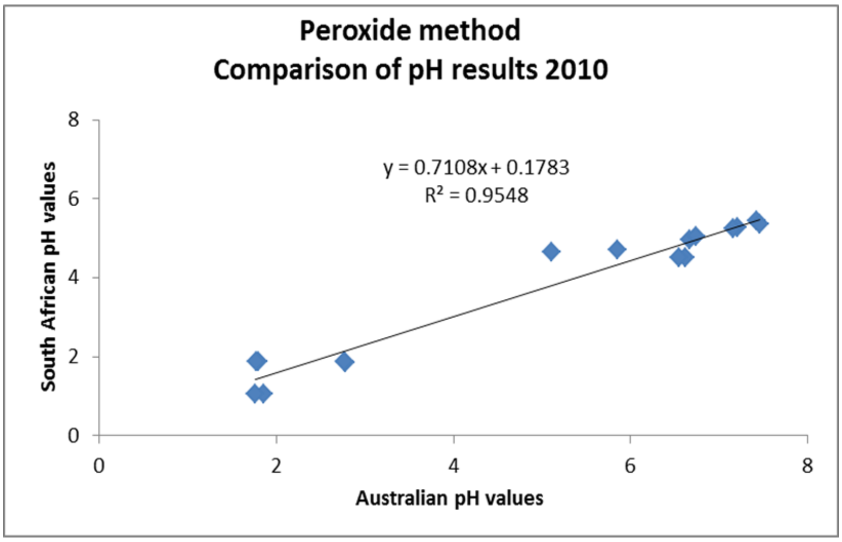


Figure 3-12 Comparison of pH results, peroxide methods (2010).

With the assumption that complete oxidation of pyrite occurred during the peroxide methods, calculation of the TPA (mol/t) were converted to kg SO_4/t (See Appendix 3) so that the results of the Australian peroxide method could be compared to the South African peroxide method. The EAS 61-10 and EAS 64-10 results confirm the high SO_4 percentage with the high TPA and AP values. EAS 61-10 already showed a high TAA (Figure 3-3) indicating that the sample is already acidic but because of the high TPA value and AP (Figure 3-13) this means the sample still has the potential to be more acidic. EAS 64-10 also has the high TPA indicating that the sample has the potential to generate acidic conditions upon oxidation. The South African AP values were lower than the Australian methods except in the case of EAS 63-10. This distinction might be because this sample was subjected to carbonate modification and without the use of an auto-titrator it is very difficult to standardise and be consistent. All South African samples were subjected to carbonate modification, but EAS 63-10 was the most difficult to standardise with consistency since the maximum recovery of the carbonate needs a slow titration.

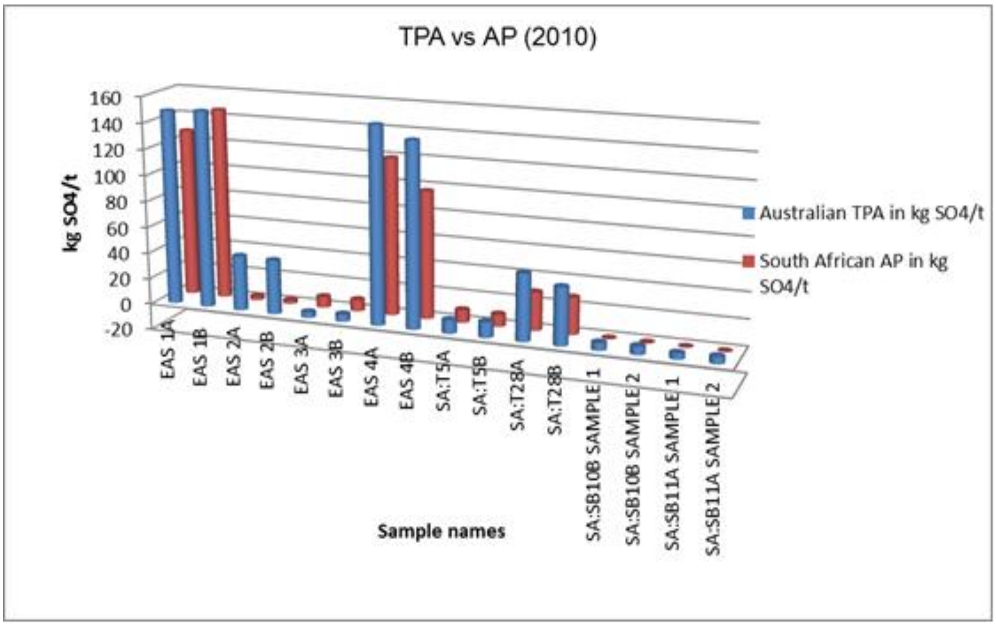


Figure 3-13 Titratable Potential Acidity versus Acid Potential 2010.

All the graphs in Figure 3-14 show a correlation greater than 0.90 therefore the duplicates values are consistent in South African and Australian peroxide methods. However, when the methods are compared to each other there are at least 2 units in variance evident with each sample that causes the results of the overall correlation (Figure 3-16) to be low. The South African method in Figure 3-14B shows a lower correlation of 0.944 that is lower than the Australian method (0.997) in Figure 3-14A. EAS 64-10 and EAS 61-10 duplicates are inconsistent and do not illustrate the same percentage of SO_4 in the South African method, this might be due to analytical, personal or instrumental error.

South African samples in both methods (Figure 3-14C and Figure 3-14D) show more than double the amount of the South African value in the Australian methods with regards $\%SO_4$. It is still unclear if carbonate modification plays a role in the difference of the values since T5 duplicate was not subjected to carbonate modification.

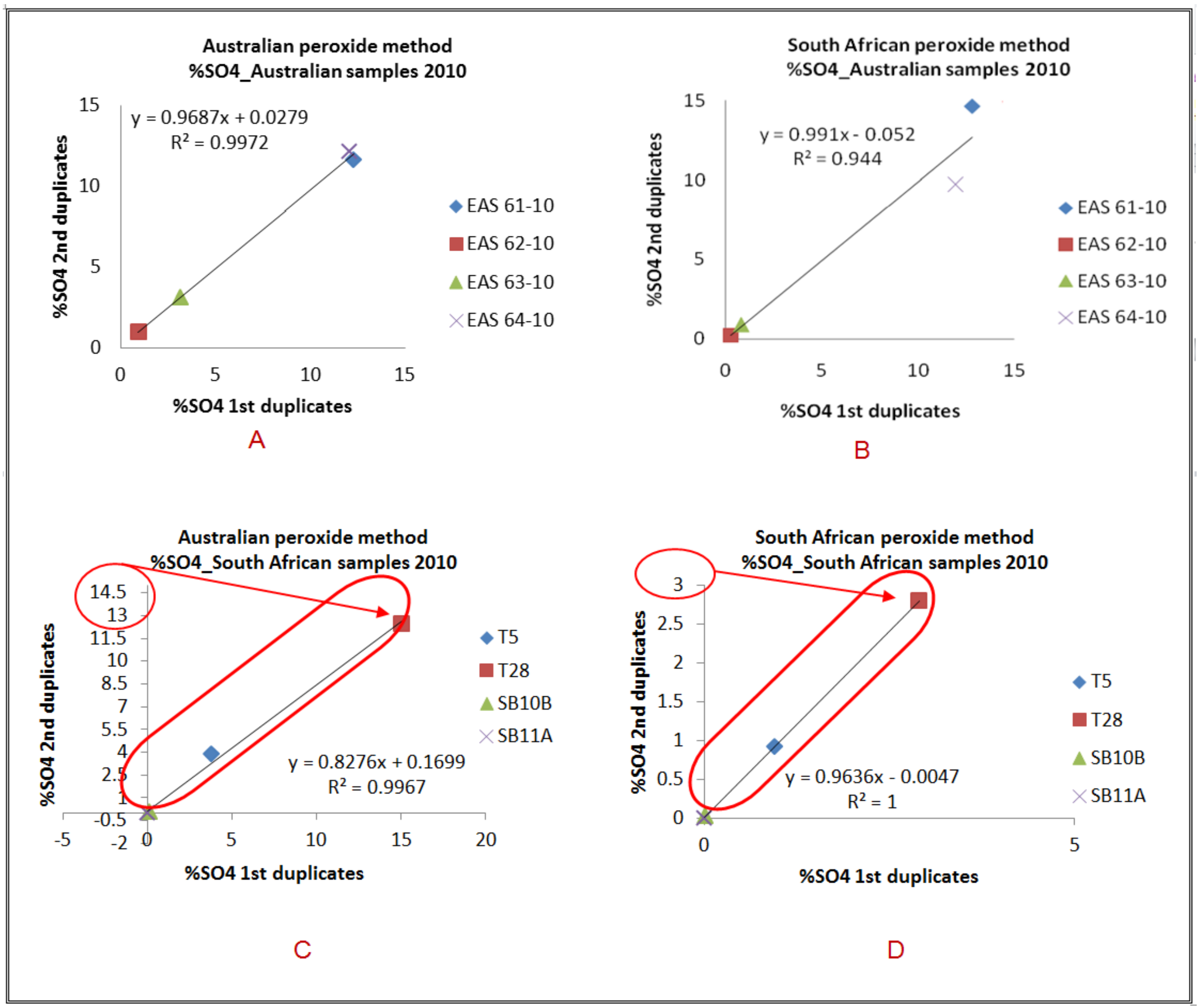


Figure 3-14 %SO_4 precision/accuracy of the peroxide methods (2010).

EAS 63-10 in Australian versus the South African method in Figure 3-15A and Figure 3-15 B show inconsistent percentage values which is interesting since that is the only sample in those figures that was subjected to carbonate modification. The trend seen in Figure 3-14C and Figure 3-14D is also evident in Figure 3-15C and Figure 3-15D. South African samples in both methods show more than double the amount of the South African value in the Australian methods with regards %Mg or %SO_4. In this case all the samples subjected to carbonate modification show a large variance in percentage values.

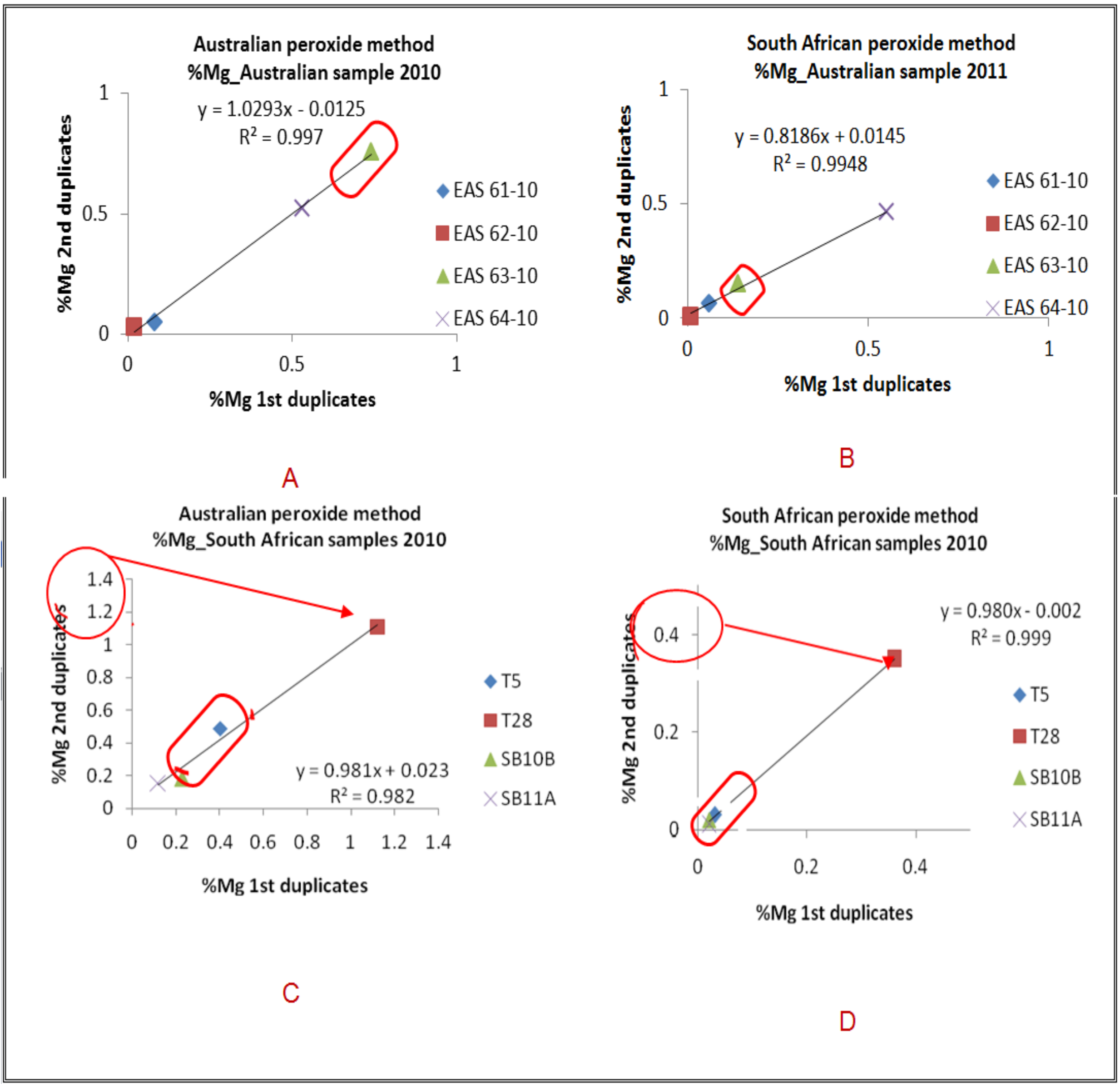


Figure 3-15 %Mg precision/accuracy of the peroxide methods (2010).

The overall %cation comparison of the peroxide methods is shown in Figure 3-16. Ca percentage values have a linear and a higher correlation with %Mg and SO_4% showing a very low correlation. %SO_4 showed the most erratic results and an unmistakeable non-linear relationship in Figure 3-16. The %SO_4 and %Mg is discussed in detail in the above figures.

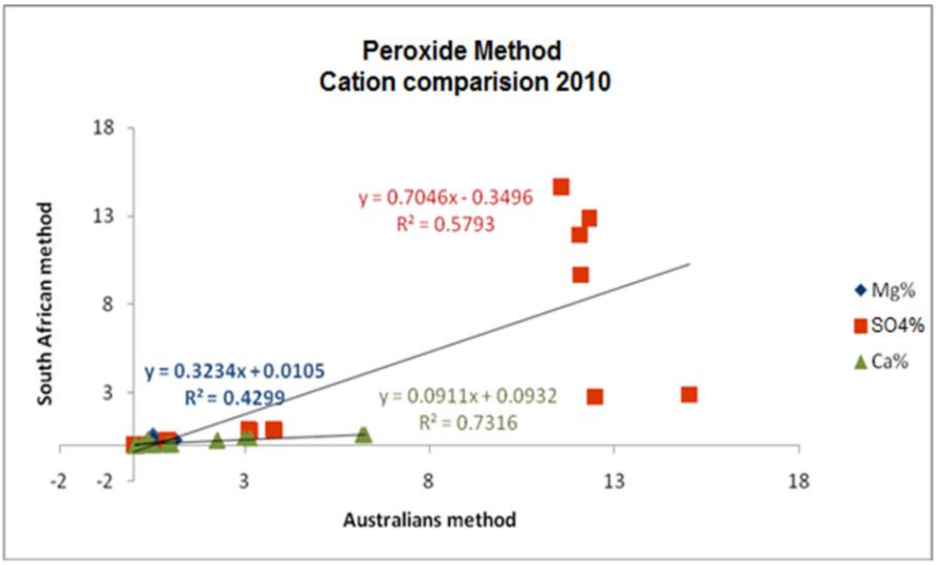


Figure 3-16 %Cation comparisons, peroxide methods (2010).

Comparison of the 2011 results

From the Australian peroxide guidelines in the year 2011, all of the South African samples had to be "treated" to carbonate modification along with one Australian sample (EAS 64-11 duplicates) because of their high pH even after peroxide digestion was done. According to the South African peroxide method, one South African sample (FEM duplicates) has a low risk of generating acid, one Australian sample (EAS 64-11) has no risk of generating acid and the rest have a high risk of generating acid.

Comparing the pH values (Figure 3-17) determined from both these methods a good correlation is observed.

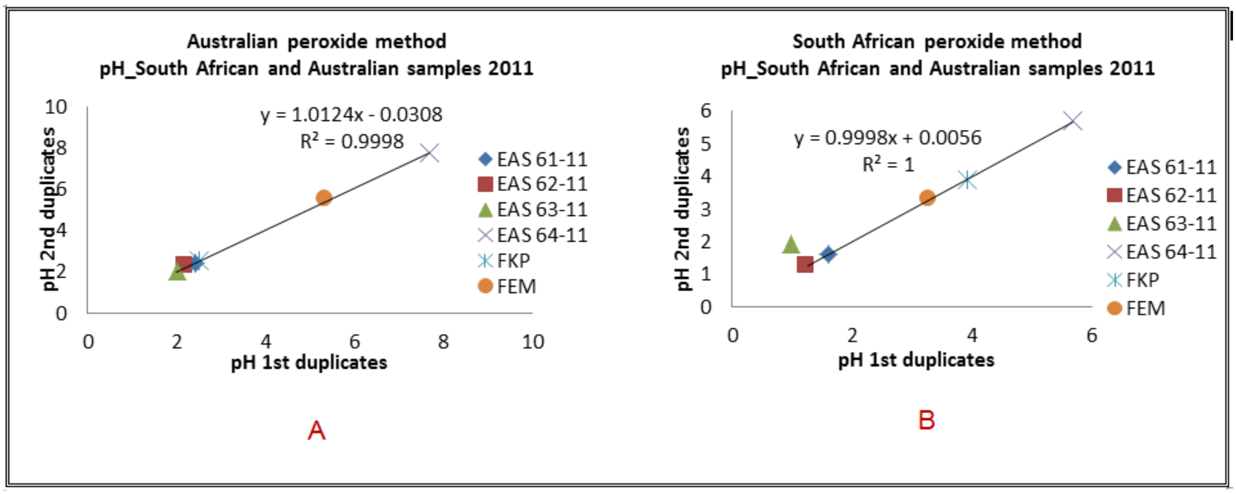


Figure 3-17 pH precision/accuracy of the peroxide methods (2011).

The correlation of pH, as already observed in Figure 3-17 is high and indicates that the pH values of the Australian methods are approximate to the South Africans. Although there is a non-linear relationship, similar pH values are evident in Figure 3-18. The correlation of pH is lower in the year 2011 compared to the 2010 results. FKP duplicate as shown in Figure 3-17 has different values in the South African peroxide method as compared to the Australian peroxide methods this causes the lower correlation viewed in Figure 3-18.

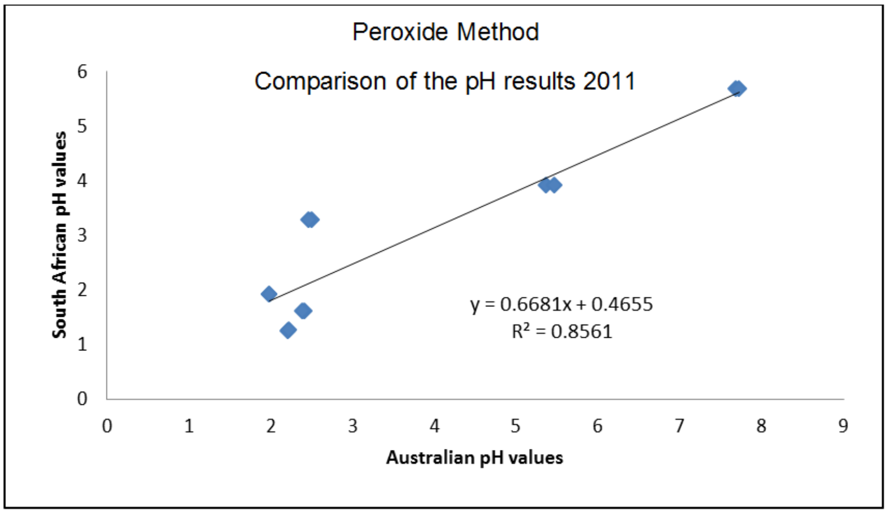


Figure 3-18 Comparison of pH results, peroxide methods (2011).

With the assumption that complete oxidation of pyrite occurred during the peroxide methods, calculation of the TPA (mol/t) were converted to kg SO_4/t (See Appendix 3) so that the results of the Australian peroxide method could be compared to the South African peroxide method. The EAS 63-11 duplicates results confirm the high SO_4 percentage with the high TPA and AP values. The high value was expected since the sample violently reacted when increments of peroxide was added. EAS 63-11 has the high TPA indicating that the sample has the potential to generate acidic conditions upon oxidation. The South African AP values were lower than the Australian methods except in the case of EAS 63-11, EAS 64-11 and FKP duplicates. It is unclear if distinction was because of the carbonate modification step since only EAS 64-11 was subjected to the step.

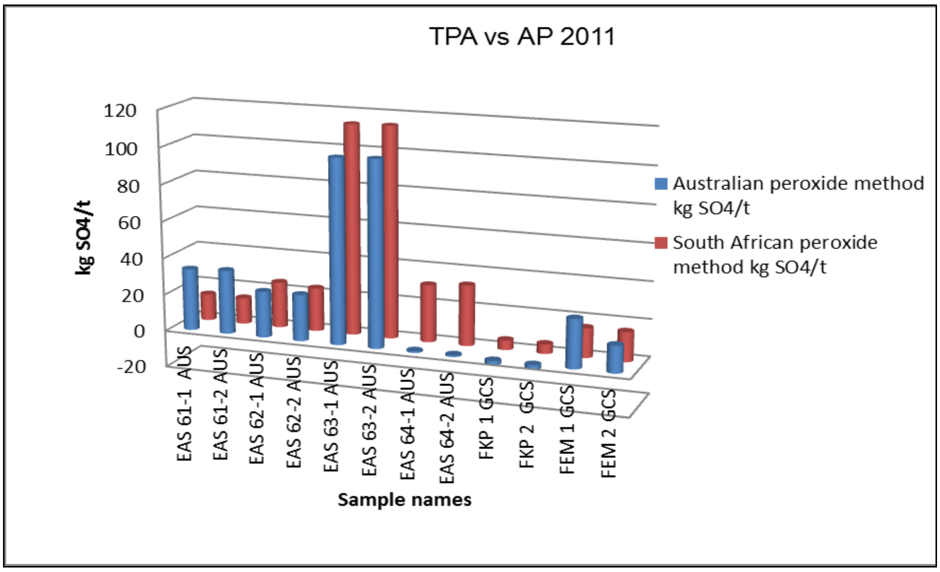


Figure 3-19 Titratable Potential Acidity versus Acid Potential 2011.

FKP duplicates in Figure 3-20A and Figure 3-20B show inconsistent percentage values. It is the only sample that has more than double the value in the South African methods compared to the Australian methods. Figure 3-20A has a linear relationship and a higher correlation value as compared to Figure 3-20B. Once again the differences are circled with red.

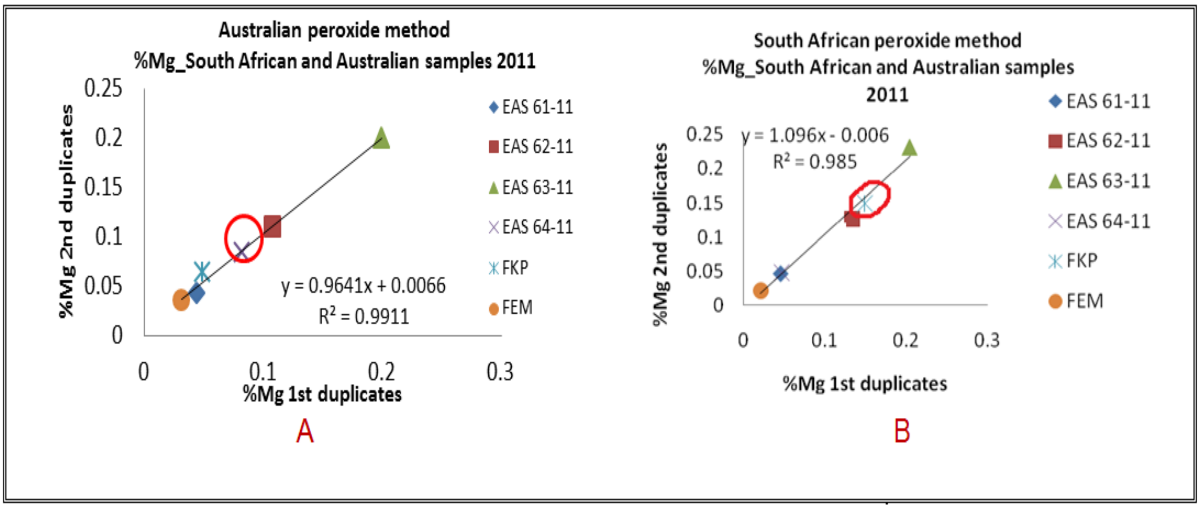


Figure 3-20 %Mg precision/accuracy of the peroxide method (2011).

All the graphs in Figure 3-21 show a correlation greater than 0.95 therefore the duplicates values are consistent in South African and Australian peroxide methods. The South African method in Figure 3-21B shows a lower correlation of 0.999 that is higher than the Australian method (0.987) in Figure 3-21A.

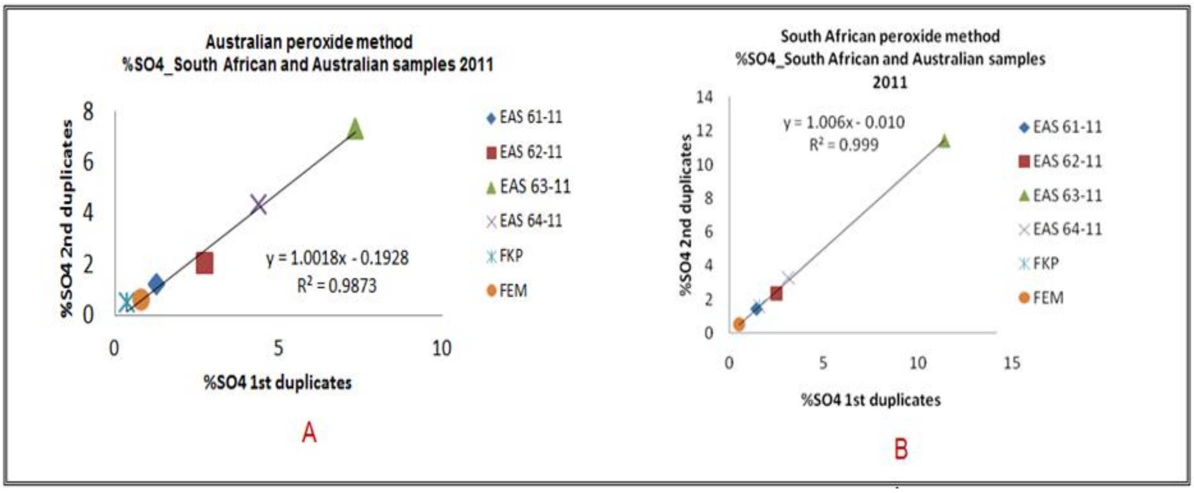


Figure 3-21 %SO4 precision/accuracy of the peroxide method (2011).

The overall %cation comparison of the peroxide methods is shown in Figure 3-22. %Ca values have a linear and a higher correlation with %Mg and SO_4% showing a very low correlation. %SO_4 showed the most erratic results and an unmistakable non-linear relationship in Figure 3-22. The %SO_4 and %Mg is discussed in detail in the above figures. A similar trend was observed in the year 2010.

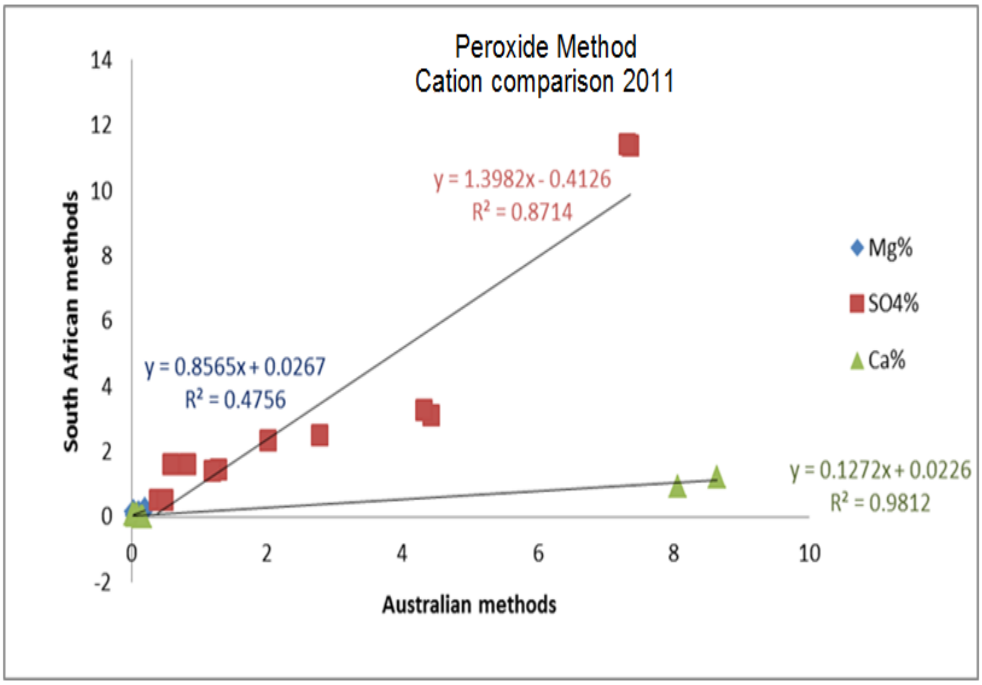


Figure 3-22 %Cation comparisons, peroxide method (2011).

3.3.3 Neutralising potential method

This method is used to calculate the buffering ability of the sample to see if it is capable of resisting the lowering of the pH. However, it is important to emphasise that the presence of carbonates, in excess of the potential acidity, will not necessary mean that the buffering ability is not readily or rapidly available because of the assumptions of the experiments and the samples are pulverised. Formation of insoluble or sparingly soluble surface coatings can limit the neutralising potential and reactivity of the Calcium Carbonate (McElnea et. al., 2004b). The correct conventional way to report the acid neutralising capacity is to convert it to %$CaCO_3$ equivalent. The reason for this is $CaCO_3$ is commonly used as a source of neutralising acidic conditions.

Comparison of the 2010 results

The Australian Neutralising potential method show 3 Australian samples with no buffering capacity (negative values in Figure 3-23). The EAS 63-10 has a higher percentage and this is proven by the alkaline pH it showed during the KCL method and the peroxide method. EAS 63-10 was also subjected to carbonate modification and had a higher excess acid neutralising capacity (See Appendix 3) and all the samples that went through carbonate modification have a higher percentage of the $CaCO_3$. The Australian methods require references samples and they should yield 100% CaCO3 equivalent; however the values showed an average of 8.83%. Errors might be sourced from the grade of the $CaCO_3$ used, analytical or systematic errors. Figure 3-23A shows negative values while and Figure 3-23B shows values above 2 percent. The negative values are seen with samples that were not subjected to carbonate modification. This proves that the samples that was subjected to carbonated modification by titration of HCL and had a high alkaline pH after peroxide digestion had excess carbonate which may have interfered with the efficiency of the oxidation.

With the South African Neutralising method, samples that had alkaline initial and final pH higher than 5 had a base potential however some of them seem to not have sufficient buffering capacity in a closed system.

The South African samples seem to have a higher neutralising potential in both the Australian and South African methods. The South African method shows a linear relationship with a higher correlation than that of the Australian neutralising potential method. Figure 3-23C and Figure 3-23D show a high correlation and a similar trend of results even when the percentage values are not approximate.

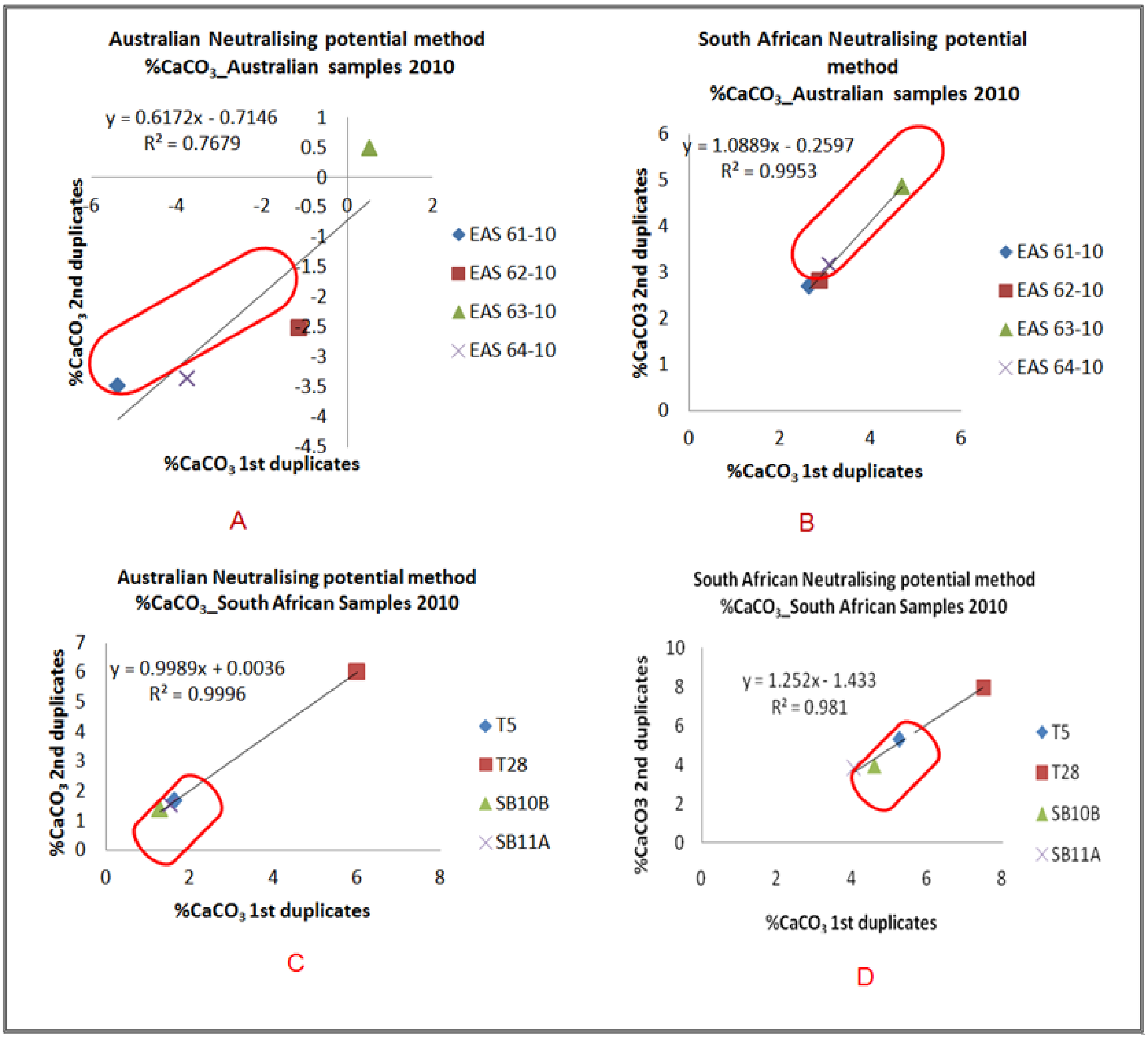


Figure 3-23 %CaCO3 precision/accuracy of the Neutralising potential methods (2010).

Negative values in the following figure (Figure 3-24) indicate that there is no neutralising capacity. The correlation of the CaCO$_3$ is not satisfactory but high and samples values seem to be erratic. The correlation of the two methods proves that there might be a good relation of the methods compared.

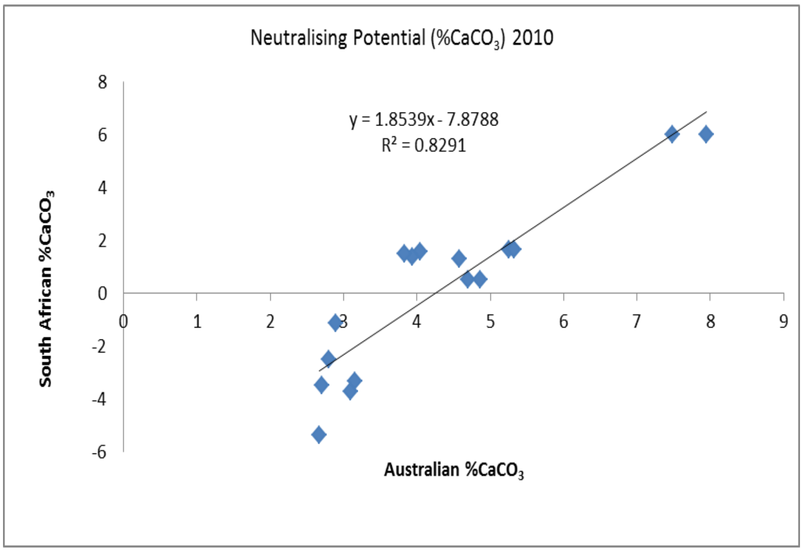


Figure 3-24 Comparison of %CaCO$_{3,}$ Neutralising potential methods (2010).

Comparison of the 2011 results

The Australian Neutralising potential method show 3 Australian samples with no buffering capacity (negative values in Figure 3-25). The EAS 64-11 has a higher percentage and this is proven by the alkaline pH it showed during the KCl method and the peroxide method. EAS 63-11 was also subjected to carbonate modification and had a higher excess acid neutralising capacity (See Appendix 3) and all the samples that went through carbonate modification have a higher percentage of the CaCO$_3$. The Australian methods require references samples and they should yield values of 100% CaCO$_3$ equivalent; however the values showed an average of 161.48% through calculations (See Appendix 3). Errors might be sourced from the grade of the CaCO$_3$ used and/or the time and temperature at which the CaCO$_3$ was dried prior to use.

Figure 3-25A shows negative values while and Figure 3-25B shows values above 3 percentage. The Australian method show that EAS 64-11 has the highest neutralising potential proving the sample had excess carbonate which could interfere with the efficiency of the oxidation.

The South African method has a low correlation and a non-linear relationship showing that the duplicates results accuracy is low.

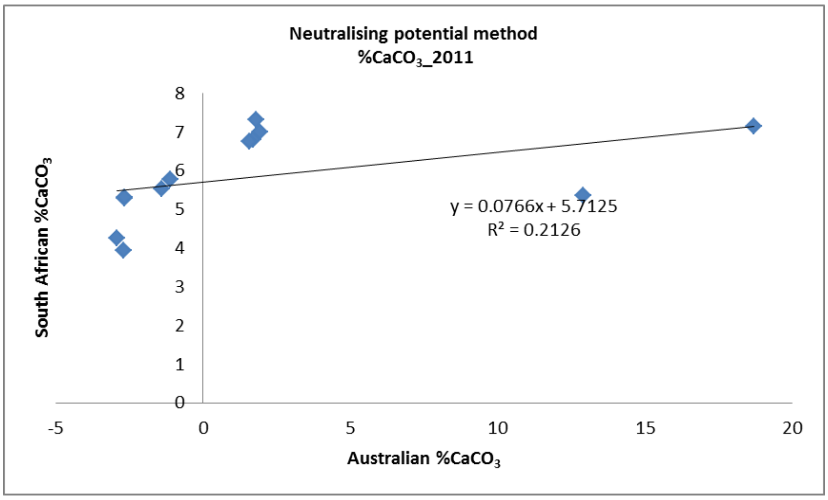


Figure 3-25 CaCO3 precision/accuracy of the Neutralising potential methods (2011).

The correlation is not satisfactory and the %$CaCO_3$ (Figure 3-26) values are erratic. The comparison between the two methods is in question as the correlation in 2010 is very high compared to the correlation obtained in 2011.

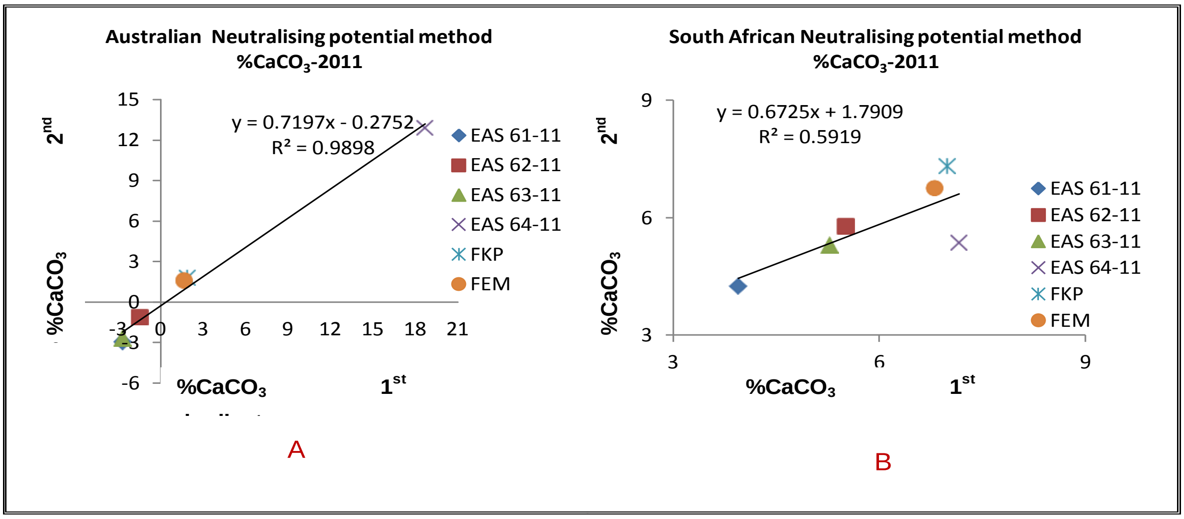


Figure 3-26 Comparison of %$CaCO_3$, Neutralising potential methods (2011).

3.4 Conclusion and Recommendations on Chapter 3

- The South Africa Actual Acidity method compared to the Australian showed that pH correlation was good even though the percentages of cations are not identical to each other but approximate. In 2011 %Ca had a low correlation as compared to the year 2010; however the %Ca consistency graphs in 2010 and 2011 showed erratic values. The erratic values are evident in the samples that were subjected to NaOH titration and these samples yielded half the values of the

South African %Ca. When the pH is high and the sample is not subjected to NaOH titration, the %Ca values of the Australian methods are double the %Ca values of the South African methods therefore the Australian method might be misleading with the %Ca results. The comparison range of %Mg is low whereas the range of $\%SO_4$ is highest.

- Australia's versus the South African peroxide method show a very good pH correlation but in the year 2010, the Mg and SO_4 percentage correlation was poor. The South African methods have a higher correlation compared to the Australian methods. It is unclear if the carbonate modification step has an influence on the result variance; since in the year 2010 the South African samples that were subjected to carbonate modification showed more than double the amount of the South African value in the Australian methods with regards $\%SO_4$ and %Mg. However, the 2011 samples that went through carbonate modification only have at least 2 units in variance.

- In the Actual and Peroxide acidity methods, Australia's results show that the %Ca or Carbonate modification has a significant role in the erratic values evident when comparing to the South Africa's methods.

- The Australia's neutralising potential method is derived from lime analysis disciplines and can be an overestimate of the neutralising capacity. When Australia's neutralising potential method was compared to the South African method, the hypothesis whether the methods are comparable or not was inconclusive. Recommendation to this uncertainty is performing tests on the same samples to verify if personal, analytical or instrumental error was significant.

- To omit re-occurring errors and to conclude whether the Australian methods and South African methods yield the same values, samples should be repeated by two different personnel and compared to the results in this chapter.

During the Precambrian era, South Africa and Australia had gold (pyrite associated) and other sulphide-bearing minerals such as banded iron formation and uranium deposited. Therefore both countries show a geological history of the formation of sulphide-bearing minerals that causes AMD and/or ASS. Despite similar geological history, different ABA methodologies are used to analysis the environmental impact of sulphide-bearing minerals. The analysis done in this chapter to determine why Australia uses different methodologies shows there are similarities in the results but are not necessarily applicable to South Africa’s geology because of the expense of extra reagents used, overestimate/underestimates of the sample’s effective Acid Neutralising Capacity (ANC) and the fact that Australia geology was waterlogged (Steyl, 2010). Furthermore, Chapter 4 uses only South African methods for the Middelburg area case study since it is more logical to use. The South African Static methods used in this chapter is explained in detail in Chapter 4 and the output of results is made simpler to read. Kinetic methods are also used to determine the metal load in the investigated area over extended period of time.

Chapter 4

Due to the location and the number of coal mines in the upper Olifants River catchment, Witbank dam was the first to suffer mining related impacts but recently the Middelburg dam has attracted attention from the water, environmental and mining regulators as well (Usher et al., 2003). The community would ask why the operations are not stopped or decreased if they pose huge environmental threats but the important question is how will this be done if the socio-economic development of the upper catchment is interdependent on coal mining, farming, power generation, metallurgic industries and eco-tourism? The options to be strongly considered are simply prevention and remediation.

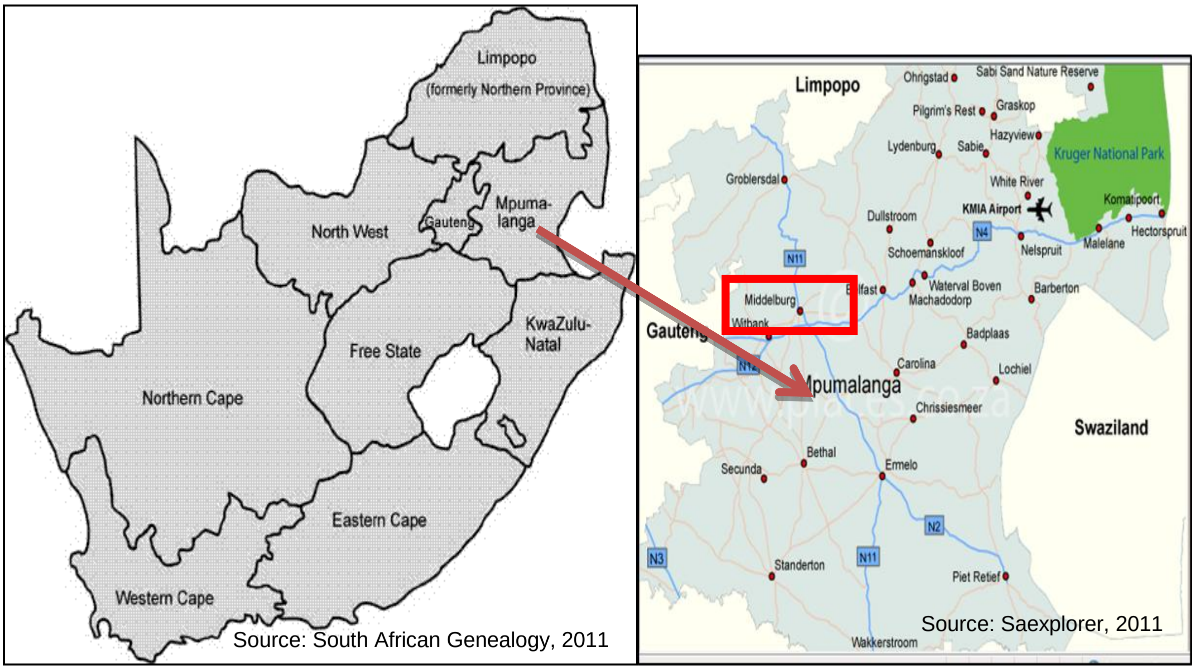
4. Case study: Prediction of AMD in the Middelburg area

The Institute for Groundwater Studies (IGS) was approached by Middelburg mine services to update the 2006 groundwater model at Goedehoop, Hartebeesfontein, Bankfontein and Klipfontein Collieries and at a later stage, Acid-Base Accounting (ABA) methods were requested. The aim of the project was to do groundwater assessment of the collieries and predict future impacts of AMD. The project had various stages that entailed the review of the initial assessment, development of numerical groundwater flow model, mineralogical analyses, static and kinetic tests.

The geochemical modeling was done by senior personnel at the IGS department therefore this chapter emphasis on the South African static and kinetic analysis (the Australian methods are not performed on these samples).

4.1 Locality of the Study Area

The locality of the investigated area is in the Middelburg area which falls in the central Highveld of the Mpumalanga province in South Africa (Figure 4-1).

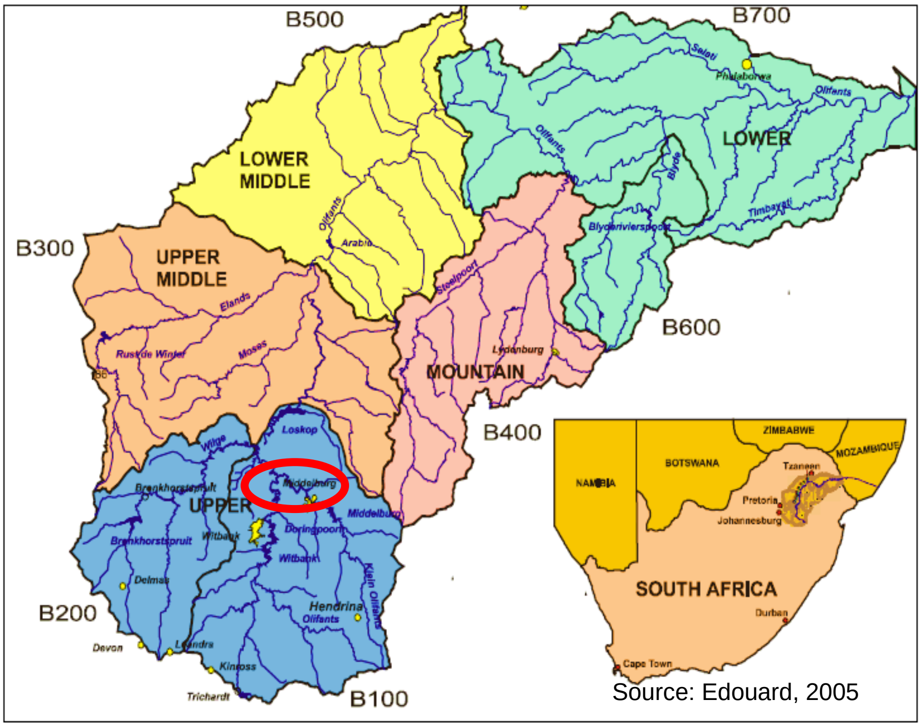

Limpopo
(formerly Northern Province)
North West
Gauteng
Mpuma-
langa
KwaZulu-
Natal
Free State
Northern Cape
Eastern Cape
Western Cape
Limpopo
Ohrigstad
Sabi Sand Nature Reserve
Pilgrim's Rest
Graskop
Hazyview
Lydenburg
Sabie
Kruger National Park
Groblersdal
White River
KMIA Airport
Komatipoort
Dullstroom
N4
Hectorspruit
Malelane
Nelspruit
Schoemanskloof
N11
Belfast
Waterval Boven
Machadodorp
Barberton
Middelburg
Witbank
Gauteng
Badplaas
N12
Carolina
Lochiel
Mpumalanga
Chrissiesmeer
Swaziland
Bethal
Secunda
Ermelo
N2
N3
Standerton
N11
Piet Retief
Wakkerstroom

Source: South African Genealogy, 2011

Source: Saexplorer, 2011

Figure 4-1 Locality of the study area (Mpumalanga province: Middelburg).

The Olifants River Catchment is situated in the north east of South Africa with upper streams that drain into the Witbank and Middelburg Highveld regions (Aston, 2000). Middelburg area is part of Olifants River Catchment in the secondary catchment named B100 (Figure 4-2). This project is based at the Open-cast coal mining in Klipfontein, Hartebeesfontein and Goedehoop. Klipfontein is along south of the Vaalbankspruit while Hartebeesfontein and Goedehoop spreads north of the Spookspruit. Figure 4-3 shows surface hydrology and the current mining operations at the investigated area. The area is located in the Karoo Supergroup (Figure 4-13) which underlines more than half of the total area of the Republic of Africa with typical rocks like sandstone, mudstone and shale.


B500
B700
B300
B600
B400
B200
B100
LOWER MIDDLE
UPPER MIDDLE
LOWER
MOUNTAIN
UPPER
Selati
Phalaborwa
Olifants
Birds
Timbavati
Blyderivierspoort
Steelpoort
Lydenburg
Arabie
Elands
Rust de Winter
Moses
Loskop
Wilge
Bronkhorstspruit
Middelburg
Doringpoort
Witbank
Delmas
Hendrina
Klein Olifants
Devon
Leandra
Kinross
Trichardt
ZIMBABWE
MOZAMBIQUE
BOTSWANA
NAMIBIA
Tzaneen
Pretoria
Johannesburg
SOUTH AFRICA
Durban
Cape Town

Source: Edouard, 2005

Figure 4-2 Catchment map showing that the study area falls under the B100.

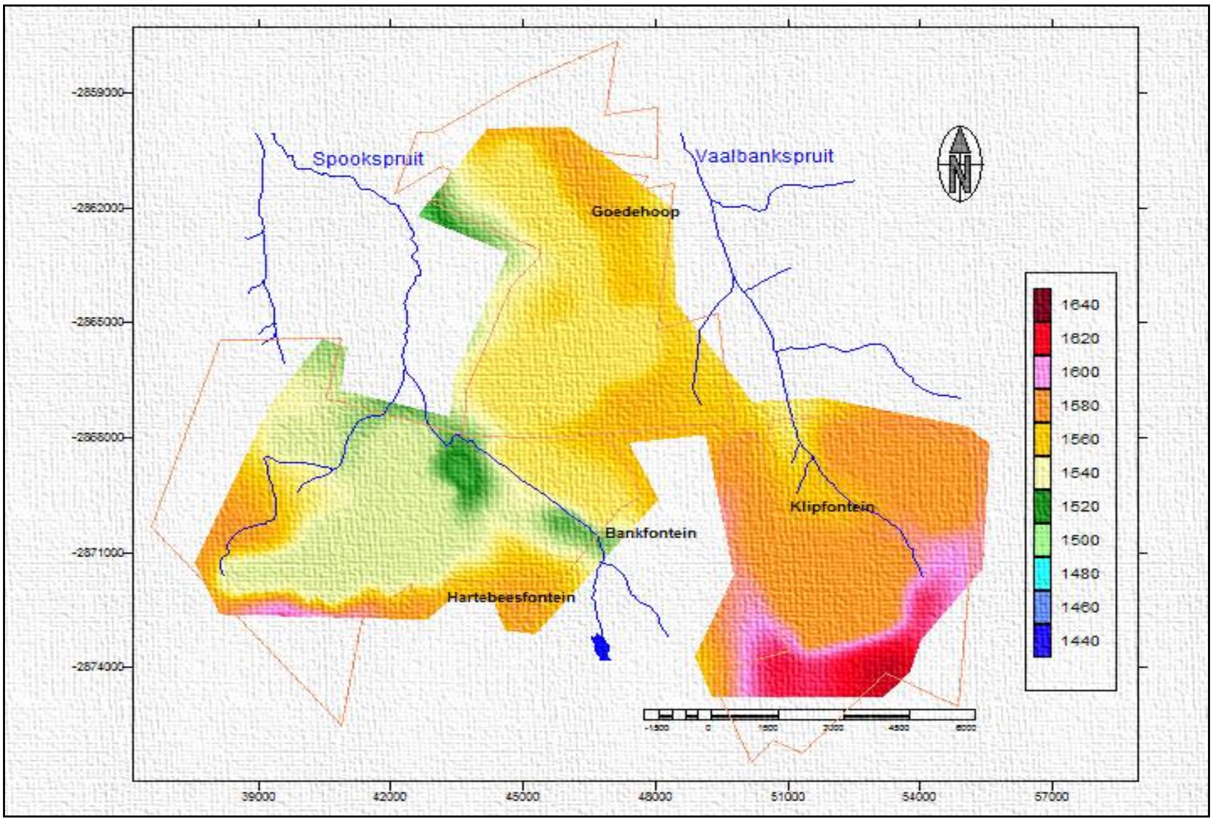

Spookspruit
Vaalbankspruit
N
Goedehoop
Bankfontein
Klipfontein
Hartebeesfontein
-2859000
-2862000
-2865000
-2868000
-2871000
-2874000
39000
42000
45000
48000
51000
54000
57000
1640
1620
1600
1580
1560
1540
1520
1500
1480
1460
1440
-1500
0
1500
3000
4500
6000

Figure 4-3 Open cast mining at the Middelburg North mines.

4.2 Objectives

The scope of investigation is a geochemical investigation and evaluation of the status quo at the Middleburg North mines by identification of soluble metals, mobile metals, prediction of the maximum metal concentration and the maximum metal loadings with respect to time. Therefore the objective of this case study is to predict and evaluate the current and future production of AMD in the Middelburg area.

4.3 Methodology

To understand the production of acid mine drainage and potential salt loads, laboratory methods such as ABA are used to predict the potential of AMD or acid generation. ABA is a procedure that predicts acid-neutralising potential, acid-generating potential of soil/rock samples and the net neutralising potential.

ABA therefore helps with the identification of: metal carbonates, metal sulphate, metal hydroxide and dissolved ions (acidity and carbonate minerals) in the geology/soil.

To achieve this, the following where performed:

- Kinetic and static tests are used for laboratory analysis.
- Software ABACUS developed by Usher (2003) is used for the output of the results and easy interpretation.
- WISH developed by E. Lukas is used for the maps showing location of the samples and chemistry illustrations.

4.3.1 Sampling

Sampling points are indicated in (Figure 4-4) where a total of 127 samples were collected for ABA analysis. The number of samples taken from Hartebeesfontein was 24, Goedehoop 44, Klipfontein North 10, Klipfontein South 28, Slurry ponds 10 and discard dumps 7 samples. The samples were dried, coned, quartered, milled and pulverised.

An additional 14 borehole samples and 8 final voids (referred to as pits in this chapter) were taken for water quality assessment.

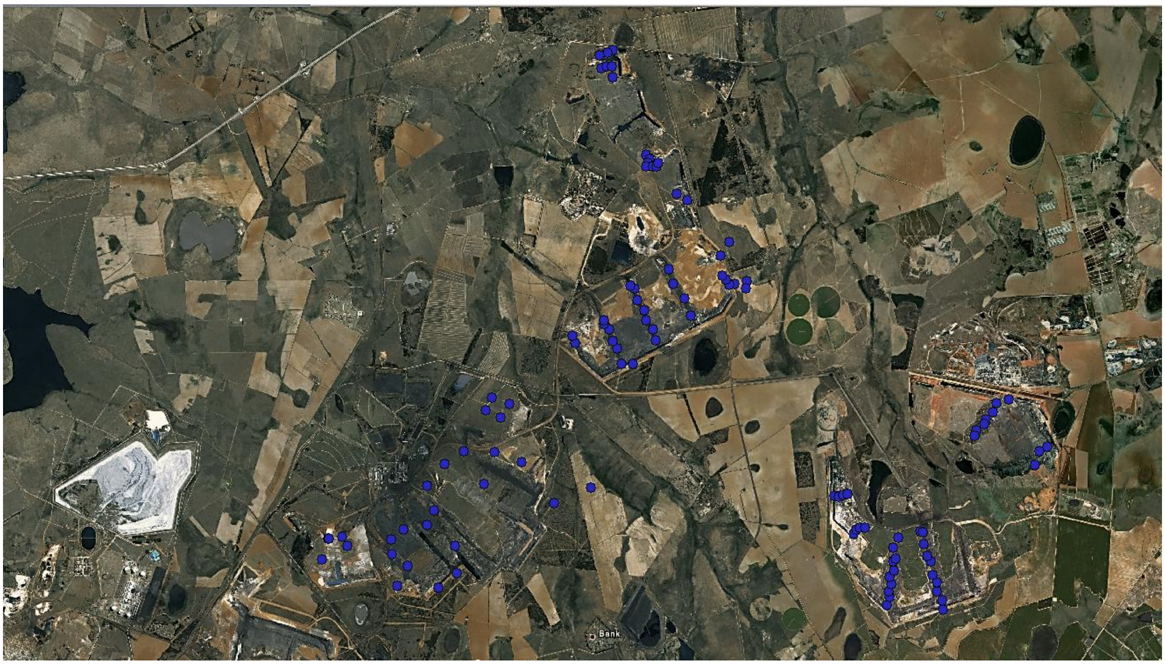


Figure 4-4 Sampling points of the Middelburg AMD Case Study.

4.3.2 Static tests

Static tests are the analytical tests used as a screening criterion of the samples; used to determine the difference between the acid-generating capability and the acid-neutralising potential of the samples. They provide the worst and the best case scenario of the current and potential AMD generation. The limitations of these tests is that the reaction rates are not considered, an assumption that reactive species are available instantly is made and that the extrapolation to the field is not accurate since the results are obtained from pulverised samples. The advantages of these test is that the turn-around time for the results is relatively short, economically viable for the company concerned and the analytical procedures are simple (Usher *et al*., 2003).

To simplify the interpretation of the static test results, the following categories are defined:

- Actual Acidity
- Potential Acidity
- NAG test
- Neutralising/ Base potential (CaCO3 kg/t)
- Net Neutralizing potential
- Net Potential Ratios (NPR)
- %S and NPR reporting

Actual Acidity

This method (also referred to as the paste pH method) was done with the addition of water to the sample and then taken to ICP analysis for major element concentration. The results obtained provides the current state of the sample and the pH recording is informative of whether the sample is already acidic on not.

Potential Acidity

Potential Acidity methodology subjects a sample to peroxide digestion and then ICP analysis for major element concentration. The higher the sulphur content of the sample, the violently it will react with the peroxide. Darker samples are known to have higher sulphate content and a smaller amount of sample mass is often used to avoid loss of a sample during the peroxide reaction.

$$\text{Acid open (AP } CaCO_3 \text{ kg/t)} = ((\text{kg } SO_4/\text{t})*50)/48$$

$$\text{Acid closed} = \text{Acid open} *2$$

Equation 4-1 Acid potential.

The sulphate content is also important in this method as it is used to calculate the acid potential (Equation 4-1) of the sample. Acid potential is then achieved by multiplying the percentage of sulphur with 31.25 (Usher *et al*., 2003). That multiplication is derived from taking into account the volume of the peroxide used and the weight of the sample. The difference between open and closed system is discussed under the Neutralising/ Base potential (CaCO3 kg/t) section.

NAG test

The pH value from the potential acidity method is used to do the NAG test. pH's are categorized into three groups to determine the sample's potential acid generation. The Net Acid Generating (NAG) test is used to categorise (Table 4-1) samples and should not be used alone as a criteria for acid generating samples. The reason for pH higher than 5.5 not being acidic is due to an average pH value (5.9) of deionised water in equilibrium with CO_2.

Table 4-1 Rough guidelines for categorizing samples (Price *et al.,* 1997).

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

Neutralising/ Base potential ($CaCO_3$ kg/t)

$$\text{Base potential (NP)} = CaCO_3\ \text{kg/t} = (\text{N } H_2SO_4 * \text{ml acid}) - (\text{N NaOH} * \text{ml alkali/weight (g)} * 50)$$

Equation 4-2 Base potential.

The Neutralising potential method indicates the buffering capacity of the sample and also referred to as the base potential of the sample. Since H_2SO_4 is present in the expected AMD environment, it is only logic to use it to acidify the samples to a pH value of 2 then back-titrated to a neutral pH (7) with NaOH. This is done to test the ability of the sample to consume acid. The higher the volume of NaOH added to the sample the less neutralising potential it will have should the sample acidify in the field. Therefore to attain a result that is equivalent to kg/t of $CaCO_3$, the normality of the acid (H_2SO_4) and base (NaOH) are taken into account along with the volumes used and the mass of the sample (Equation 4-2).

$$\text{NNP open} = \text{Base (NP)} - \text{Acid open (AP)}$$

Equation 4-3 Net Neutralising Potential open (NNP).

$$\text{NNP closed} = \text{Base (NP)} - \text{Acid open (AP*2)}$$

Equation 4-4 Net Neutralising Potential closed (NNP).

It is important to differentiate between “**open**” (NNP open) and “**closed**” (NNP closed) systems when interpreting the results. The difference between the two systems is because of the transfer of carbon among solid, liquid and gas phases.

The open system is based on 1 mole of FeS_2 (64 g sulphur) neutralised by 2 moles of $CaCO_3$ (200 g) and in the closed system, 1 mole of FeS_2 neutralised by 4 moles of $CaCO_3$ (that is why we multiply the AP by 2). The open system (Equation 4-3) in the field would be for example the waste rock pile while tailings vary from open and closed systems (Equation 4-4). The negative values indicate that there is insufficient neutralising capacity of the sample (Usher *et al*., 2003).

Net Neutralizing potential

The difference of neutralising potential from the acid potential of a sample represents the net neutralising potential. The result is usually presented with the initial and final pH of the sample on a graph such as Figure 4-5 below. The values that are greater than zero on the x-axis are considered as samples with the potential to neutralize acid and the values that are smaller than zero the opposite. One of the relations between final pH (potential acidity) and NNP is when a negative NNP is portrayed the pH of the sample should also be low.

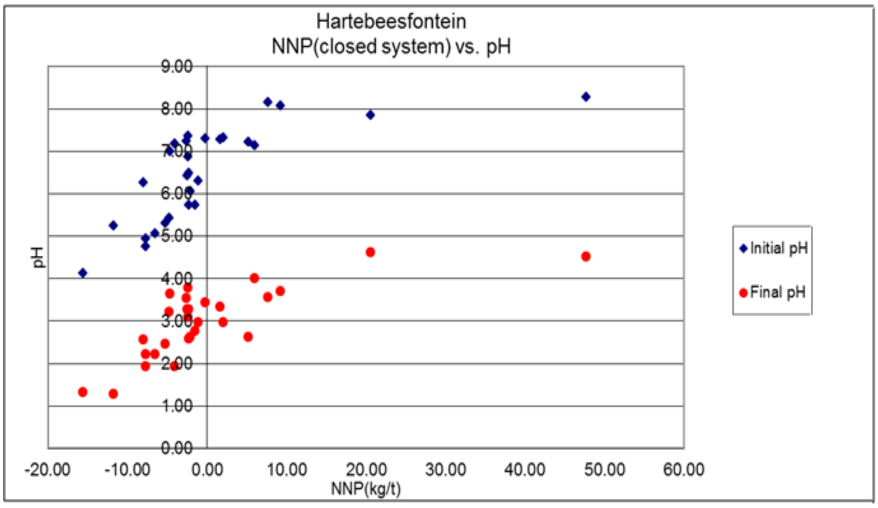


Figure 4-5 A graph example defining NNP.

Net Potential Ratios (NPR)

The guidelines (Table 4-2) are used to categorise the different acid-generation potential samples derived from the ratio of Acid potential (AP) and Neutralising potential (NP). This serves as a visual guide of acid generation probability of samples. The Figure 4-6 shows an output from ABACUS as an example of the Net Neutralising Ratio.

Table 4-2 Guidelines for ABA screening criteria (Price *et al.*, 1997).

ARD POTENTIAL	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 samples plotted (Figure 4-6) are both from the open and closed system scenario. Open system is shown with the blue dot while the pink one represents samples in a closed system. The samples above the red line show that acidification of the sample is likely to occur and the samples under the green line represent samples that are unlikely to have the potential to generate acid. Therefore, naturally if the NP has a higher value than the AP it is unlikely that the sample will generate acidic conditions.

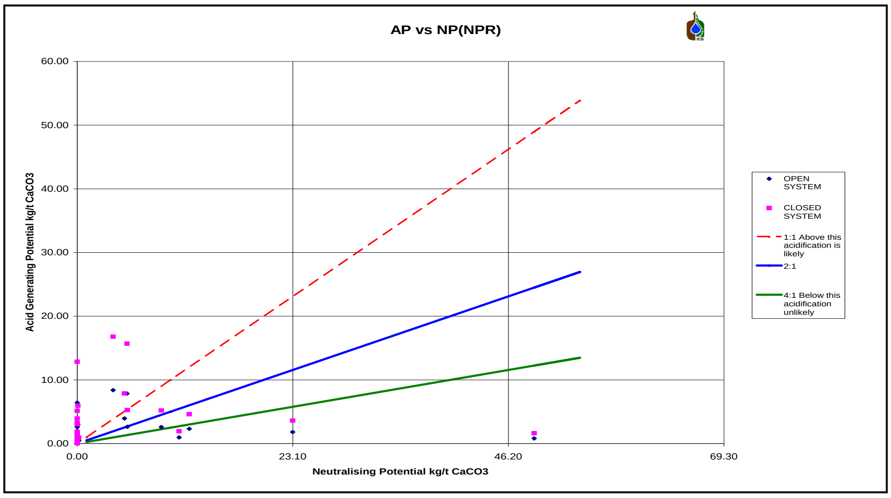


Figure 4-6 An example of a graph showing the categories of NPR.

%S and NPR reporting

This visual interpretation of the results is based on a set of rules pertaining to the sustainable long-term generation of acid such as a certain percentage of Sulphur (0.3 %) and the Net Neutralising Potential (NPR).

The red area shows NPR values below a ratio of 1:1 and sulphide values that have a percentage higher than 0.3 %. The blues dots represent the samples analysed. Any samples under the red area (Figure 4-7) have a high probability of sustaining sulphur. Samples that are considered inconclusive have an NPR value of 3:1 to 1:1. The samples in a blue have a high enough neutralising capability while the ones in the green area have a very low probability of acidifying. Very high sulphide values would plot in the white area when the sample also has a very high neutralising potential.

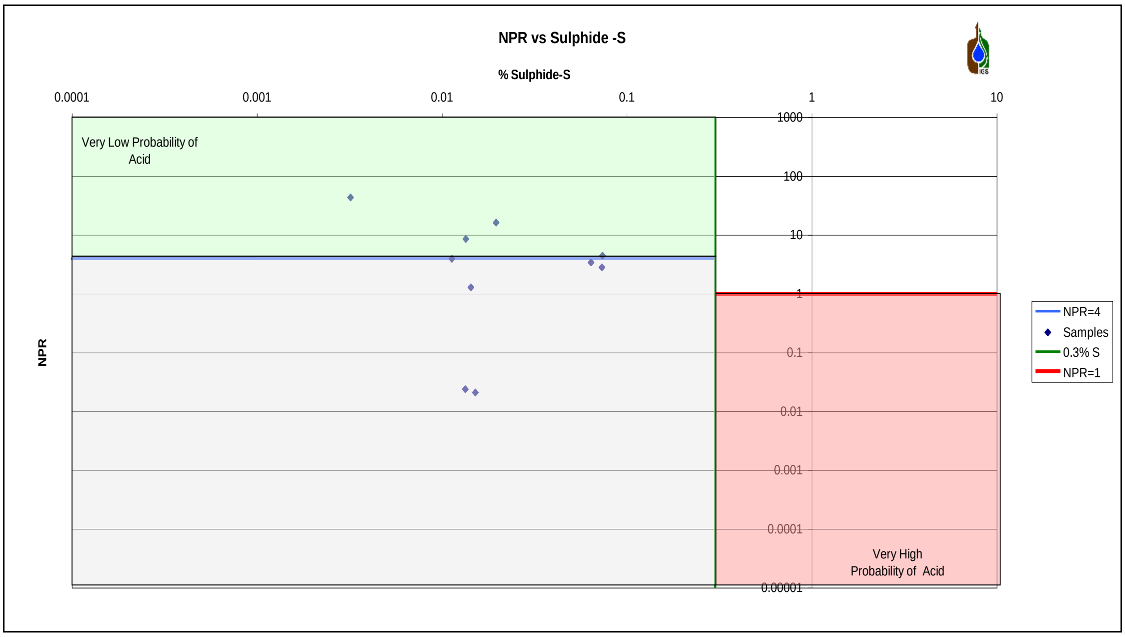


Figure 4-7 A graphical example of the NPR vs. % S.

4.3.3 Kinetic tests

The kinetics tests are used to define acid generation characteristics whereby the samples leachate is measured with respect to time (i.e. Humidity cells, field tests, column tests etc).

Humidity Cells were used in this case study to simulate accelerated weathering of samples. Not all samples collected from the study area were used for the kinetic test, samples that showed uncertain or erratic results in static tests were chosen for these tests. ASTM Standards (1996) suggest that the kinetic tests be done for 20 weeks minimum but this case study carried on with the pH and EC evaluation for a period of 20 additional weeks. The EC results are represented in Appendix 5.

Figure 4-8 shows the work station of this project. A cylinder fitted with a perforated base plate was filled with a representative 1 kg of each sample and placed in temperature controlled room. The temperature was kept constant at 30 degree Celsius since the optimal temperature for the *Thiobacillus* bacteria is 30 degrees (Usher *et al*., 2003). Drain hole tubing was inserted so that the weekly leachate is collected into the 1 litre bottle efficiently. Air supply used to mimic the conditions in the field would be changed from dry to humid air using the humidifier and an electric air pump. The humidifier used was a 25 litre plastic container filled with distilled water and was regulated constant pressure. The cap of the plastic container had in- and outlet holes drilled to hole the aerator (tube from the electric pump to the container) and another tube that connects to the cylinders. Sealing of these areas were done by silicon so that significant amount of air pressure is not lost through leakage. The challenging factor about this test is the regulation of air supply to each cell because of the different grain size and material of the sample. A more calibrated supply of air was achieved by forming a “loop” (connected tubing) of air supply to the system, using in-line tabs and tight-fitting lids with tubing into separate water containers for efficient bubbling. Longer hours of the collection of leachate were spent on samples that had low permeability.

A weekly procedure referred to in this thesis as a **3-3-1** was followed to obtain metal leach rates and pH values. **3-3-1** procedure is a an episode of **3** day supply of dry air to the samples then **3** day supply of wet air, followed by **1** day of collecting leachate(sampling).

To collect leachate from the cylinders, the main air supply was shut down then the draining hole was clamped with a peg. 1 L of deionised was added to the cylinders and soaked for approximately for an hour. The peg was then removed to drain out the leachate from the humidity cells and collected for ICP, EC and pH analysis.

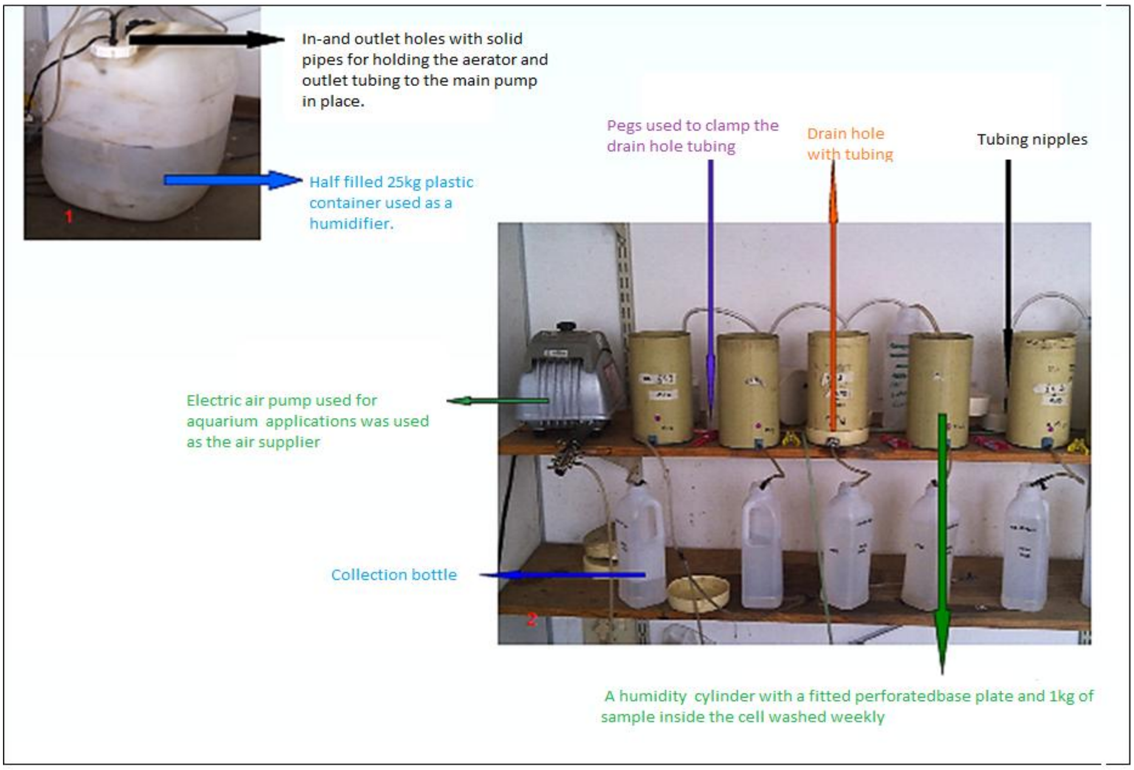

In-and outlet holes with solid pipes for holding the aerator and outlet tubing to the main pump in place.
Half filled 25kg plastic container used as a humidifier.
1
Pegs used to clamp the drain hole tubing
Drain hole with tubing
Tubing nipples
Electric air pump used for aquarium applications was used as the air supplier
Collection bottle
2
A humidity cylinder with a fitted perforatedbase plate and 1kg of sample inside the cell washed weekly

Figure 4-8 Components used in Kinetic testing for this case study.

4.3.4 The importance of pH in the prediction of AMD

pH is not necessarily a true indication of acidity nor a good determining with regards to AMD. pH measures the activity of hydrogen ions an intensity factor to gives us an indication of how much hydrogen ions are in excess over other ions to neutralize bases. This is referred to as total acidity $CaCO_3$ (often calculated in kg/t).

Despite the arguments about the role that pH plays in the acid mine drainage prediction results, a fairly good linear relationships between pH and the log of total acidity on the acid mine drainage water is evident (Figure 4-9). The values used are from the South African ABA methods in chapter 3 and are tabulated in Table 4-3.

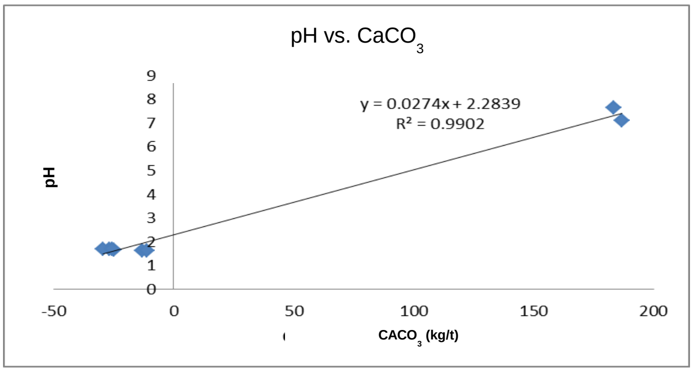


Figure 4-9 Correlation of pH with $CaCO_3$.

Table 4-3 Values used to verify that the pH is related to the buffering capacity of the sample.

Sample names	Lab names	pH	$CaCO_3$ kg/t		Duplicates Lab names	pH	$CaCO_3$ kg/t
EAS 61-11	EAS 61-1 AUS	1.7	-26.900215		EAS 61-2 AUS	1.71	-29.32735
EAS 62-11	EAS 62-1 AUS	1.64	-12.91855		EAS 62-2 AUS	1.64	-11.311855
EAS 63-11	EAS 63-1 AUS	1.67	-24.8833		EAS 63-2 AUS	1.7	-25.84048
EAS 64-11	EAS 64-1 AUS	7.12	186.766175		EAS 64-2 AUS	7.64	183.484415

Another reason why pH is important is because the lower the pH, the higher the probability for it to destroy the bicarbonate buffer system. Once the buffer system is destroyed, it would not regenerate without the addition of more buffer material (Kelly, 1988). With that in mind, once the pH reaches below 4.2 the carbonate and bicarbonates turn into carbonic acid (Kelly, 1988). For these reasons I therefore continued to pH recordings after the recommended ASTM standard time.

4.4 Overall climate

4.4.1 Temperature

Table 4-4 Temperature over the Middelburg area (Steve Tshwete Municipal, 2005).

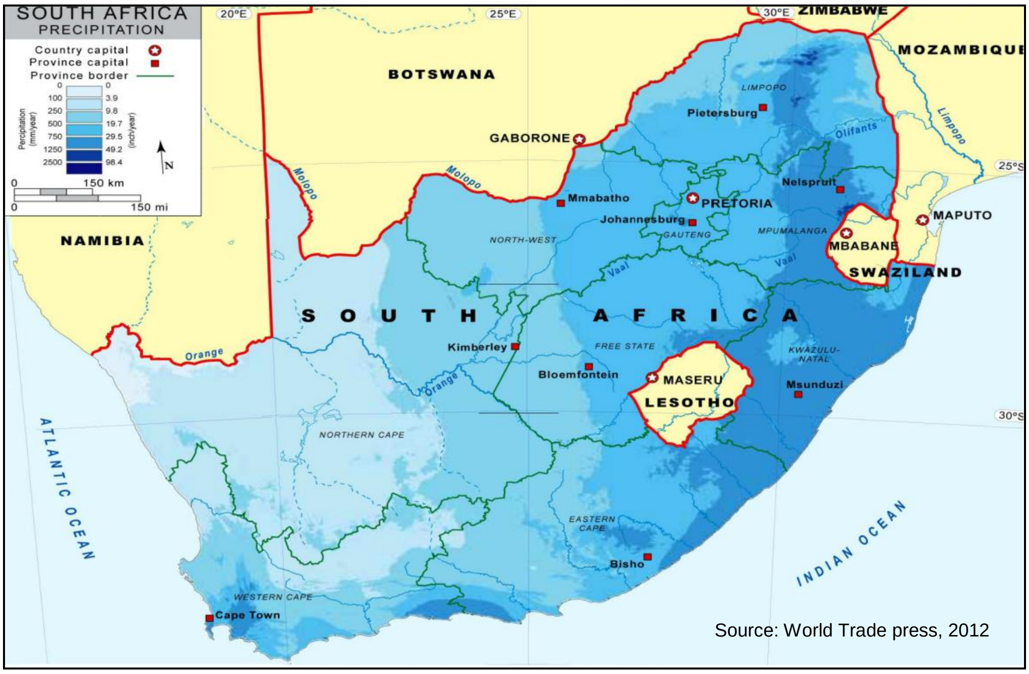
Averages	Dec, Jan, Feb	Mar	Apr	May	Jun, Jul, Aug	Sep	Oct	Nov
Temperature	23.6	21.8	18.9	16.0	14.3	18.9	21.9	22.6
Night Temperature	17.6	15.8	12.7	9.4	7.5	12.8	15.9	16.8
Day Temperature	29.6	27.8	25.1	22.6	21.1	25.0	27.9	28.4
Maximum Temperature	33.0	31.2	28.6	26.4	25	28.5	31.3	31.4
Minimum Temperature	14.2	12.4	9.2	5.6	3.6	9.5	12.4	13.5

Temperature is the highest during October, November, December, January and February in the Middelburg area (Table 4-4). The temperature at night and in winter months is not as high as the temperature during the day. It is important to consider the temperature of the investigated area so that the kinetic tests could mimic the field conditions as closely as possible and for the fact that some AMD generation factors are influenced by temperature. The ASTM method specifies that the humidifier temperature has to be between 28- 32 degree Celsius during the kinetic testing (ASTM, 1996). For this project an average of the 30 degree Celsius was used to receive optimum results.

4.4. 2 Precipitation

Most rainfall occurs during summer with an average midday temperature of 17.3 °C in June to 25.5 °C in January. The region is the coldest in July when the mercury drops to 2 °C on average during the night. It rains more in the summer months (October to April) than in the winter because air flows in from the Indian ocean during summer months, penetrates the interior and gives rise to rain and thunderstorm activity. In the winter months the high pressure systems causes an inversion layer that prevents air from reaching the interior, minimizing winter rainfall (Woodford *et al*., 2002). The mean annual precipitation for the Middelburg area varies from 500mm – 700mm (Figure 4-10).

Recharge in the study area has average assumption of 16 %. This assumption was made from the last model done by the IGS. In the year 2011 IGS reported the recharge of undisturbed aquifer formations between 1.5 % and 3% and for the rehabilated open cast the range was between 10 and 17 % (Vermeulen *et al.*, 2011).

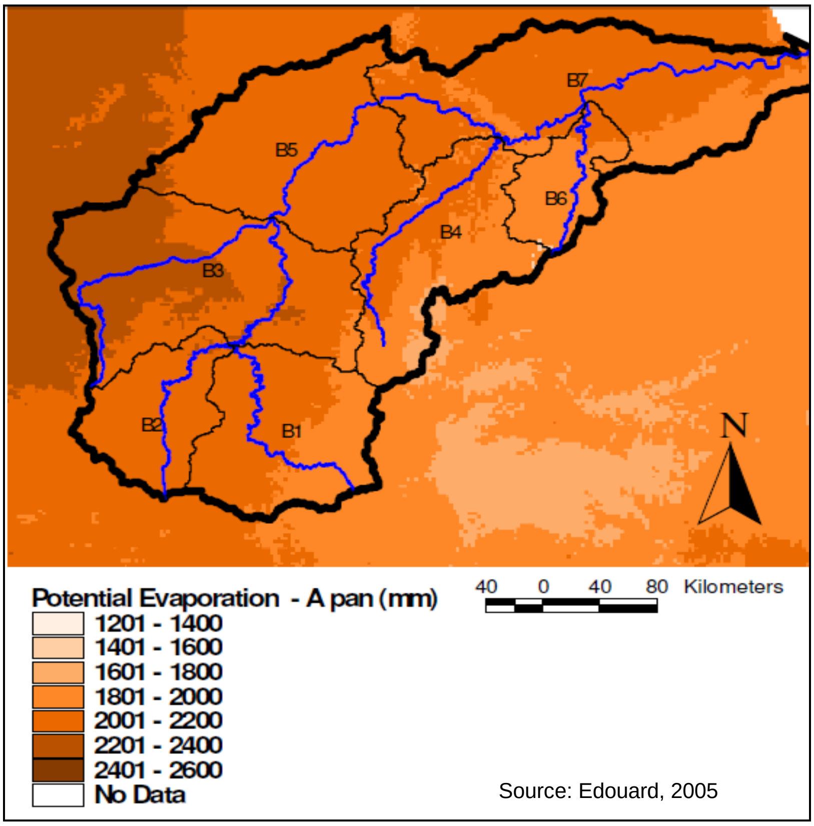

SOUTH AFRICA
PRECIPITATION
Country capital
Province capital
Province border
Percipitation (mm/year)
0
100
250
500
750
1250
2500
(inch/year)
0
3.9
9.8
19.7
29.5
49.2
98.4
N
0
150 km
0
150 mi
20°E
25°E
30°E
25°S
30°S
ZIMBABWE
MOZAMBIQUE
BOTSWANA
NAMIBIA
GABORONE
MAPUTO
MBABANE
SWAZILAND
MASERU
LESOTHO
S O U T H A F R I C A
LIMPOPO
Pietersburg
Limpopo
Olifants
Molopo
Mmabatho
PRETORIA
Johannesburg
GAUTENG
NORTH-WEST
Nelspruit
MPUMALANGA
Vaal
Kimberley
FREE STATE
Bloemfontein
Orange
KWAZULU-NATAL
Msunduzi
NORTHERN CAPE
EASTERN CAPE
Bisho
WESTERN CAPE
Cape Town
ATLANTIC OCEAN
INDIAN OCEAN

Source: World Trade press, 2012

Figure 4-10 Mean Annual precipitation.

4.4.3 Evaporation

Evaporation rate is increased as the heat increases, therefore during the summer months the evaporation rate elevates. Evaporation is also one of the largest consumers of water in this area. Using the adapted methodology of a standard US Weather Bureau Class A pan, the evaporation rate of the Middelburg area is estimated to range from 1801 to 2200 mm per annum (Figure 4-11).


B7
B5
B6
B4
B3
B2
B1
N
Potential Evaporation - A pan (mm)
1201 - 1400
1401 - 1600
1601 - 1800
1801 - 2000
2001 - 2200
2201 - 2400
2401 - 2600
No Data
40 0 40 80 Kilometers

Source: Edouard, 2005

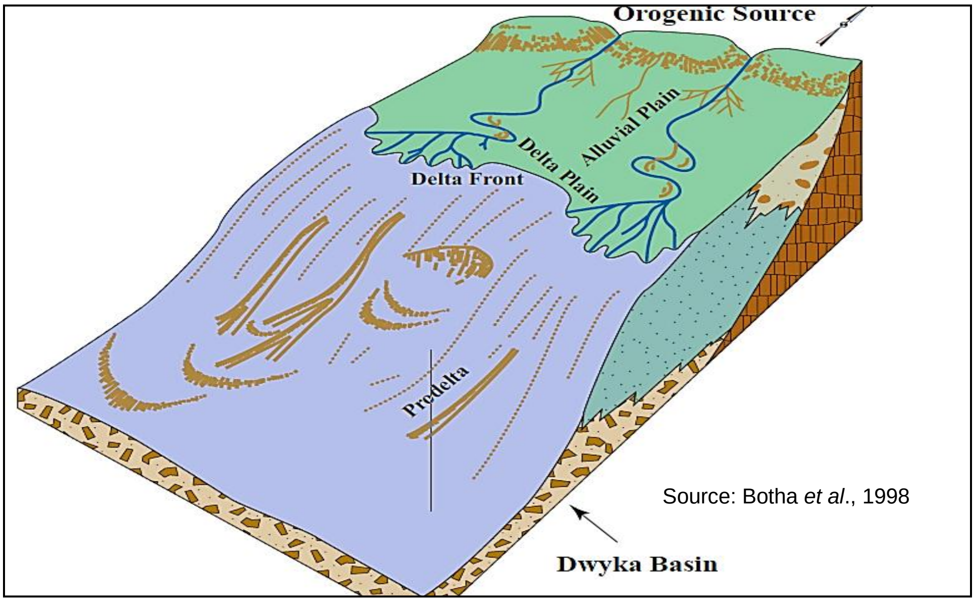
Figure 4-11 Potential evaporation in the Olifants catchment.

4.5 Geology and Mining

4.5.1 Basin shape and tectonic setting of the Karoo Supergroup

After the Cape fold belt formation, the Karoo sedimentation began. Continental Sedimentation began in 280 Ma (Permo-Carboniferous) which ended 100 million years later during the early Jurassic. The depositional style of the Karoo sequence shows effects of more localised tectonic basins and this is proved by palaeo-environmental analysis of the major stratigraphic units. A major ice sheet covered the early Karoo basin and surrounding highlands as a result of the Southern Gondwana part moving over the South Pole, the glacial sedimentation formed the Dwyka group in the Karoo.

After glaciation large volumes of melt ice remained as an extensive self-fed shallow sea, black shales and muds accumulated under relatively cool climatic conditions leading to the formation of the Lower Ecca. Subducting palaeo-pacific plate caused deformation of the Southern rim which resulted in the mountain ranges far to the South. Large deltas derived material from this source and built out the Ecca Sea (Upper Ecca), other material were derived from granitic uplands to the west and north-east. Promotion of thick accumulation of peat on the delta and coastal plains which now constitute the major coal reserves of South Africa was due to the cool climate and lowland setting (Botha *et al*., 1998). This formation is the one relevant in this chapter (Figure 4-12). Prograding deltas later cleaved to fill most of the basin after fluvial sedimentation (Beaufort Group domination).



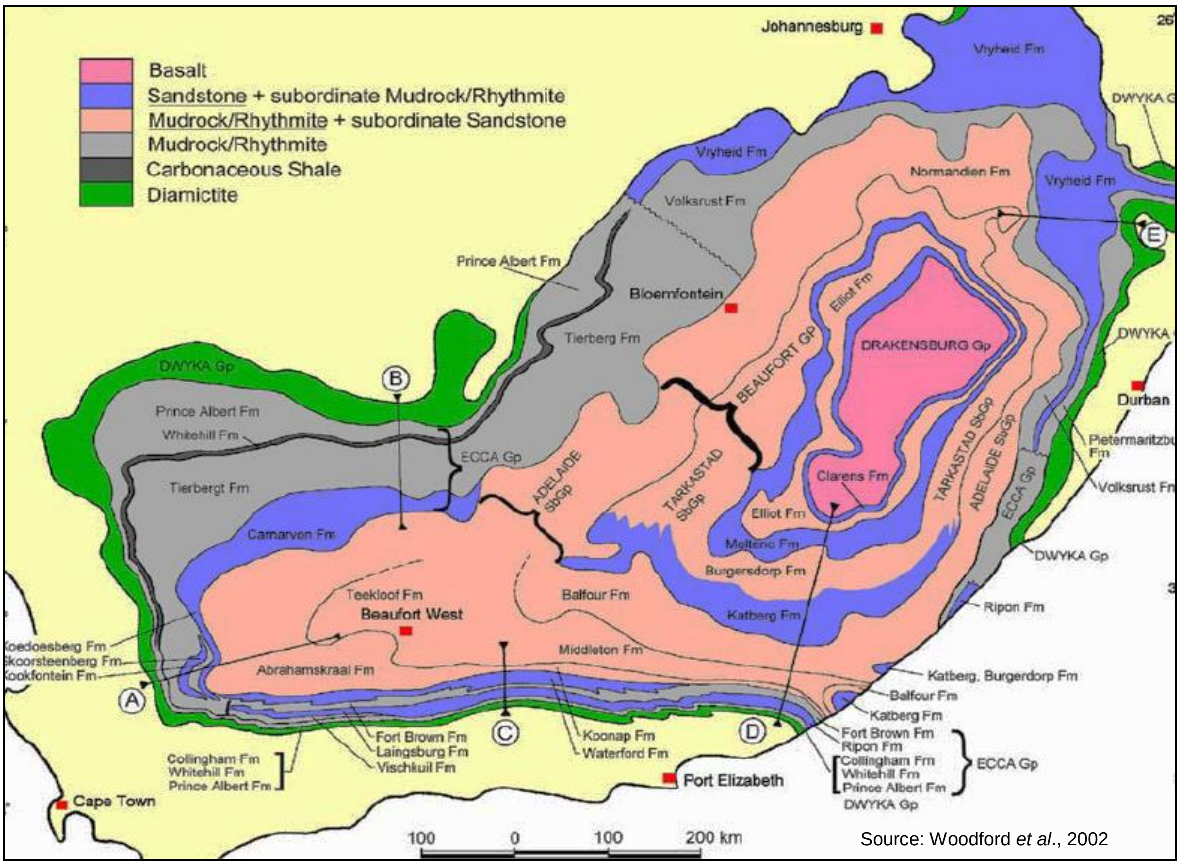
Source: Botha *et al*., 1998

Figure 4-12 Diagrammatic illustration of the Ecca formation.

Various compressional events were defined when the deposition of the Beaufort group occurred. The deposition of the Beaufort Group took place at an east linear basin with a recess in a coastline forming a bay towards the north over South Africa just like the Ecca Group. The difference between the Ecca and the Beaufort Group is that the latter's axis shifted further northwards, the basin was more enclosed and the geology is completely different (Botha *et al*., 1998).

4.5.2 Geology

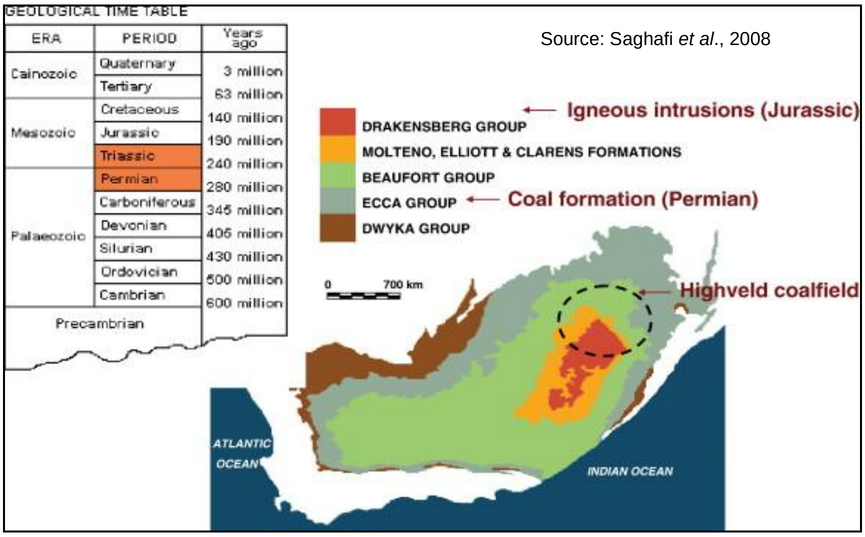
Almost two thirds of South Africa is covered with the Karoo Supergroup, the investigated area is in the Karoo Supergroup (Ecca group) therefore consists of typical Karoo sandstone and mudstone (Figure 4-13).


Basalt
Sandstone + subordinate Mudrock/Rhythmite
Mudrock/Rhythmite + subordinate Sandstone
Mudrock/Rhythmite
Carbonaceous Shale
Diamictite
Johannesburg
Vryheid Fm
DWYKA G
Vryheid Fm
Normandien Fm
Vryheid Fm
Volksrust Fm
E
Prince Albert Fm
Bloemfontein
Elliot Fm
DRAKENSBURG Gp
DWYKA
Tierberg Fm
BEAUFORT GP
Durban
DWYKA Gp
B
Prince Albert Fm
Whitehill Fm
Pietermaritzbu Fm
ECCA Gp
ADELAIDE SbGp
TARKASTAD SbGp
TARKASTAD SbGp
ADELAIDE SbGp
ECCA Gp
Volksrust Fn
Tierbergt Fm
Clarens Fm
Elliot Fm
Carnarvon Fm
Molteno Fm
DWYKA Gp
Burgersdorp Fm
Teekloof Fm
Beaufort West
Balfour Fm
Ripon Fm
Katberg Fm
Koedoesberg Fm
Skoorsteenberg Fm
Kookfontein Fm
Middleton Fm
Abrahamskraal Fm
Katberg, Burgerdorp Fm
Balfour Fm
A
Katberg Fm
Fort Brown Fm
Laingsburg Fm
Vischkuil Fm
C
Koonap Fm
Waterford Fm
D
Fort Brown Fm
Ripon Fm
Collingham Fm
Whitehill Fm
Prince Albert Fm
ECCA Gp
DWYKA Gp
Collingham Fm
Whitehill Fm
Prince Albert Fm
Port Elizabeth
Cape Town
100
0
100
200 km
26
3

Source: Woodford *et al*., 2002

Figure 4-13 Lithostratiographic map of the Karoo Supergroup.

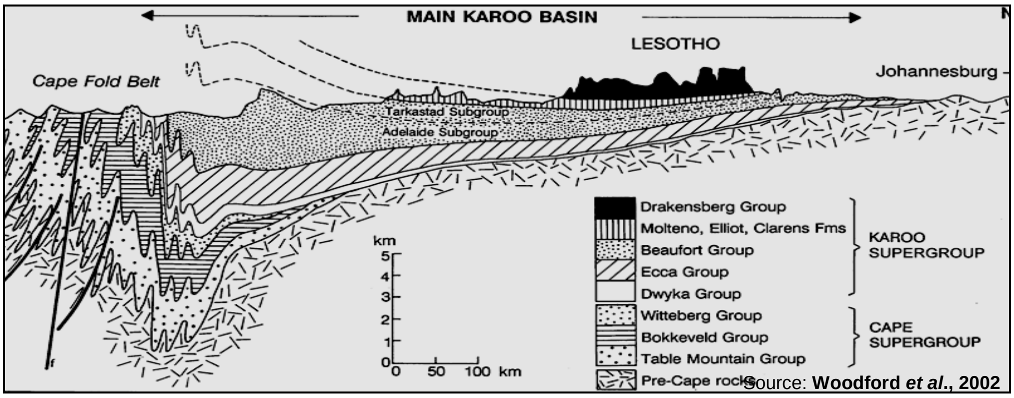
The Ecca group was formed in the Permian age (Figure 4-14) and has 16 formations which can be categorised in the southern, western –northwestern and northeastern geographical zones. Prince Albert and Whitehill Formation are basal sediments that make the Lower Ecca. The common rocks of these formations are dark-grey to black carbonaceous shale, black carbonaceous pyrite-bearing shale and siltstone. The Upper Ecca comprises of Vischkuil Formation, Collingham Formation, Waterford Formation of the Southern Zone, Tierberg Formation, Skoorsteenberg Formation, Waterford Formation of the Western Zone, Waterford Formation of the North-Western Zone, Kookfontein Formation with a mineralogical composition that varies from sandstones, shales, yellow tuff to rhythmite.


GEOLOGICAL TIME TABLE
ERA
PERIOD
Years ago
Cainozoic
Quaternary
Tertiary
Mesozoic
Cretaceous
Jurassic
Triassic
Permian
Palaeozoic
Carboniferous
Devonian
Silurian
Ordovician
Cambrian
Precambrian
3 million
63 million
140 million
190 million
240 million
280 million
345 million
405 million
430 million
500 million
600 million
Igneous intrusions (Jurassic)
DRAKENSBERG GROUP
MOLTENO, ELLIOTT & CLARENS FORMATIONS
BEAUFORT GROUP
ECCA GROUP
Coal formation (Permian)
DWYKA GROUP
0
700 km
Highveld coalfield
ATLANTIC OCEAN
INDIAN OCEAN

Source: Saghafi *et al*., 2008

Figure 4-14 Geological time table with emphasis on the Highveld Coalfield.

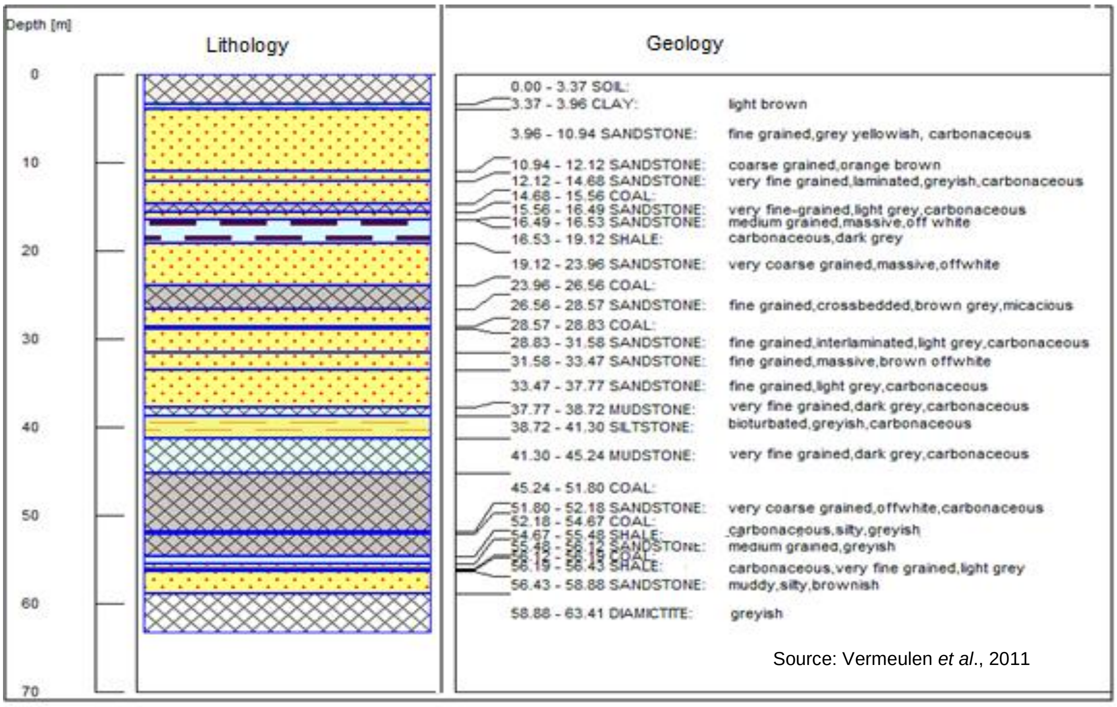
The Middle Ecca has Ripon Formation, Fort Brown Formation, Laingsburg Formation, Pietermaritzburg Formation, Vryheid Formation and Volksrust Formation with rocks such as mudstone, sandstone and coal seams. Coal deposits in South Africa are wide spread in the Middle Ecca of the Karoo sequence however, the Ecca group thins out North. With the lower Ecca absent the coal measures often rest directly on the Dwyka group (Figure 4-15).


MAIN KAROO BASIN
N
LESOTHO
Cape Fold Belt
Johannesburg
Tarkastad Subgroup
Adelaide Subgroup
km
5
4
3
2
1
0
0
50
100 km
Drakensberg Group
Molteno, Elliot, Clarens Fms
Beaufort Group
Ecca Group
Dwyka Group
KAROO SUPERGROUP
Witteberg Group
Bokkeveld Group
Table Mountain Group
CAPE SUPERGROUP
Pre-Cape rocks

Source: **Woodford *et al*., 2002**

Figure 4-15 Cross sectional view of the Karoo and Cape Supergroup.

A typical lithological unit of the studied area is shown in Figure 4-16. The lithology varies from sandstone, shale, mudstone, siltstone, diamicite and coal. The coal seams are at 15m, 24m and 50m approximately with sandstone above, the sandstone is often the water-bearing stratum. The water in/from the sandstone is therefore one of the possible contributors to the oxidation of sulphur minerals (Vermeulen *et al*., 2011).


Depth [m]
Lithology
Geology
0
10
20
30
40
50
60
70
0.00 - 3.37 SOIL:
3.37 - 3.96 CLAY: light brown
3.96 - 10.94 SANDSTONE: fine grained,grey yellowish, carbonaceous
10.94 - 12.12 SANDSTONE: coarse grained,orange brown
12.12 - 14.68 SANDSTONE: very fine grained,laminated,greyish,carbonaceous
14.68 - 15.56 COAL:
15.56 - 16.49 SANDSTONE: very fine-grained,light grey,carbonaceous
16.49 - 16.53 SANDSTONE: medium grained,massive,off white
16.53 - 19.12 SHALE: carbonaceous,dark grey
19.12 - 23.96 SANDSTONE: very coarse grained,massive,offwhite
23.96 - 26.56 COAL:
26.56 - 28.57 SANDSTONE: fine grained,crossbedded,brown grey,micacious
28.57 - 28.83 COAL:
28.83 - 31.58 SANDSTONE: fine grained,interlaminated,light grey,carbonaceous
31.58 - 33.47 SANDSTONE: fine grained,massive,brown offwhite
33.47 - 37.77 SANDSTONE: fine grained,light grey,carbonaceous
37.77 - 38.72 MUDSTONE: very fine grained,dark grey,carbonaceous
38.72 - 41.30 SILTSTONE: bioturbated,greyish,carbonaceous
41.30 - 45.24 MUDSTONE: very fine grained,dark grey,carbonaceous
45.24 - 51.80 COAL:
51.80 - 52.18 SANDSTONE: very coarse grained,offwhite,carbonaceous
52.18 - 54.67 COAL:
54.67 - 55.48 SHALE: carbonaceous,silty,greyish
55.48 - 56.12 SANDSTONE: medium grained,greyish
56.12 - 56.19 COAL:
56.19 - 56.43 SHALE: carbonaceous,very fine grained,light grey
56.43 - 58.88 SANDSTONE: muddy,silty,brownish
58.88 - 63.41 DIAMICTITE: greyish

Source: Vermeulen *et al*., 2011

Figure 4-16 Typical stratigraphy map of the Middelburg mines.

4.5.3 Mining operations at the Study area

Mining of coal has been operational for more than 100 years. Only 15 years ago, strict legislation was put into place. In 1991 the mineral acts was re-enforced on mines. Act 50 of 1991 stated that the land (i.e. the mines) remained property of the owner until they are issued a certificate of closure. This was substituted by the mineral and petroleum act of 2002 that stated that no closure certificate would be issued unless management of potential pollution to water resources has been addressed (Hodgson *et al*., 2007). Therefore the prediction of AMD in the investigated area is essential for the environmental impact assessment as well as the planning and management of the mine. According to Hodgson *et al*., (2001) planning could minimize or control the pollution potential during or after mining activities. 40 % of coal mining in South Africa is by means of open cast as the coal occurs as thick seams that are shallow (Usher, 2003). Open cast mining is in operation at the investigated area.

4.6 Surface hydrology and Geohydrology of the investigated area

4.6.1 Surface hydrology

The study area is located in the Middelburg area (Figure 4-17), large water impoundments such as the Witbank dam, Middelburg dam and Loskop dam control the streams flows along the main Olifants and the Klein Olifants river system. The Klein Olifants River is the primary drainage valley in the Middelburg Dam (Mey & Van Niekerk, 2009). Approximately 13 km to the Northwest of the Middelburg North Colliery the surface water drainage flows into the Olifants River by first going through Spookspruit (Figure 4-18) whereas Klipfontein goes through Vaalspruitbank (Figure 4-18) into Pienars dam.

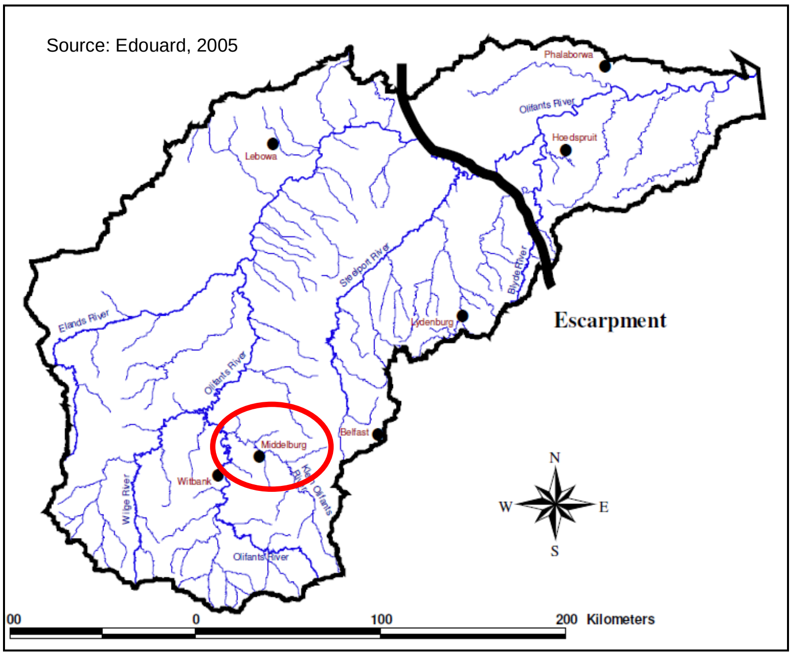

Source: Edouard, 2005
Phalaborwa
Olifants River
Hoedspruit
Lebowa
Steelpoort River
Blyde River
Elands River
Lydenburg
Escarpment
Olifants River
Belfast
Middelburg
Witbank
Wilge River
Klein Olifants
Olifants River
N
W
E
S
00
0
100
200 Kilometers

Figure 4-17 Olifants catchment showing the main tributaries and urban centres.

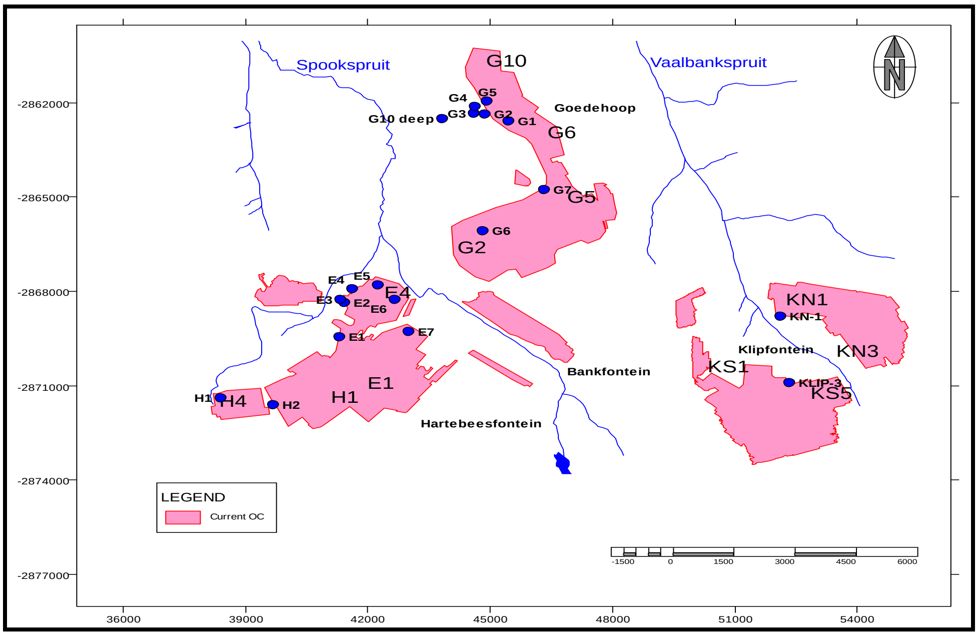

Spookspruit
G10
Vaalbankspruit
G4
G5
Goedehoop
G10 deep
G3
G2
G1
G6
G7
G5
G6
G2
E4
E5
E4
E3
E2
E6
E7
E1
E1
H1
H4
H2
H1
Bankfontein
Hartebeesfontein
KN1
KN-1
KN3
Klipfontein
KS1
KLIP-3
KS5
LEGEND
Current OC
-1500
0
1500
3000
4500
6000
-2862000
-2865000
-2868000
-2871000
-2874000
-2877000
36000
39000
42000
45000
48000
51000
54000

Figure 4-18 Surface hydrology with the current open cast operation (pink).

Dams (dams 1-10) and voids (also known as pits where the water has already filled up) were analysed for the water quality. Figure 4-19 shows the points were surface water quality was investigated. The water quality was analysed by the IGS Laboratory.

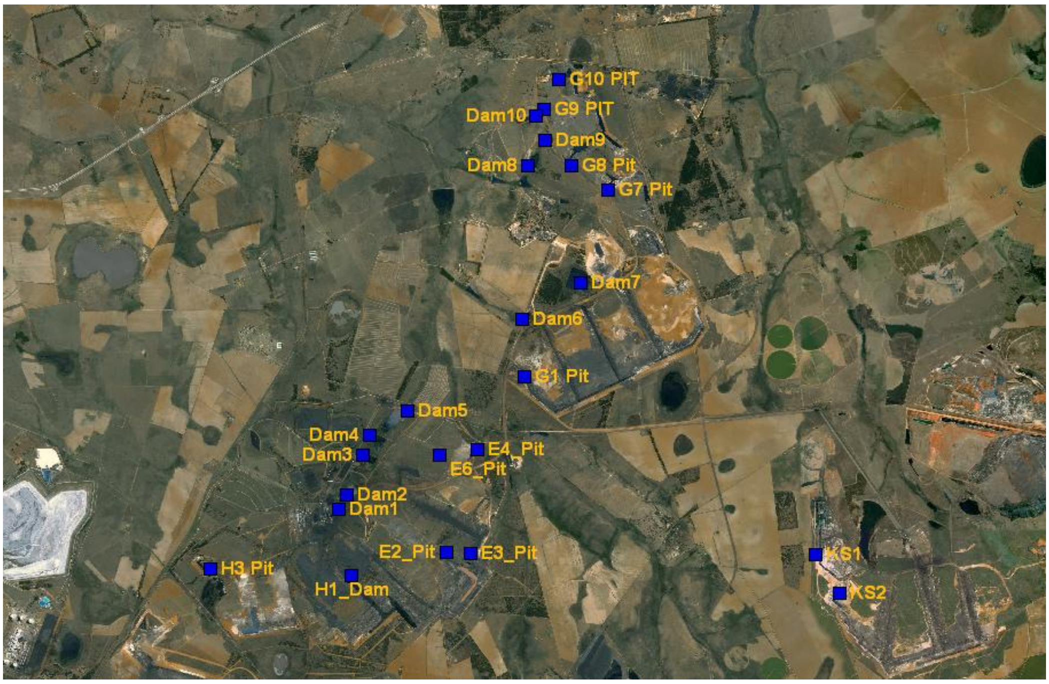

G10 PIT
Dam10
G9 PIT
Dam9
Dam8
G8 Pit
G7 Pit
Dam7
Dam6
G1 Pit
Dam5
Dam4
Dam3
E4_Pit
E6_Pit
Dam2
Dam1
E2_Pit
E3_Pit
H3 Pit
H1_Dam
KS1
KS2

Figure 4-19 Dam and pit points of the analysed water chemistry for surface hydrology.

The voids (pits) and some dams are heavily contaminated with SO_4, indicating AMD. H3 and Dam 9 have the lowest SO_4 values in Figure 4-20. Therefore, according to the laboratory analysis, H3 serves as an indication that the water flow is down-gradient towards the north east since it is located west of the opencasts. The surface water dams further down the Hartebeesfontein are polluted due to this reason.

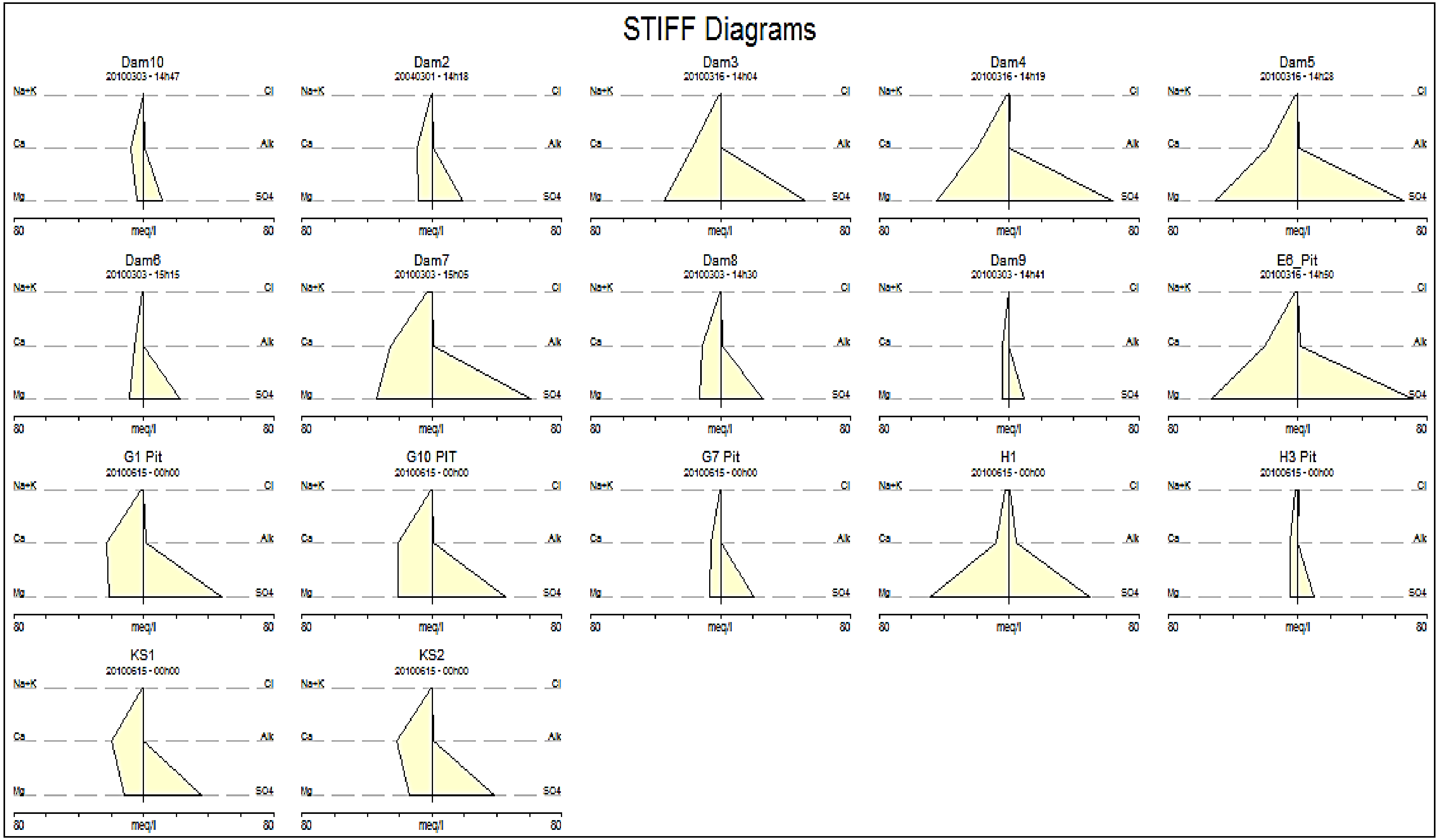


Figure 4-20 Stiff diagrams for the surface hydrology.

The percentage plotting of cations and anions are plotted on the piper diagram (Figure 4-21), it shows that the water is dominantly CaCl classified with about 2 samples that are $CaNaHCO_3Cl$.

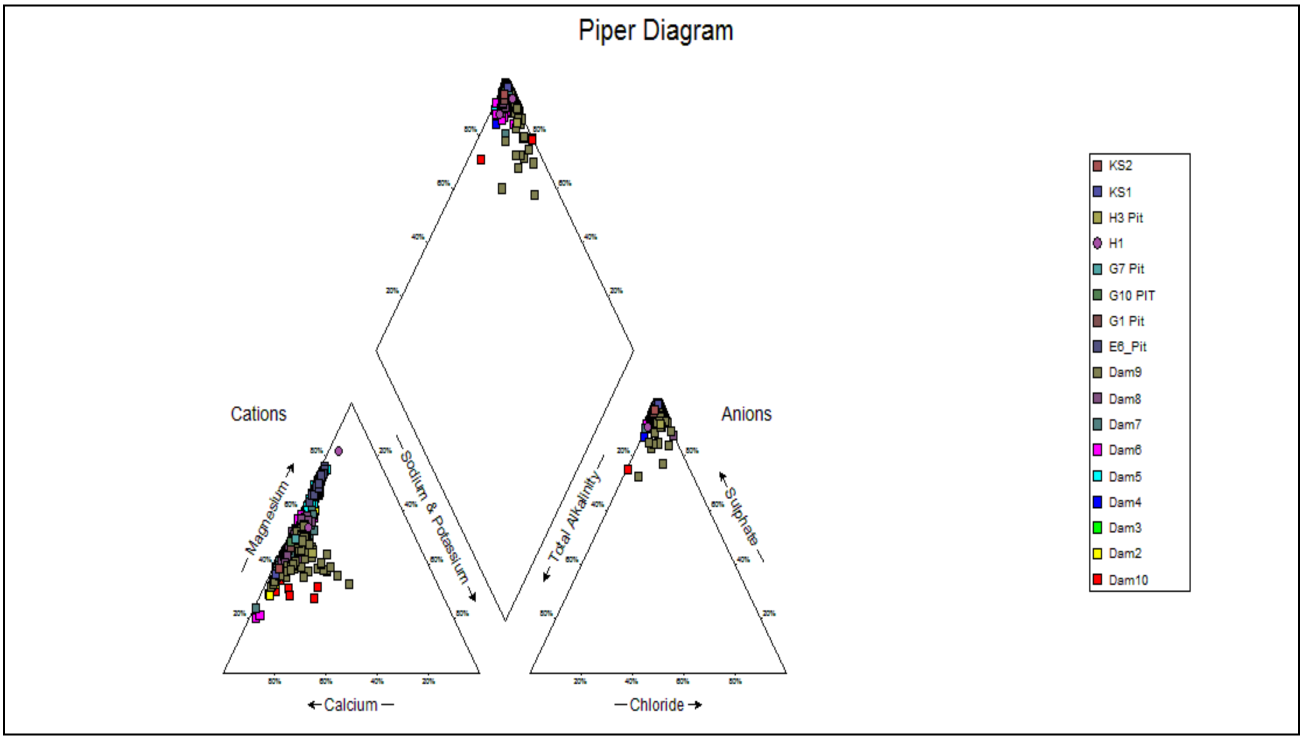


Figure 4-21 Piper diagrams for the surface hydrology.

The EC value of the voids varied from 174- 324mS/m while the lowest EC value was from the dams at the value of 88 mS/m. The highest values are marked with a red square; the proportionality of each is shown by the size of the square (Figure 4-23). Appendix 5 has detailed data of the major and minor analysed ions in water. The EC time graph (Figure 4-22) indicates that the water quality varies between sampling runs with E6 having the highest TDS concentration.

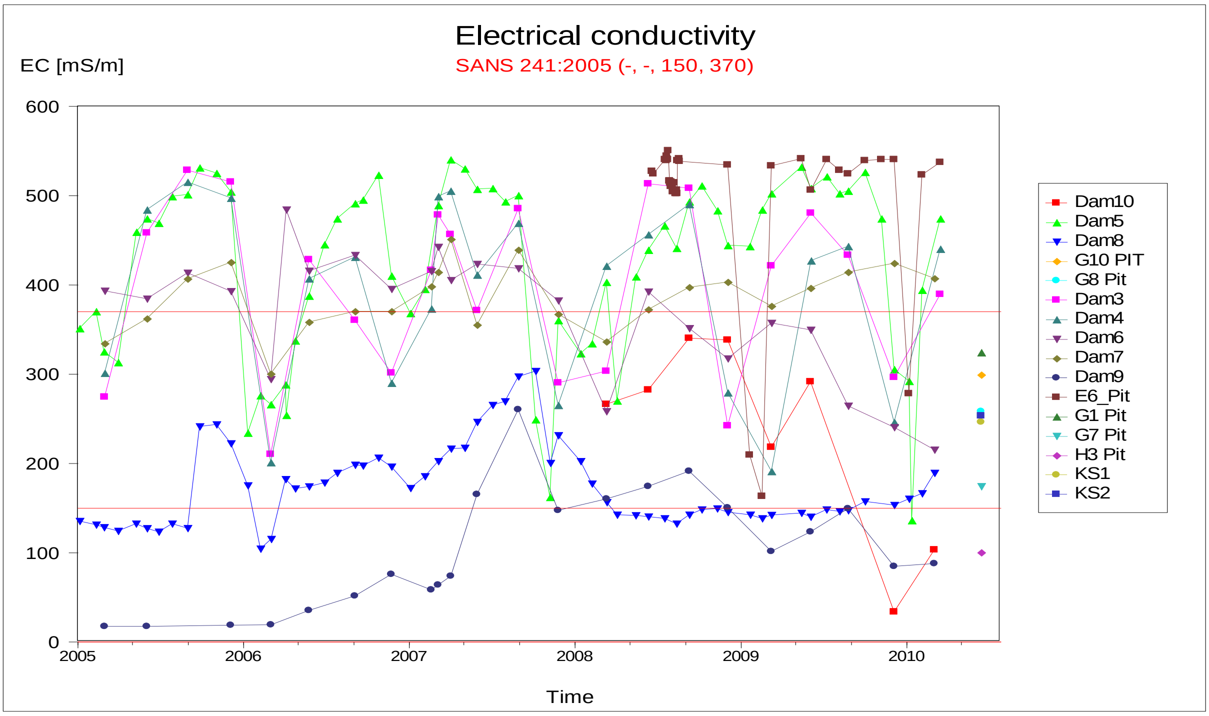


Figure 4-22 EC measurements of the surface hydrology.

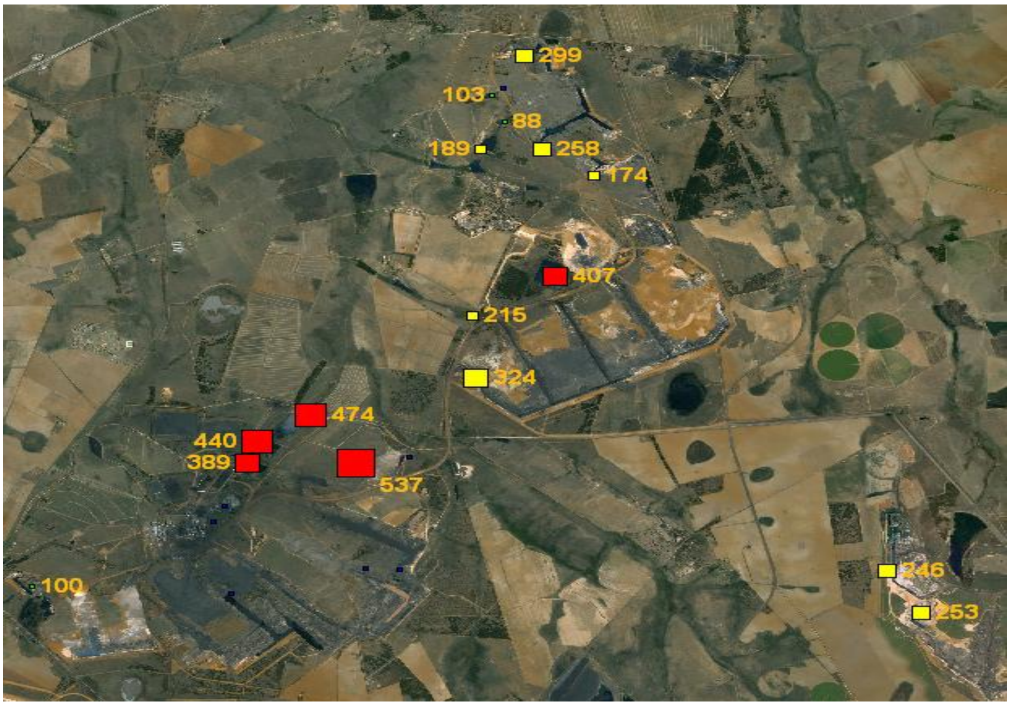

299
103
88
189
258
174
407
215
324
474
440
389
537
100
246
253

Figure 4-23 EC distribution of the surface hydrology.

The H1, Dam 3, Dam 4, Dam 5, Dam 7, E6 pit and G1 pit have relatively high SO_4 values as shown in the stiff diagram and also the time graph below (Figure 4-24). High sulphate values (Figure 4-25) are relative to the high EC (Figure 4-23). The EC values illustrate that Hartebeesfontein opencasts are the reason for the polluted down-gradient surface water dams.

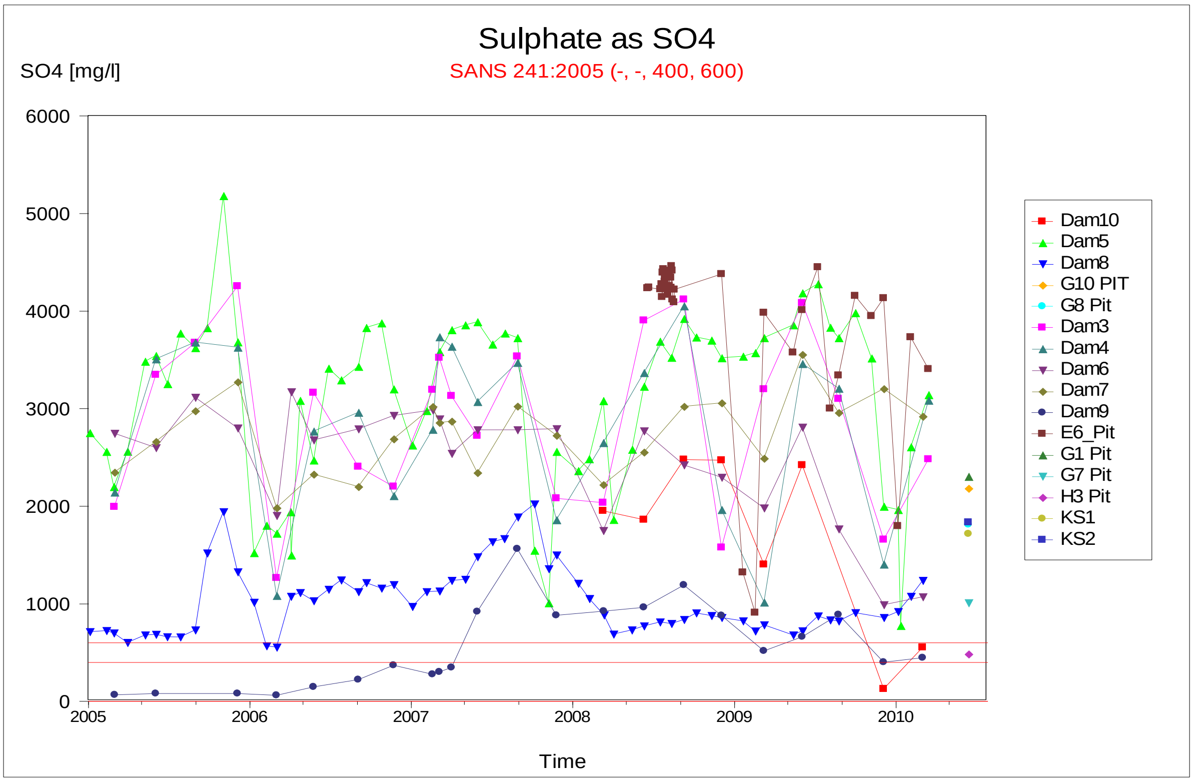


Figure 4-24 Time graph of SO_4.

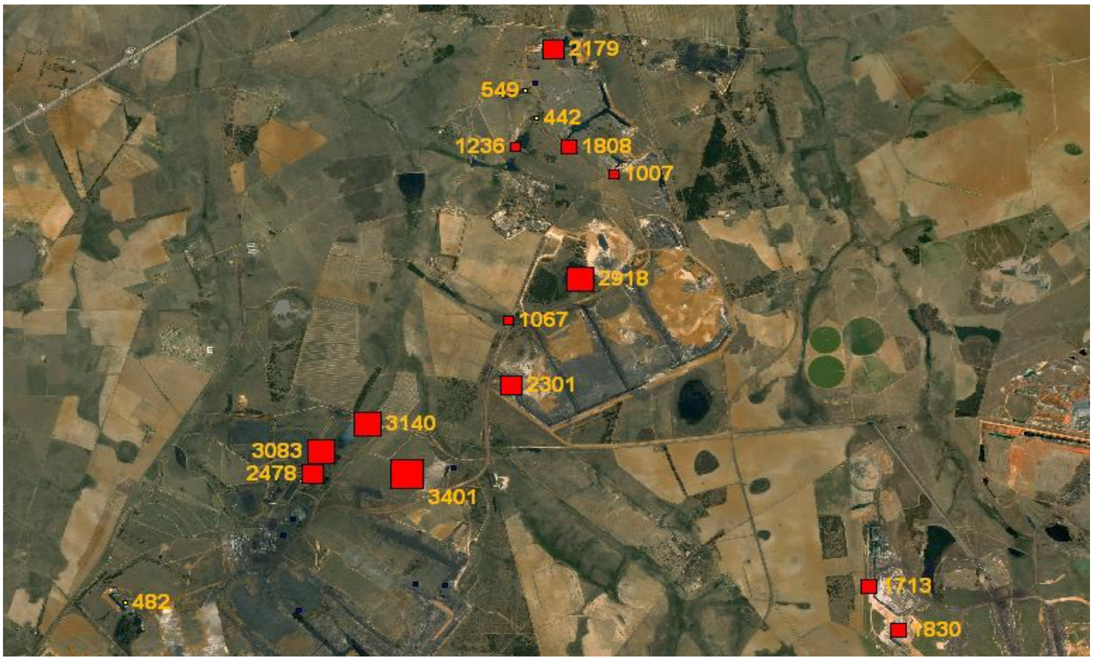
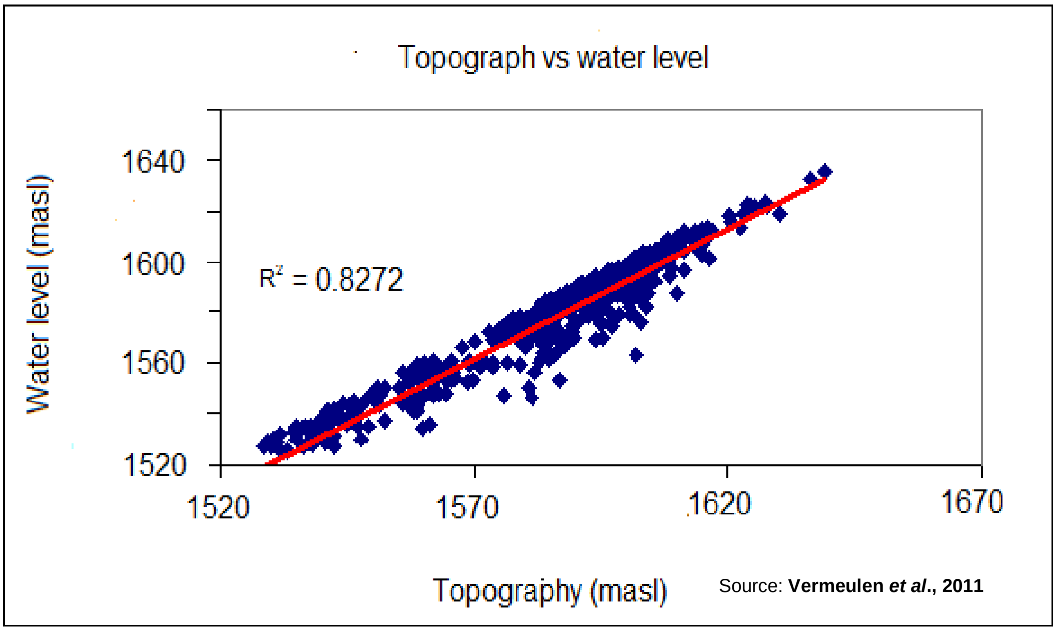

2179
549
442
1236
1808
1007
2918
1067
2301
3140
3083
2478
3401
482
1713
1830

Figure 4-25 SO_4 proportional distribution for Surface hydrology.

4.6.2 Geohydrology

There are four types of aquifers in the Olifants catchment but only 2 of the 4 aquifers systems are revised at the investigated study area. The Middelburg area has weathered rock and structural/fractured aquifer systems. Vermeulen *et al*., 2011 constructed Figure 4-26 to show whether the groundwater level follows topography using 600 boreholes data that was surveyed. The figure shows a correlation coefficient that is high enough to make an assumption that the groundwater level follows the surface topography. The low T-values of the geological formation and Kinematic porosities also implied the water levels are nearly or completely horizontal in the opencast areas (Vermeulen *et al*., 2011).



Source: **Vermeulen *et al*., 2011**

Figure 4-26 Correlation between surface topography and groundwater leve

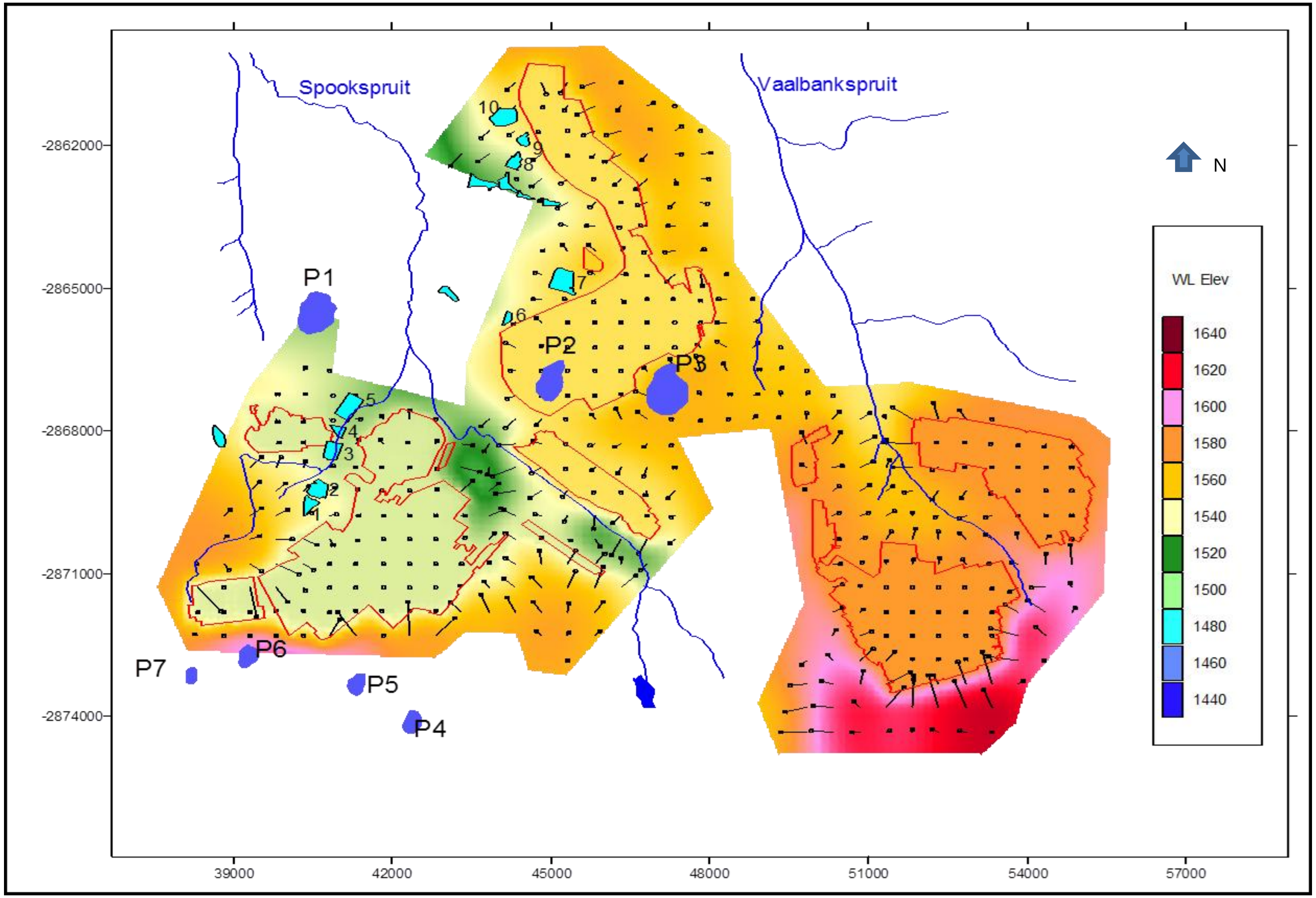

Spookspruit
Vaalbankspruit
N
WL Elev
1640
1620
1600
1580
1560
1540
1520
1500
1480
1460
1440
P1
P2
P3
P4
P5
P6
P7
1
2
3
4
5
6
7
8
9
10
-2862000
-2865000
-2868000
-2871000
-2874000
39000
42000
45000
48000
51000
54000
57000

Figure 4-27 Groundwater flow direction with the water levels.

About 14 borehole water samples were analysed in the previous 2006 groundwater assessment done by the IGS laboratory (Figure 4-28). The time graph (Figure 4-29) shows that the groundwater rose about 4m till presently but only further sampling can verify the trend in this area.

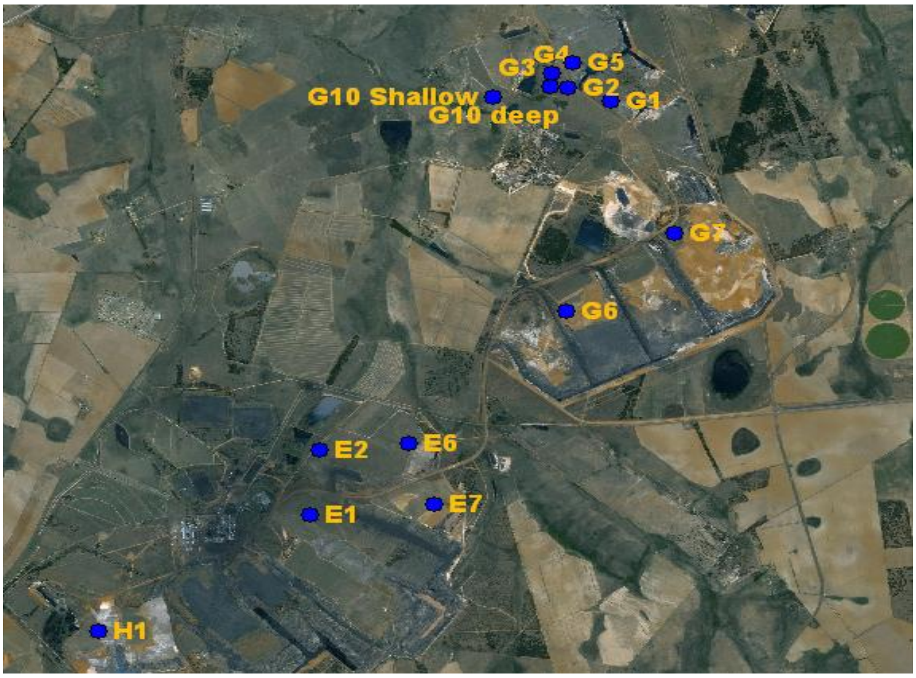


Figure 4-28 Sampling points for groundwater assessment.

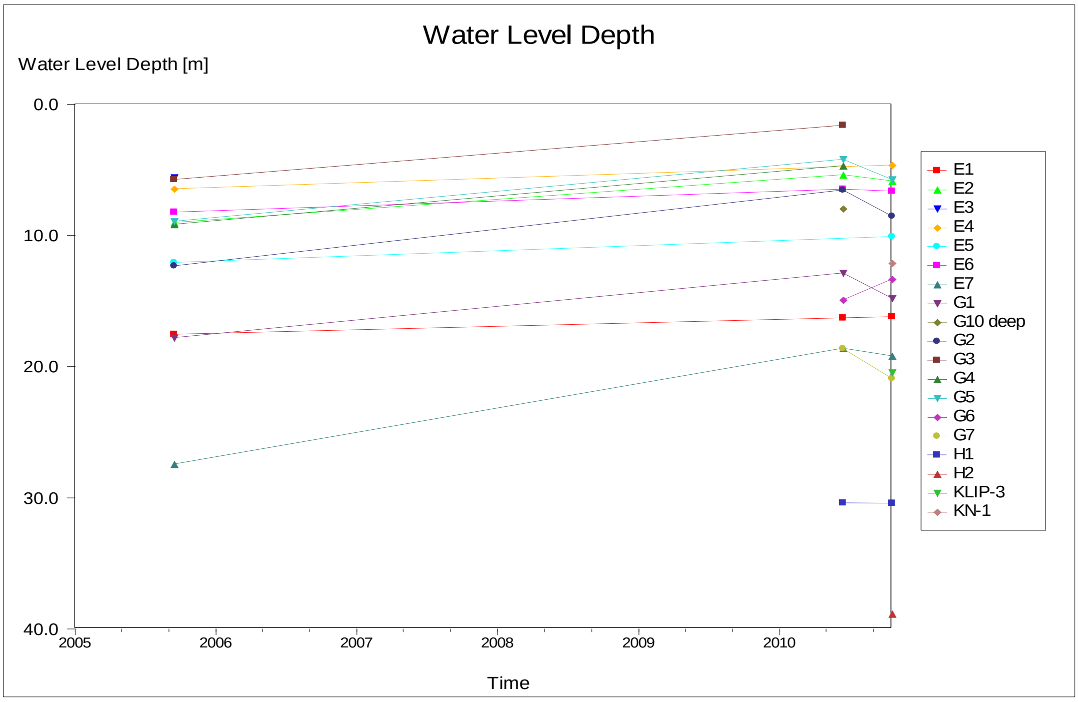


Figure 4-29 Time graph of Geohydrology of the investigated area.

High sulphate values (Figure 4-30) are clear in at the Hartebeesfontein and E7 indicating AMD presence. The voids discussed above are also heavily contaminated but this does not correspond with the groundwater quality from Goedehoop that indicates that the polluted water from the opencasts do not affect the water in the surrounding aquifer as yet.

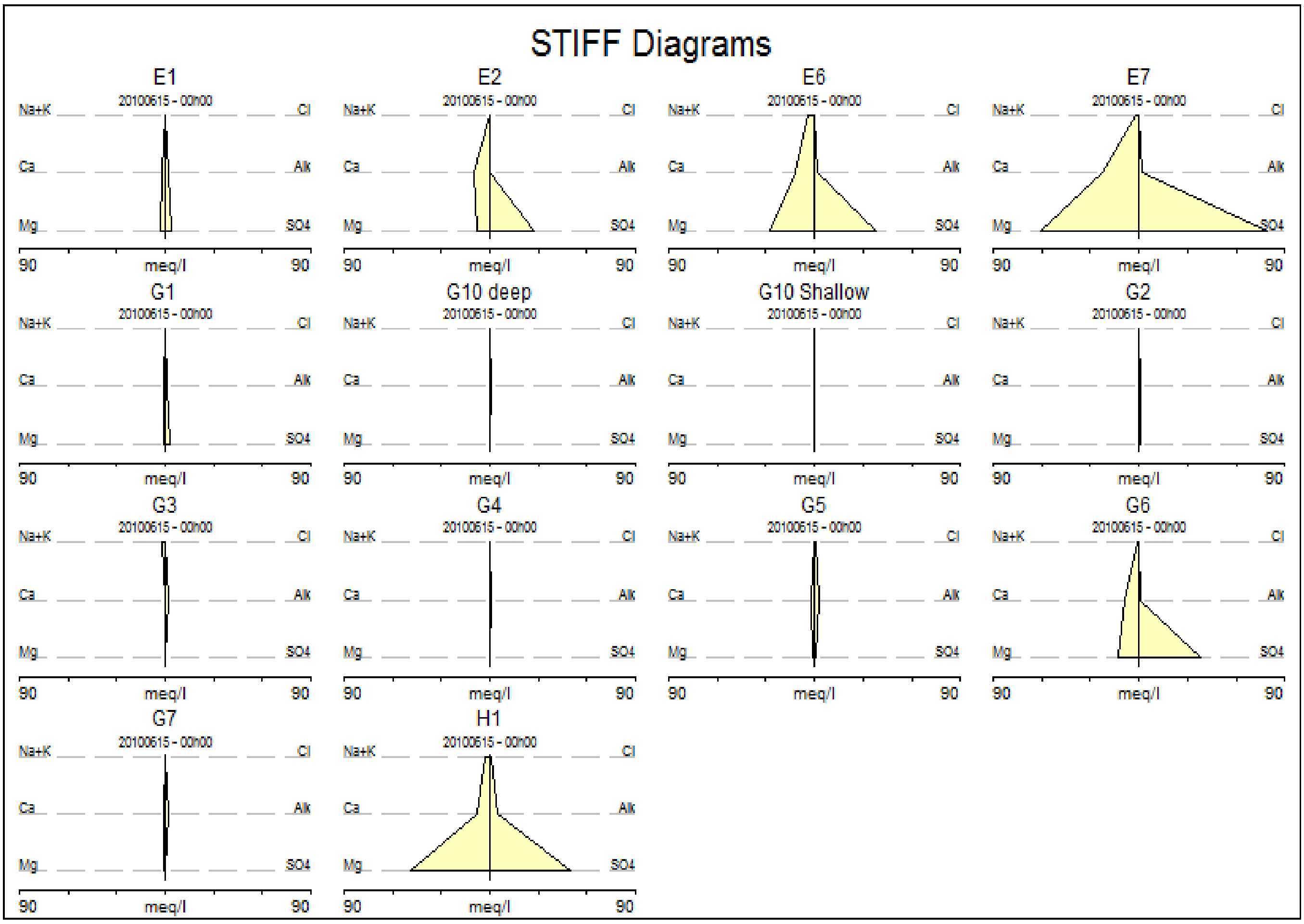


Figure 4-30 Stiff diagrams for the groundwater.

The piper diagram (Figure 4-31) illustrated the chemistry of the groundwater to be under the $CaHCO_3$, $CaNaHCO_3Cl$, $NaHCO_3Cl$, NaCl and CaCl types with the classification that alkaline earths exceed alkalies, weak acids are greater than strong acids, carbonate hardness exceeds 50 % or no one cation-anion pair exceeds 50 %.

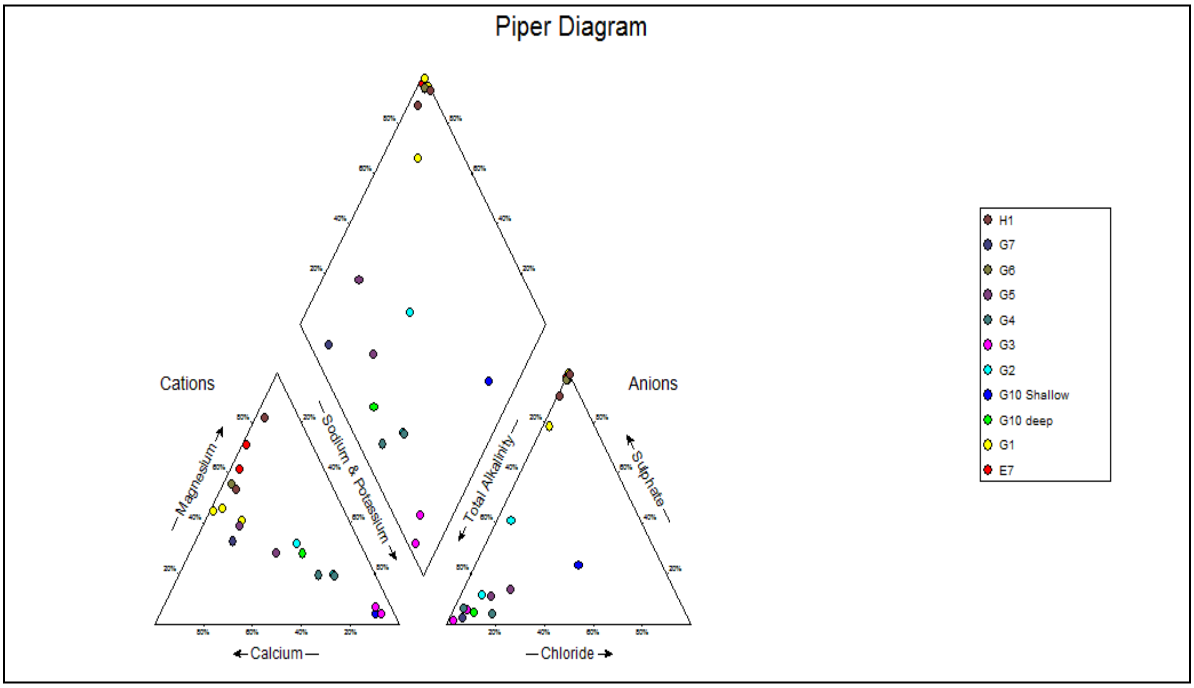


Figure 4-31 Piper diagrams for the groundwater.

According to Figure 4-32, the EC values of E6, E1 and G1 decrease (showing improvement of water quality) with time while G5, G2 and G4 stay constant. The high values of EC indicated in red circles in Figure 4-33 shows a trend in surface EC whereby the values are relatively high.

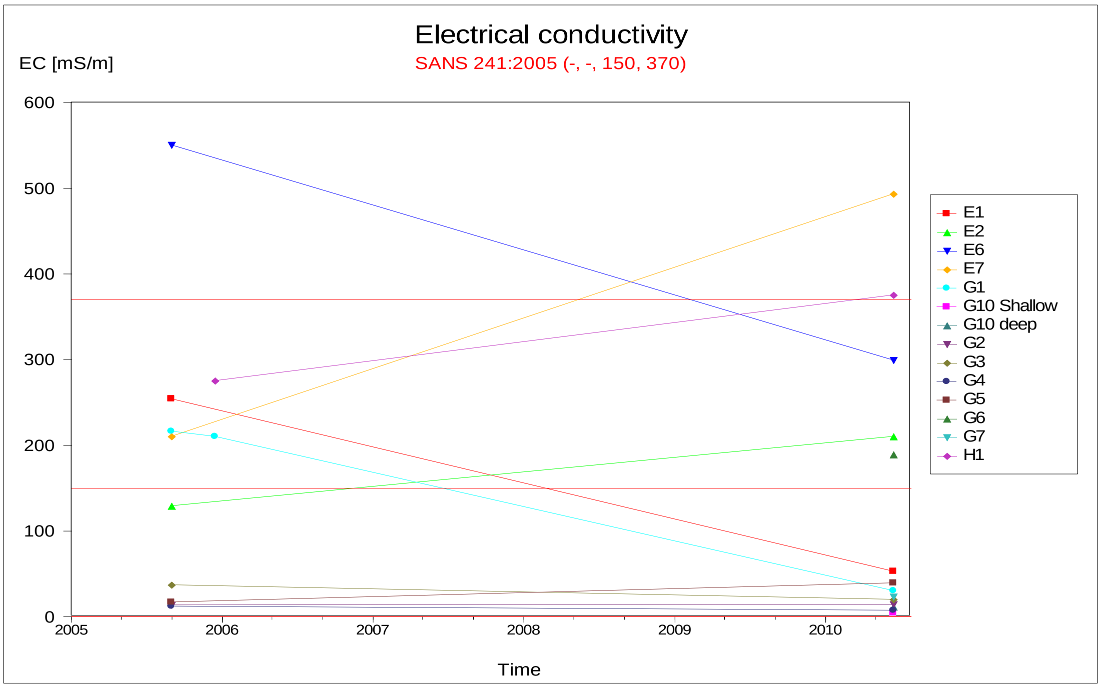


Figure 4-32 Time graph of EC values of groundwater.

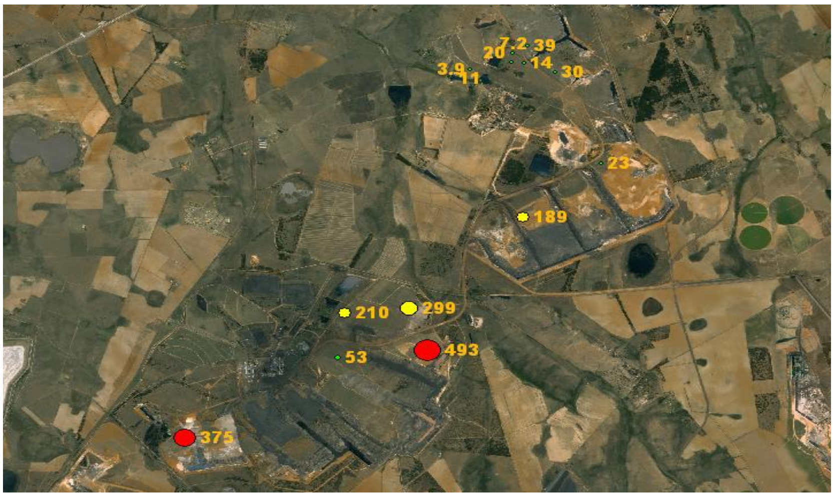

20
7.2
39
3.9
11
14
30
23
189
210
299
53
493
375

Figure 4-33 EC proportional distribution of the geohydrology.

4.6.3 Decant

Water levels inside the collieries are flattened and as a result decant occurs at the minimum surface elevation above the open cast mines (Figure 4-34). Material above the mined out area is therefore recharged mainly by the decant. The relationship of the decant with the mined out area has a close correlation thus when the acid-generating material is below mine water level the SO_4 generation value decreases.

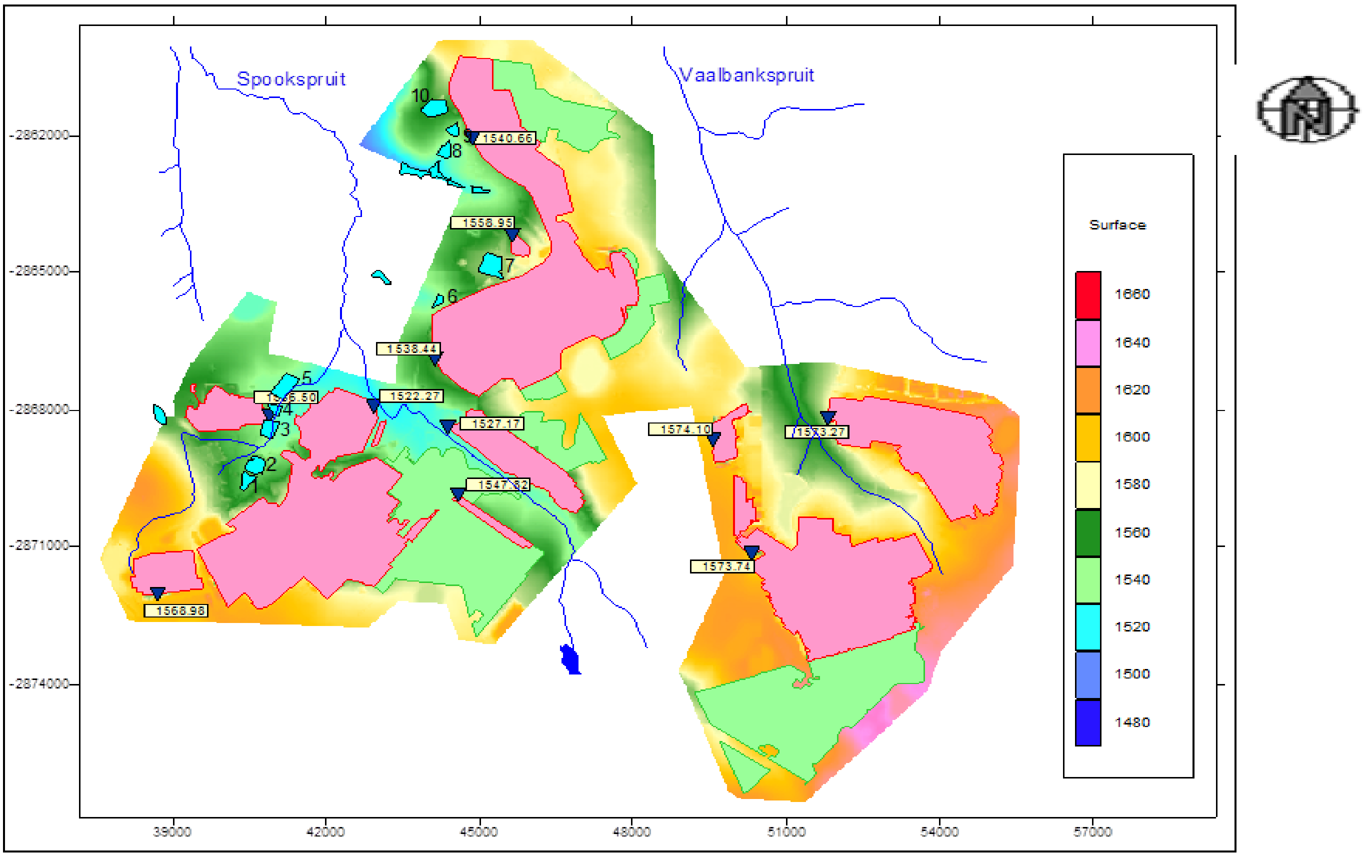

Spookspruit
Vaalbankspruit
10
1540.66
8
1558.95
7
6
1538.44
5
1536.50
4
3
2
1
1522.27
1527.17
1547.82
1574.10
1573.27
1573.74
1568.98
Surface
1660
1640
1620
1600
1580
1560
1540
1520
1500
1480
-2862000
-2865000
-2868000
-2871000
-2874000
39000
42000
45000
48000
51000
54000
57000

Figure 4-34 Decant point at the investigated area.

4.7 Sites investigated, results and interpretation

As mentioned in the sampling section, 127 samples were collected from various locations and analysed for AMD prediction. This chapter and/or section emphasis on three locations to avoid repetition of interpretations. The rest of the locations are discussed in Appendix 5.

4.7.1 Goedehoop Ramp 4

Forty four samples were collected over the ten Goedehoop Ramps. Only Ramp 4 will be discussed in this chapter. Four samples were analysed for Goedehoop Ramp 4 as illustrated in Figure 4-35.

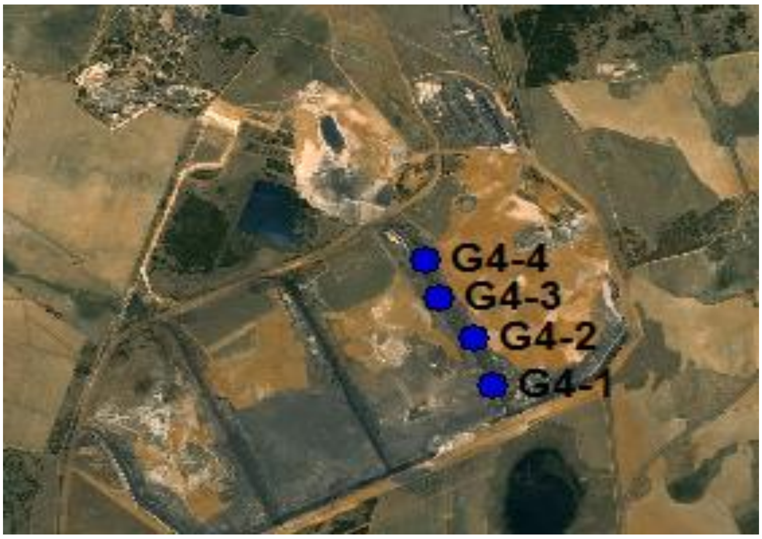


Figure 4-35 Sampling point of Goedehoop Ramp 4

Mineralogical analysis of Goedehoop Ramp 4

Table 4-5 illustrates a key to for reading all the mineralogical results in this chapter. Goedehoop Ramp 4 mine consists predominantly of quartz and kaolinite with accessory components of gypsum and K-Feldspar (Table 4-6). The absence of buffering minerals such as calcite and dolomite suggest that the conversion of pyrite to depositional gypsum is already occurring.

Table 4-5 Classification table for mineralogical results.

Dominant	**XX**	**>40%**
Major	X	15-40%

Minor	xx	5-15%
Accessory	x	2-5%
Rare	<x	<2%

Table 4-6 Mineralogical analysis of Goedehoop Ramp 4.

Sample	Q	Kaol	Illite	Kvsp	Gyp
G4-1	XX	XX	<x	<x	
G4-2	XX	XX	<x	<x	
G4-3	XX	XX			x
G4-4	XX	XX	<x	<x	

Static results for Goedehoop Ramp 4

Static tests were performed to assess likely reacting components of Goedehoop Ramp 4. All the Goedehoop samples from Ramp 4 have a high initial value but partly oxidises in the final pH method (Table 4-7). Three out of four samples indicate that they have a medium to a high risk of acid generation.

Table 4-7 Interpretation of ABA pH and NAG results Goedehoop Ramp 4.

Site Name	Initial pH	Final pH	Interpretation
G4-1	7.12	4.07	Medium Risk Acid Generation
G4-2	8.28	4.39	Medium Risk Acid Generation
G4-3	6.93	3.95	Medium Risk Acid Generation
G4-4	7.23	3.49	Higher Risk Acid Generation

Figure 4-36 shows a proportional distribution of pH with an average initial pH of 7.4. All samples have alkaline pH, indicating that there samples are currently not acidic and poses a less threat of generating AMD.

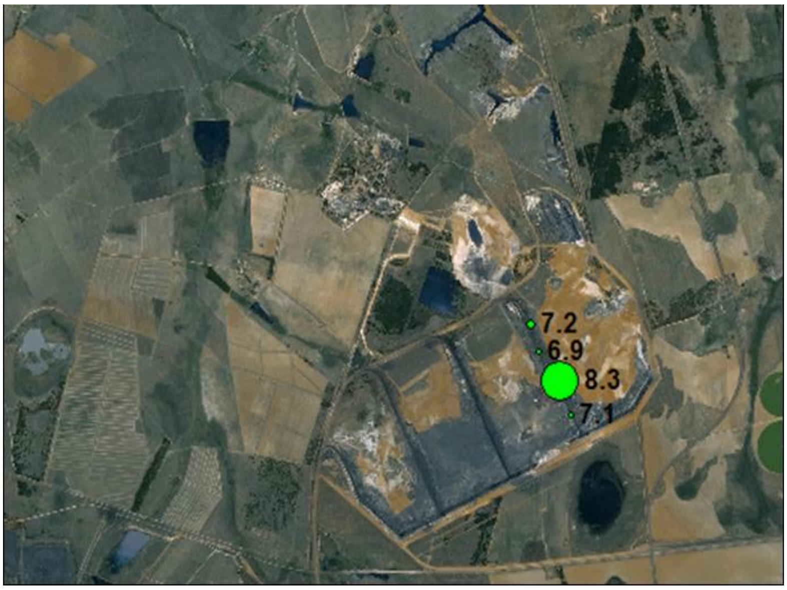


Figure 4-36 Initial pH of Goedehoop Ramp 4 samples.

The samples pH drop to values ranging from 3-4, meaning after they were exposed to peroxide digestion they oxidised. An average final pH is 4.00 is observed, indicating a medium risk of acid generation upon oxidisation (Figure 4-36).

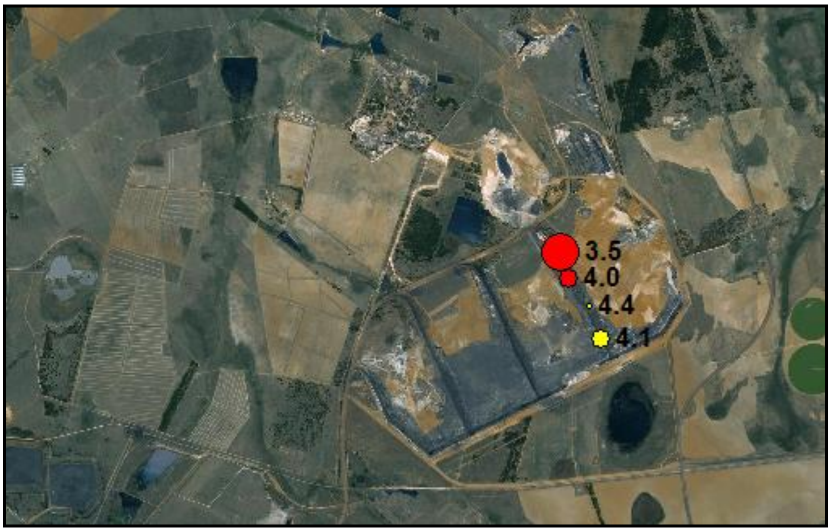


Figure 4-37 Final pH showing Goedehoop Ramp 4 samples.

Three samples out of four from the Goedehoop Ramp 4 values show a positive Net Neutralising potential that suggest the samples will unlikely generate acidic conditions, one sample shows a negative net neutralising potential (Figure 4-38) therefore suggesting that the sample will likely produce AMD. This sample had an initial pH of 7 that dropped to a pH of 4 after oxidation. Despite the low pH, the sample did not have enough neutralising potential to be regarded as samples that will unlikely produce AMD.

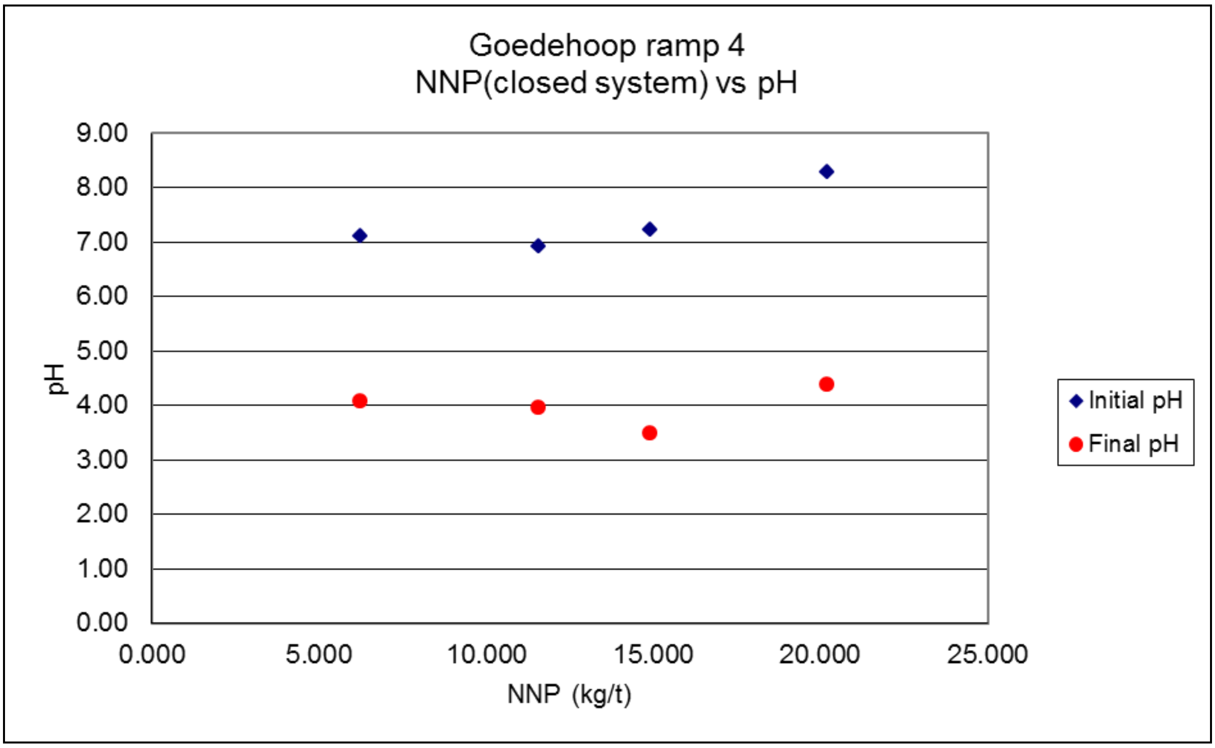


Figure 4-38 NNP Goedehoop Ramp 4.

The open and closed NNP is interpreted in Table 4-8 where samples have no negative value. Although they have positive NNP in a both the closed and open systems, values under 20 have to be verified by other tests. Therefore 3 samples have to be verified with Kinetic tests while G4-2 has a probability of having excess neutralising minerals. The NP/AP ratio in Table 4-9 suggests that there is no acid potential at this Ramp.

Table 4-8 Interpretation of ABA Net Neutralising Potential results.

Site Name	**Net Neutralising Potential (Open)**	**Net Neutralising Potential (Closed)**	**Interpretation**
G4-1	6.896	6.243	Verify with other tests
G4-2	20.621	20.196	Probably Excess Neutralising Minerals

G4-3	7.412	7.412	Verify with other tests
G4-4	15.440	14.914	Verify with other tests

Table 4-9 Interpretation and NP/AP ratios for the Goedehoop Ramp 4 samples.

Site Name	**Neutralising Potential Ratio(NP/AP) for Open System**	**Interpretation Open System**	**Interpretation Closed System**
G4-1	11.57	No Acid Potential	No Acid Potential
G4-2	49.50	No Acid Potential	No Acid Potential
G4-3	741.20	No Acid Potential	No Acid Potential
G4-4	30.35	No Acid Potential	No Acid Potential

In Figure 4-39, three samples show both in the open and closed system are unlikely to acidify, the other one is uncertain as it plots close to the zero lines.

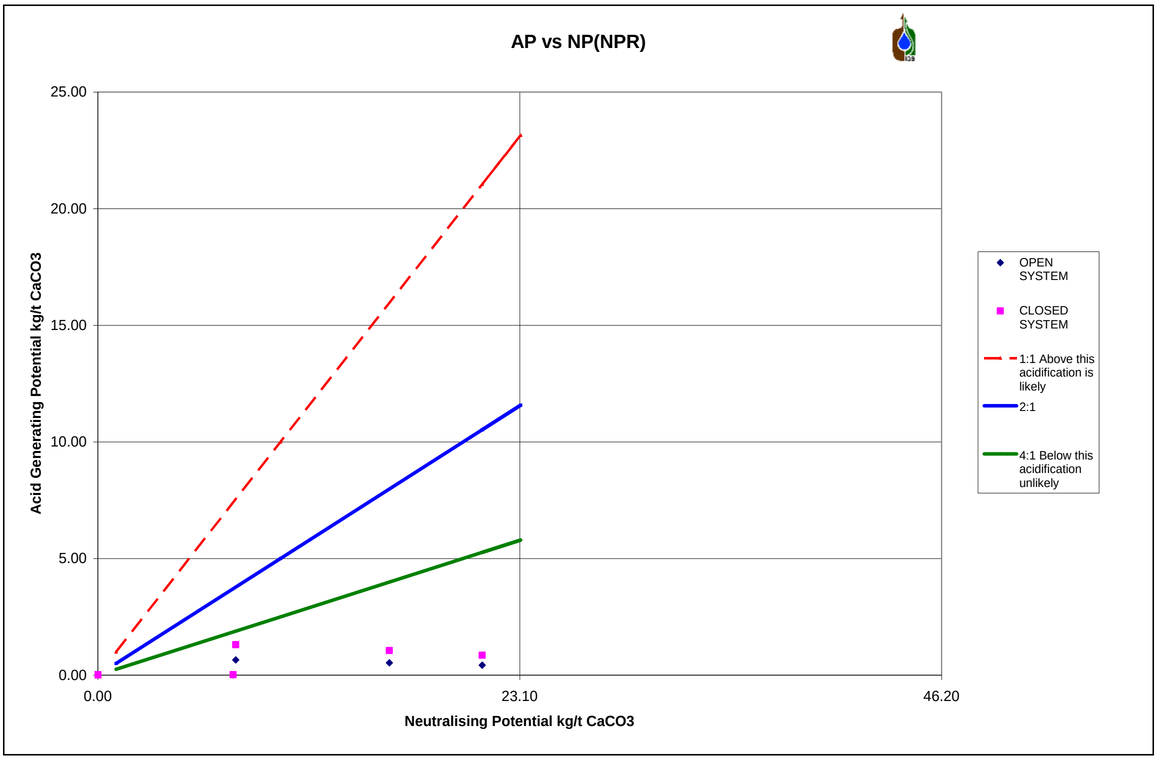


Figure 4-39 Graphical presentation of NPR results for Goedehoop Ramp 4.

The percentage sulphur in the samples plotted against the NPR (Figure 4-40) indicates all samples have a very high probability of acidifying since they are all plotted in the green area.

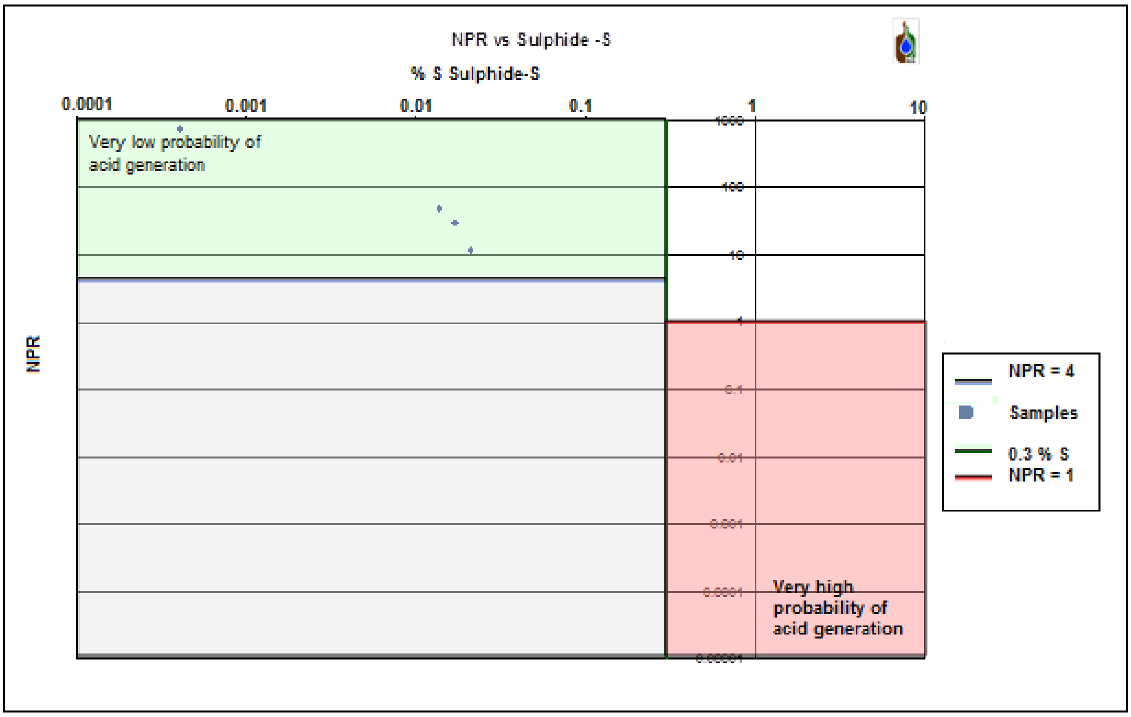


Figure 4-40 % S vs NPR for the Goedehoop Ramp 4 sample

Kinetic results for Goedehoop Ramp 4

Only one sample from the three samples is used in order to verify the Static tests because the static test results were approxiamate. Although the pH of G4-1 had an initial pH of 7.12 in the static test, the kinetic test showed a starting pH of 8.5. The pH differs because the sample used during the static test analysis is pulverised whereas chips are used in the Kinetic test. The pH in the Kinetic tests later dropped as the weeks progressed and then erratic values were effident. The six outliners circled in red might be due to personal, instrumental or analytical errors.

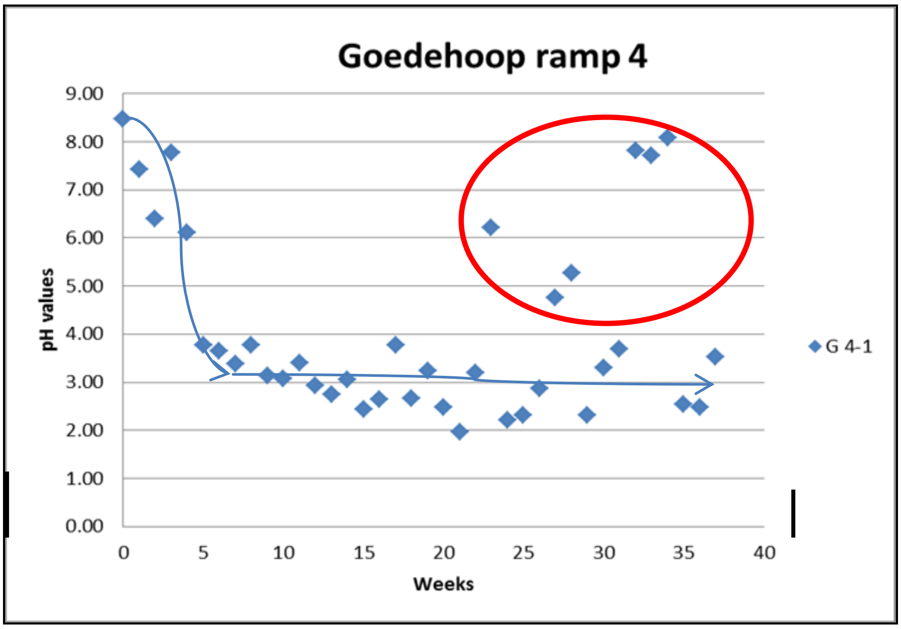


Figure 4-41 Kinetic cell pH value for Goedehoop Ramp 4.

From week 1 the pH for G4-1 shows erratic value but the SO4 load goes up to 1600 mg/kg/week in week 21 (Figure 4-42). It is usual to have erratic readings the first few weeks because of the removal of readily soluble components from prior oxidation or weathering.

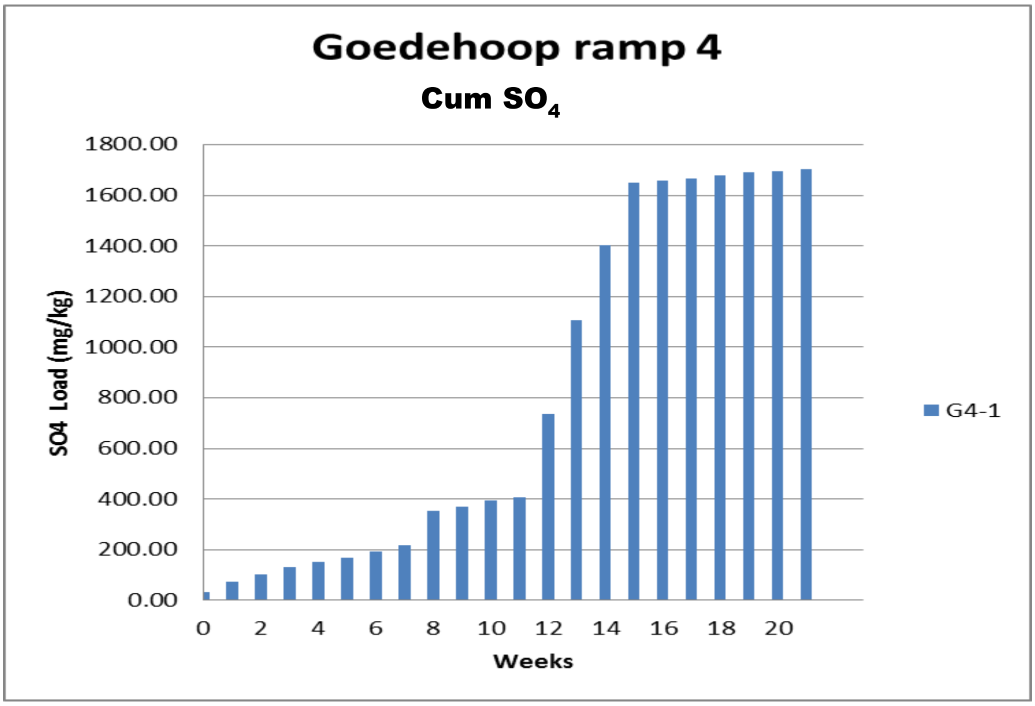


Figure 4-42 Cumulative SO_4 of Goedehoop Ramp 4 sample.

4.7.2 Hartebeesfontien

Figure 4-43 shows the location of 28 samples that were analysed for Hartebeesfontein area.

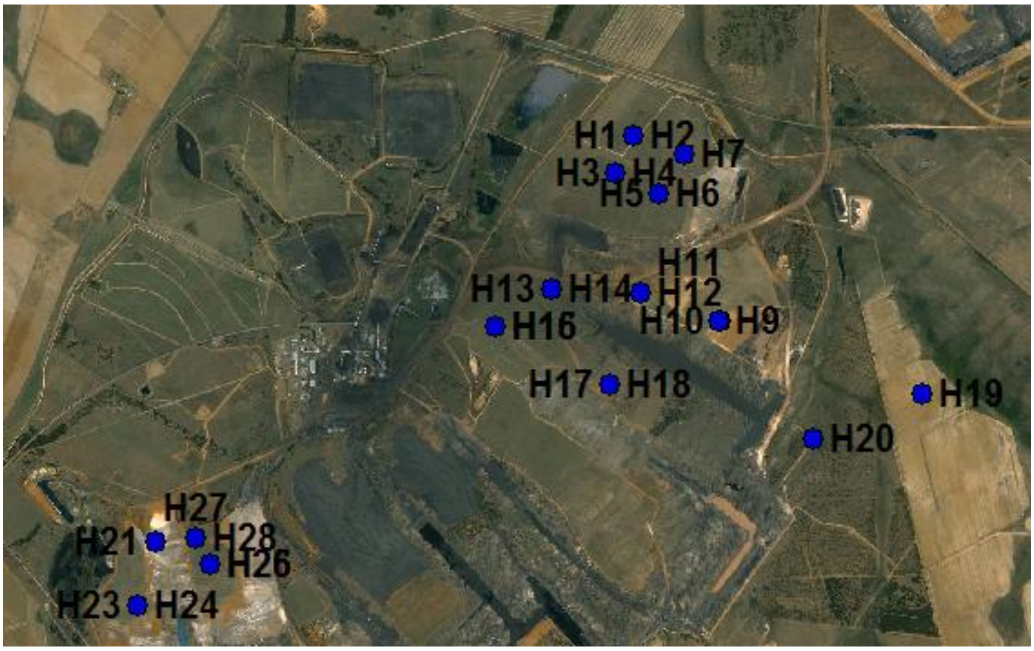


Figure 4-43 Sampling points of Hartebeesfontein area.

Mineralogical analysis of the Hartebeesfontein area

One half of the Figure 4-9 samples consist predominantly of quartz and kaolinite with traces of potassium feldspar while the other mainly consists of quartz to a lesser extent kaolinite and potassium feldspar. In both sections the presence of buffering material such as calcite or dolomite is largely absent. Two (H19 and H20) sample have an accessory mineral as pyrite (Table 4-10)

Table 4-10 Mineralogical analysis of Hartebeesfontein

Sample	**Q**	**Kaol**	**Illite**	**Kvsp**	**Pyrite**	**Calcite**	**Montm**	**Gyp**	**Sid**	**Hem**	**Pyrr**	**Dol**
H1	XX	XX		xx		<x						
H2	XX	XX		xx								
H3	XX	XX	X	x								
H4	XX	XX	x	xx								

H5	XX	XX	<x	<x								
H6	XX	XX	x	<x								
H7	XX	xx	x	xx		<x						
H8	XX	X	x	xx								
H9	XX	X	x	xx								
H10	XX	X	x	xx								
H11	XX	X	x	x					x			
H12	XX	X	x	xx					x			
H13	XX	X	x	xx								<x
H14	XX	XX	x	xx								
H15	XX	X	xx	xx								
H16	XX	X	x	xx								
H17	XX	X	xx	xx								
H18	XX	X	x	xx								
H19	XX	XX			<x							
H20	XX	XX			<x							
H21	XX	X	x	XX								
H22	XX	xx	x	XX								
H23	XX	X	xx	xx					<x			
H24	XX	X	xx	xx					<x			<x
H25	XX	XX	x	X					<x			
H26	XX	XX	x	xx					<x			
H27	XX	xx	x	xx					<x			<x
H28	XX	xx	x	xx								

Static results of the Hartebeesfontein area

Most of the samples have a pH that is slightly acidic or alkaline except for H-20 (Table 4-11). All of the samples indicate that they have a medium-high risk of acid generation.

Table 4-11 Interpretation of ABA pH and NAG results for Hartebeesfontein.

Site Name	**Initial pH**	**Final pH**	**Interpretation**
H-1	7.14	4.00	Medium Risk Acid Generation
H-2	7.29	3.33	Higher Risk Acid Generation
H-3	6.06	2.63	Higher Risk Acid Generation
H-4	5.74	2.58	Higher Risk Acid Generation
H-5	4.76	2.22	Higher Risk Acid Generation
H-6	4.95	1.94	Higher Risk Acid Generation
H-7	5.30	2.47	Higher Risk Acid Generation
H-8	5.07	2.22	Higher Risk Acid Generation
H-9	6.30	2.97	Higher Risk Acid Generation
H-10	5.74	2.76	Higher Risk Acid Generation
H-11	7.86	4.62	Medium Risk Acid Generation
H-12	8.27	4.52	Medium Risk Acid Generation
H-13	5.42	3.21	Higher Risk Acid Generation
H-14	6.48	3.27	Higher Risk Acid Generation
H-15	6.43	3.28	Higher Risk Acid Generation
H-16	7.30	3.43	Higher Risk Acid Generation
H-17	7.21	2.63	Higher Risk Acid Generation

H-18	6.26	2.56	Higher Risk Acid Generation
H-19	5.24	1.29	Higher Risk Acid Generation
H-20	4.13	1.33	Higher Risk Acid Generation
H-21	7.24	3.54	Medium Risk Acid Generation
H-22	7.37	3.79	Medium Risk Acid Generation
H-23	7.17	1.94	Higher Risk Acid Generation
H-24	7.33	2.96	Higher Risk Acid Generation
H-25	8.15	3.55	Medium Risk Acid Generation
H-26	8.07	3.70	Medium Risk Acid Generation
H-27	6.88	3.10	Higher Risk Acid Generation
H-28	6.99	3.65	Medium Risk Acid Generation

Grouped into two groups, H1-H20 samples (circled in blue) had an average initial pH of 6.1 and H21 –H28 had an average initial pH 7.4 (Figure 4-44).

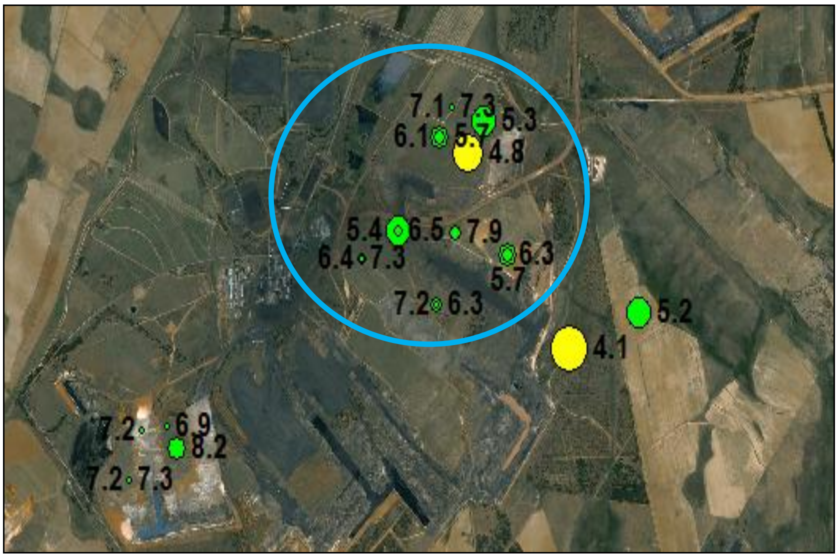


Figure 4-44 Initial pH showing Hartebeesfontein samples.

From H1-H20 an average final pH of 2.9 indicates a medium-high risk of acid generation upon oxidisation and then H21–H28 has an average final pH of 3.3, which indicates a medium-high risk of acid generation upon oxidisation. Most of the Hartebeesfontein ABA Static results had a LOW pH after complete oxidation therefore indicating a high possibility of AMD in the area (Figure 4-45).

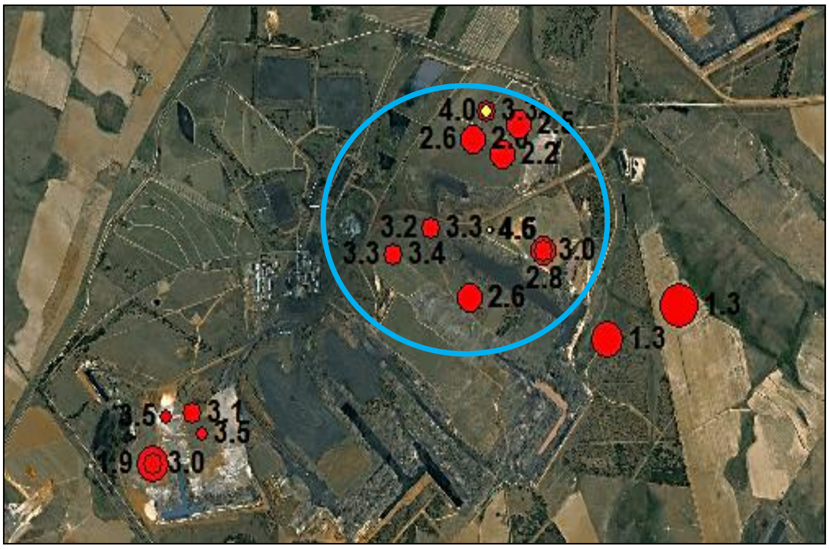


Figure 4-45 Final pH showing Hartebeesfontein samples

Hartebeesfontein values (Figure 4-46) of twenty three sample show a negative net neutralising potential therefore suggesting that the sample will likely produce acidic conditions. Five samples show a positive Net Neutralising potential suggests that the samples would unlikely generate acidic conditions.

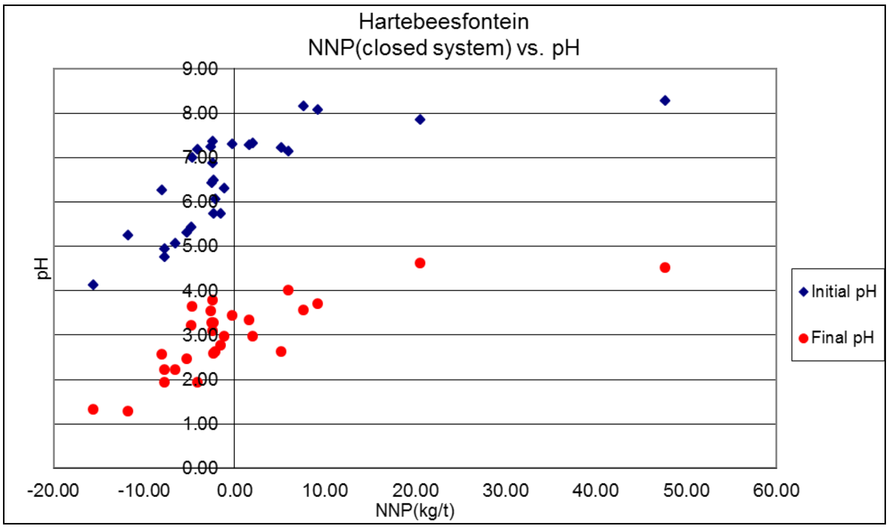


Figure 4-46 NNP Hartebeesfontein results.

The open and closed NNP is interpreted in Table 4-12 where it indicates negative values as potential acid generator and most of the samples need to be verified with Kinetic tests. Only two samples indicate the probability of having excess neutralising minerals. The orange results indicate the potential of acid generation.

Table 4-12 Interpretation of ABA Net Neutralising Potential results.

Site Name	**Net Neutralising Potential (Open)**	**Net Neutralising Potential (Closed)**	**Interpretation**
H-1	5.505	5.943	Verify with other tests
H-2	0.851	1.634	Verify with other tests
H-3	-0.590	-1.180	Verify with other tests
H-4	-0.575	-1.149	Verify with other tests
H-5	-0.291	-0.583	Verify with other tests
H-6	-0.222	-0.443	Verify with other tests
H-7	-0.275	-0.550	Verify with other tests
H-8	-0.631	-1.262	Verify with other tests
H-9	-0.256	-0.511	Verify with other tests
H-10	0.650	1.300	Verify with other tests
H-11	21.851	20.617	Probably Excess Neutralising Minerals
H-12	48.325	47.687	Probably Excess Neutralising Minerals
H-13	-0.092	-0.183	Verify with other tests
H-14	-0.163	-0.327	Verify with other tests

H-15	-0.164	-0.328	Verify with other tests
H-16	-0.029	-0.228	Verify with other tests
H-17	7.103	5.197	Verify with other tests
H-18	-1.209	-2.419	Verify with other tests
H-19	-3.970	-11.783	Verify with other tests
H-20	-4.795	-9.589	Verify with other tests
H-21	-0.128	-0.257	Verify with other tests
H-22	-0.118	-0.237	Verify with other tests
H-23	0.626	-4.086	Verify with other tests
H-24	3.698	2.023	Verify with other tests
H-25	9.858	7.715	Verify with other tests
H-26	10.070	9.225	Verify with other tests
H-27	-0.565	-1.130	Verify with other tests
H-28	-0.106	-0.213	Verify with other tests

Table 4-13 Interpretation and NP/AP ratios for Hartebeesfontein.

Site Name	**Neutralising Potential Ratio(NP/AP) for Open System**	**Interpretation Open System**	**Interpretation Closed System**
H-1	1.287	Acid under certain conditions	Likely Acid Generator
H-2	0.023	Likely Acid Generator	Likely Acid Generator
H-3	0.012	Likely Acid Generator	Likely Acid Generator

H-4	0.011	Likely Acid Generator	Likely Acid Generator
H-5	0.016	Likely Acid Generator	Likely Acid Generator
H-6	0.021	Likely Acid Generator	Likely Acid Generator
H-7	0.014	Likely Acid Generator	Likely Acid Generator
H-8	0.013	Likely Acid Generator	Likely Acid Generator
H-9	0.006	Likely Acid Generator	Likely Acid Generator
H-10	0.005	Likely Acid Generator	Likely Acid Generator
H-11	12.794	No Acid Potential	No Acid Potential
H-12	60.161	No Acid Potential	No Acid Potential
H-13	0.023	Likely Acid Generator	Likely Acid Generator
H-14	0.021	Likely Acid Generator	Likely Acid Generator
H-15	0.021	Likely Acid Generator	Likely Acid Generator
H-16	0.368	Likely Acid Generator	Likely Acid Generator
H-17	3.472	Acid under certain conditions	Acid under certain conditions
H-18	0.004	Likely Acid Generator	Likely Acid Generator
H-19	0.458	Likely Acid Generator	Likely Acid Generator
H-20	0.002	Likely Acid Generator	Likely Acid Generator
H-21	0.047	Likely Acid Generator	Likely Acid Generator
H-22	0.051	Likely Acid Generator	Likely Acid Generator
H-23	0.681	Likely Acid Generator	Likely Acid Generator
H-24	2.043	Acid under certain conditions	Acid under certain conditions

H-25	5.204	No Acid Potential	Acid under certain conditions
H-26	11.280	No Acid Potential	No Acid Potential
H-27	0.007	Likely Acid Generator	Likely Acid Generator
H-28	0.018	Likely Acid Generator	Likely Acid Generator

Majority of samples in both open and closed system showed acid generating potential since they plotted above the red line, some are inconclusive and the rest are unlikely to acidify (Figure 4-47).

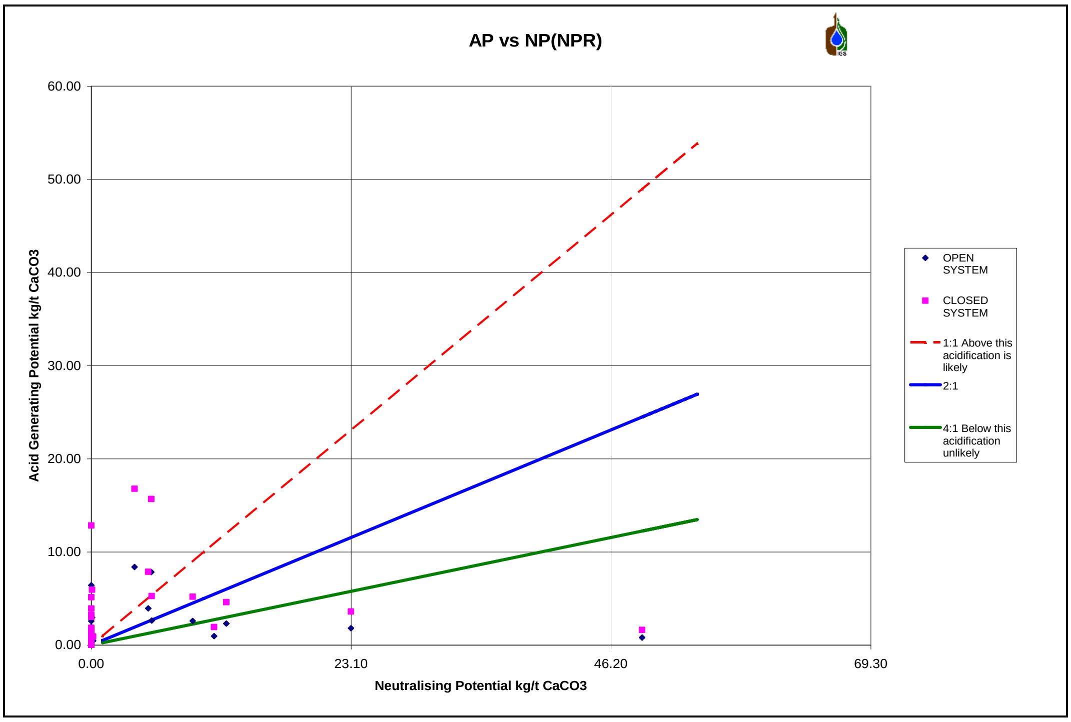


Figure 4-47 Graphical presentation of NPR results for Hartebeesfontein.

The percentage sulphur in the samples plotted against the NPR (Figure 4-48) indicates the majority of the samples as uncertain risk of acid production samples with one sample that is inconclusive. The rest of the samples show a low probability of acid generation.

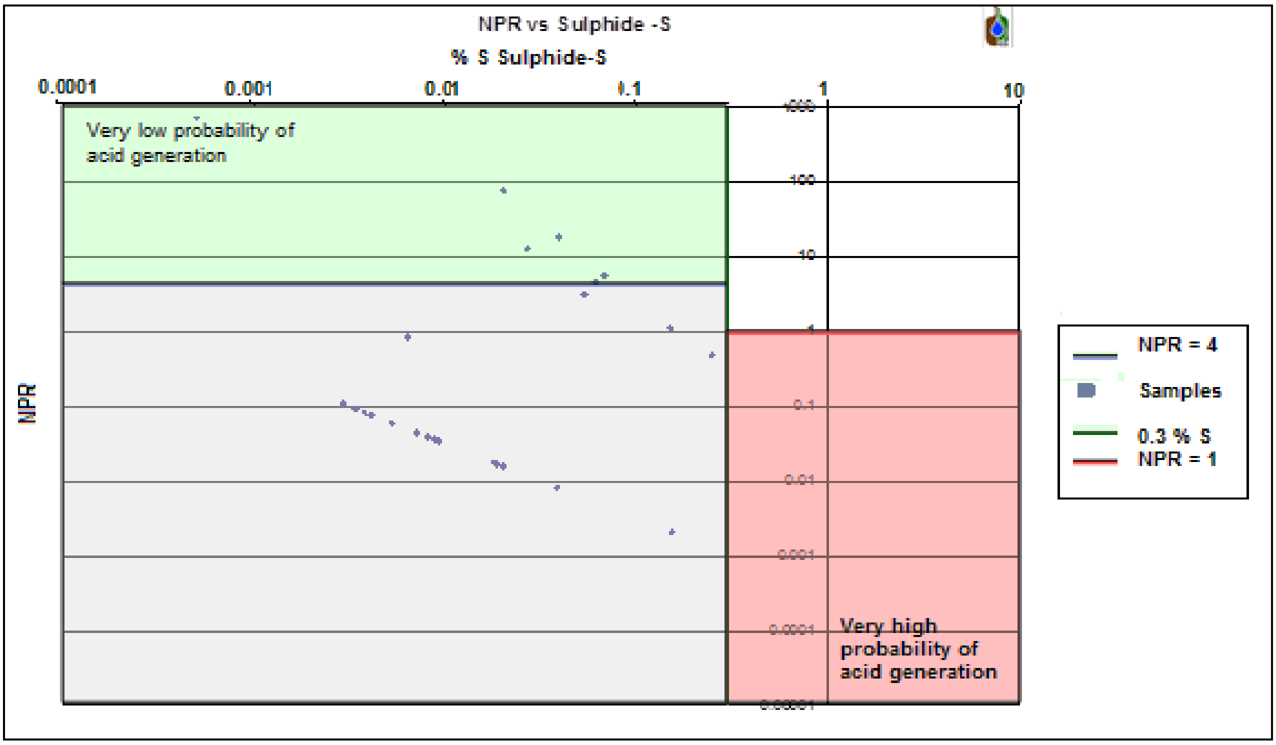


Figure 4-48 % S vs NPR for the Hartebeesfontein samples.

Kinetic results for the Hartebeesfontein area

Three samples that represented different results were chosen for the Kinetic test.

H16 had negative results in NNP closed and open system translating (Table 4-13) into the sample being likely to be an acid generator.

H17 had positive results in NNP closed and open system indicating that the sample will be acidic under certain conditions (Table 4-13) since the NNP is lower than 20 but ranges between 5 and 7 (Table 4-12).

H23 had a negative result in NNP closed system and a positive result in NNP open system that was negative. According to the NP/AP ratio (Table 4-13) the sample will likely generate acid.

All the samples pH stays contant with a little erratic period before week 40 (Figure 4-49).

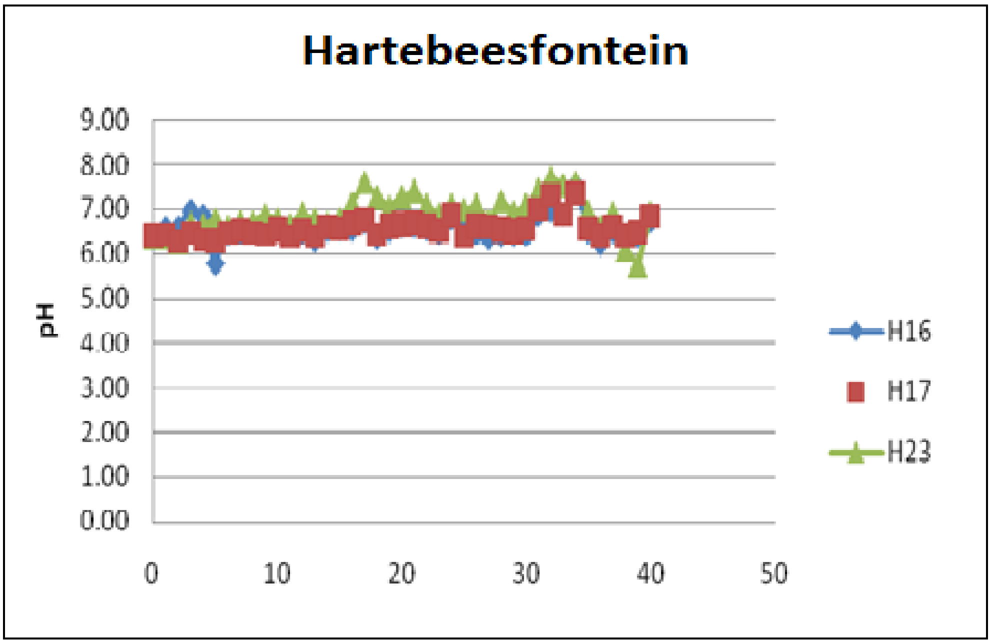


Figure 4-49 Kinetic cell pH value for the Hartebeesfontein.

In Figure 4-50, H23 has the highest value of SO_4 load with H16 showing a lowest SO_4 load. H17 that showed (Table 4-13) that the sample will acidify under certain conditions has the cumulative value that is +/- 980 cum mg/kg after week 20.

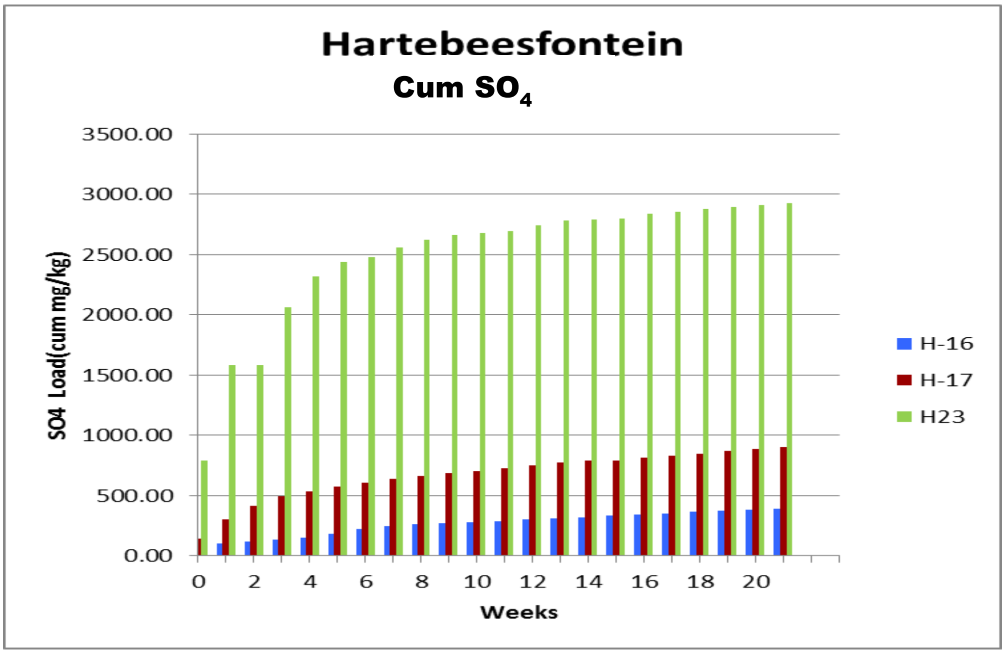


Figure 4-50 Cumulative SO_4 of the Hartebeesfontein samples.

4.7.3 Discards

Seven Samples (Figure 4-51) were taken from the investigated mine and analysed.

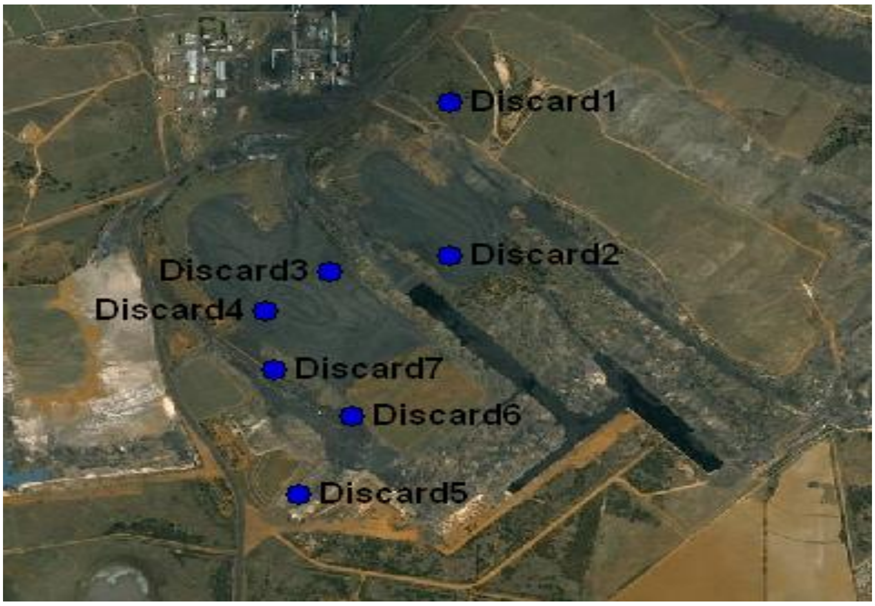


Figure 4-51 Sampling point of Discard samples.

Mineralogical analysis of Discard samples

All samples have quartz and Kaolinite as dominant minerals. The presence of Calcite and pyrite is seen in Discards 5, 6 and 7 as either an accessory or minor mineral. In the instance of the Discard mine area conversion of pyrite to depositional gypsum has occurred readily. The conversion of pyrite to sulphate containing species most likely will occur with an initial buffering reaction taking place with the calcite to form gypsum. The possibility of the oxidation of pyrite to AMD is high with an initial neutralising reaction taking place with the calcite to form gypsum (Table 4-14).

Table 4-14 Mineralogical analysis of Discard samples.

Sample	Q	Kaol	Illite	Kvsp	Pyrite	Calcite	Gyp	Sid	Hem	Pyrr
Discard 1	XX	XX			x			x	<x	
Discard 2	XX	XX	<x		<x		<x			
Discard	XX	XX	<x	<x	x		x	x		

3										
Discard 4	XX	XX	<x	<x			xx		<x	<x
Discard 5	XX	XX	x	<x	<x	x	<x	x		
Discard 6	XX	XX	x	<x	x	x		<x		
Discard 7	XX	XX	<x	<x	x	xx		<x		

Static results for Discard samples

Some of the samples were already partly oxidised prior to the final pH method (Table 4-15)

Table 4-15 Interpretation of ABA pH and NAG results for Discard samples.

Site Name	**Initial pH**	**Final pH**	**Interpretation**
Discard 1	4.57	2.01	Higher Risk Acid Generation
Discard 2	4.12	1.83	Higher Risk Acid Generation
Discard 3	4.23	1.16	Higher Risk Acid Generation
Discard 4	4.14	1.66	Higher Risk Acid Generation
Discard 5	7.69	2.36	Higher Risk Acid Generation
Discard 6	7.99	2.00	Higher Risk Acid Generation
Discard 7	7.52	2.38	Higher Risk Acid Generation

All the discard values show a negative net neutralising potential in Figure 4-52 therefore suggesting that the discards will likely produce AMD.

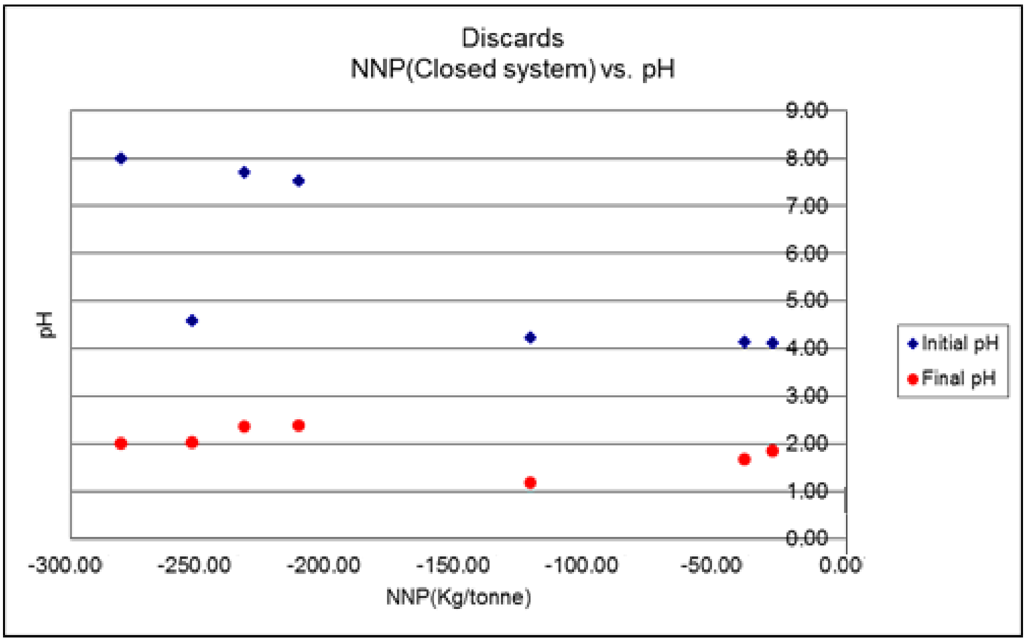


Figure 4-52 NNP results for Discard samples

The average initial pH in Figure 4-53 is 5.8 and the average final pH (Figure 4-55) is 1.9. All samples dropped to values ranging from 1 to 2.4, indicating a high of acid generation upon oxidization.

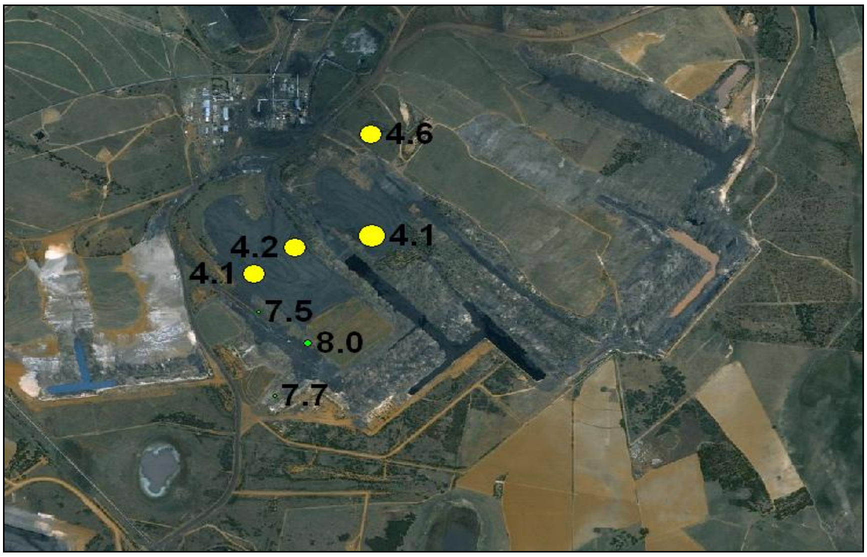


Figure 4-53 Proportional Initial pH showing discard samples.

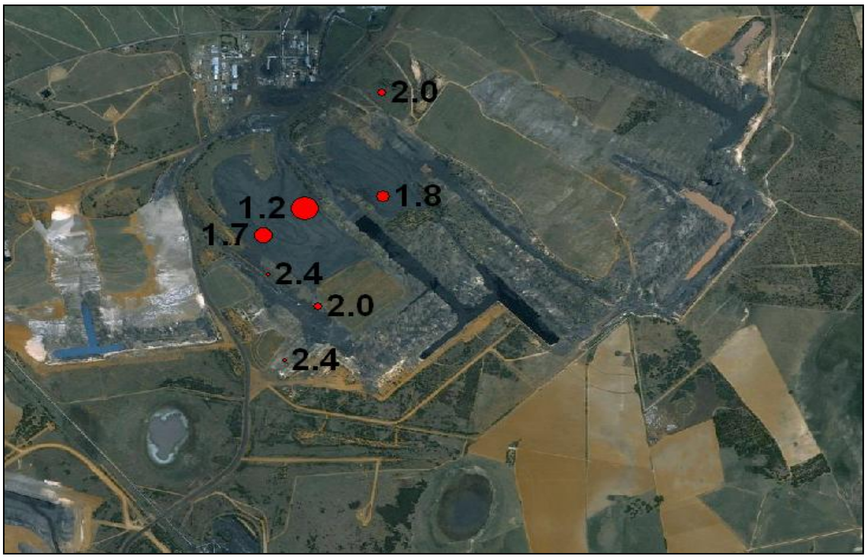


Figure 4-54 Proportional final pH showing discard samples.

The open and closed NNP is interpreted in Table 4-16, it indicates negative values as potential Acid generator. 5 out of 7 seven samples have the potential to generate acid.

Table 4-16 Interpretation of ABA Net Neutralising Potential results for Discard samples.

Site Name	Net Neutralising Potential (Open)	Net Neutralising Potential (Closed)	Interpretation
Discard 1	-113.53	-227.06	Potential Acid Generator
Discard 2	-0.55	-1.10	Verify with other tests
Discard 3	-40.88	-81.76	Potential Acid Generator
Discard 4	0.00	0.00	Verify with other tests
Discard 5	-91.19	-218.11	Potential Acid Generator
Discard 6	-126.24	-276.11	Potential Acid Generator
Discard 7	-80.34	-197.60	Potential Acid Generator

The entire Discard samples batch in both open and closed system (Table 4-17) showed acid generating potential since they plotted above the red line (Figure 4-55).

Table 4-17 Interpretation and NP/AP ratios for the Discard samples.

Site Name	**Neutralising Potential Ratio(NP/AP) for Open System**	**Interpretation Open System**	**Interpretation Closed System**
Discard 1	0.00	Likely Acid Generator	Likely Acid Generator
Discard 2	0.02	Likely Acid Generator	Likely Acid Generator
Discard 3	0.00	Likely Acid Generator	Likely Acid Generator
Discard 4	0.10	Likely Acid Generator	Likely Acid Generator
Discard 5	0.28	Likely Acid Generator	Likely Acid Generator
Discard 6	0.16	Likely Acid Generator	Likely Acid Generator
Discard 7	0.31	Likely Acid Generator	Likely Acid Generator

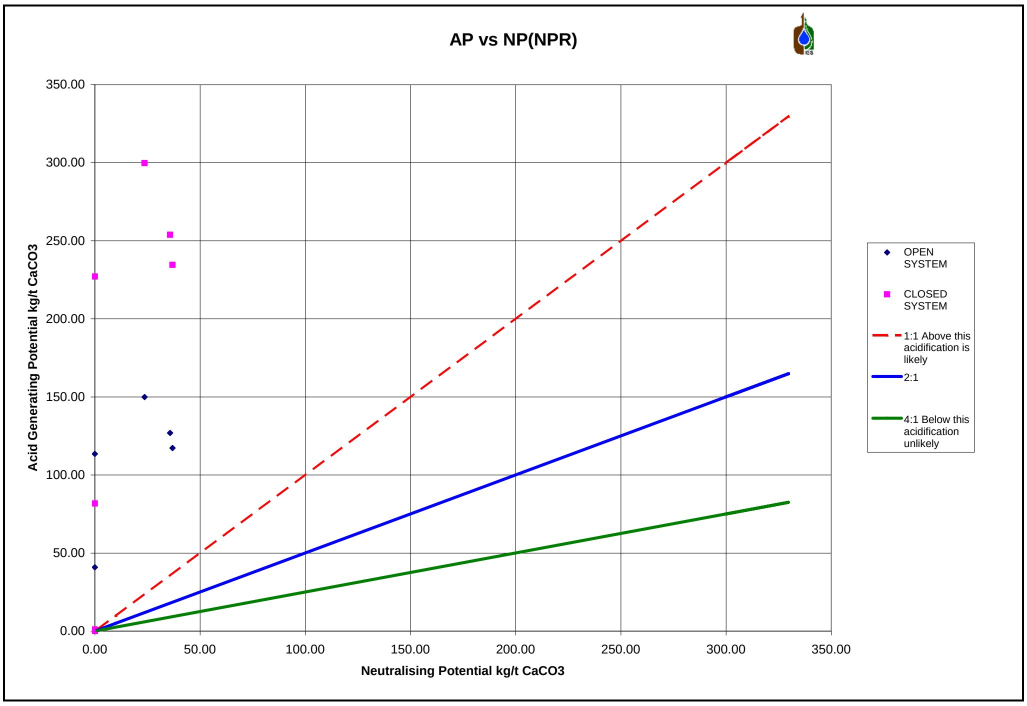


Figure 4-55 Graphical presentation of NPR results for Discards.

The percentage sulphur in the samples plotted against the NPR (Figure 4-56) indicates an uncertain risk of acid production for two of the samples while those with S % of higher than 1 and plotting in the red, indicating a high risk of AMD.

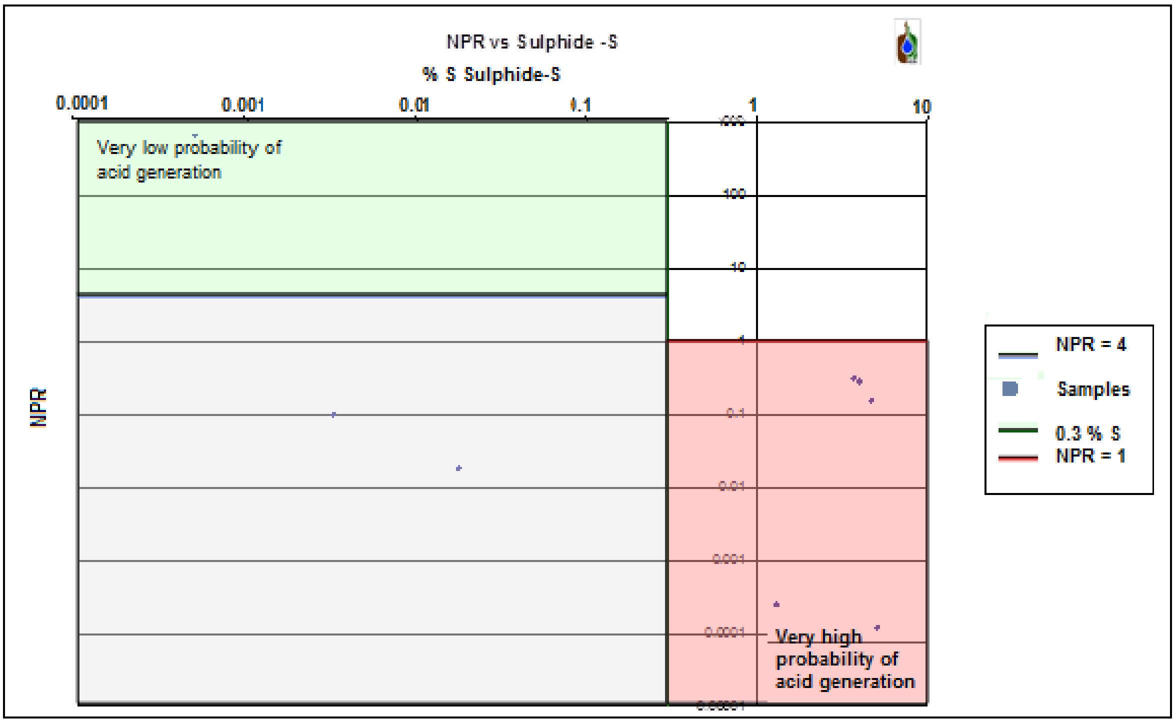


Figure 4-56 %S vs NPR for the Discard samples.

Kinetic results

Two samples that represented different results were chosen for the Kinetic test.

Discard 4 had positive results in NNP closed and open system translating into the sample being likely to be an acid generator (Table 4-17). The results therefore had to be verified by the Kinetic test.

Discard 5 had negative results in NNP closed and open system indicating that the sample is likely to generate acid.

From week 1 the pH for both Discard 4 and 5 was already acidic and stayed constant till week 40 (Figure 4-57).

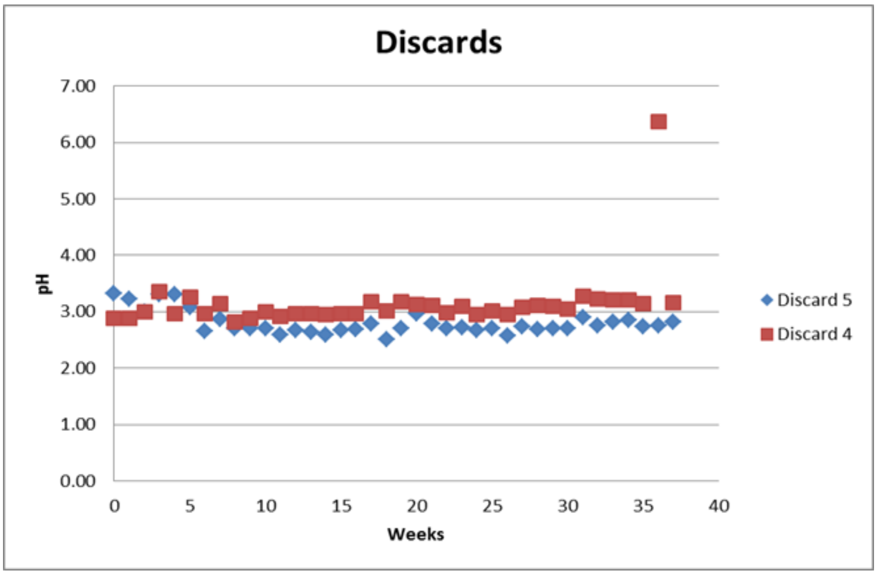


Figure 4-57 Kinetic c ell pH values of the Discard samples.

In Figure 4-58, the cummulative SO_4 of Discard 5 is higher than Discard 4 and it is almost 3000 cum mg/kg. This shows that the samples have high probability of generating AMD.

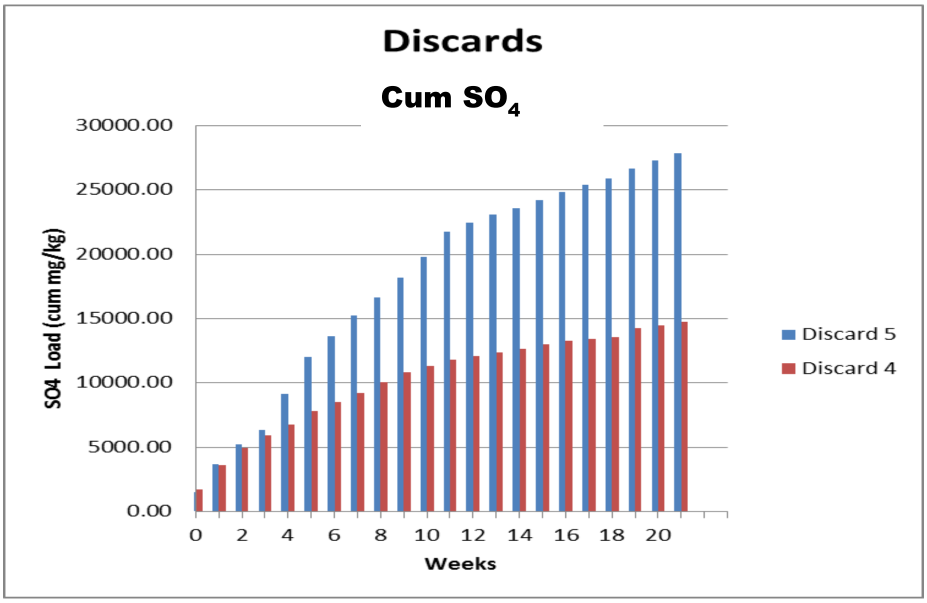


Figure 4-58 Cumulative SO_4 of Discard sample.

4.8 Summary of all sites, results and interpretation

Most of the results (Figure 4-59) fall into the grey area (with more or less 20 kg/t of NNP) and need other tests to verify. Samples that have a negative NNP are high risk acid potential and should be treated immediately.

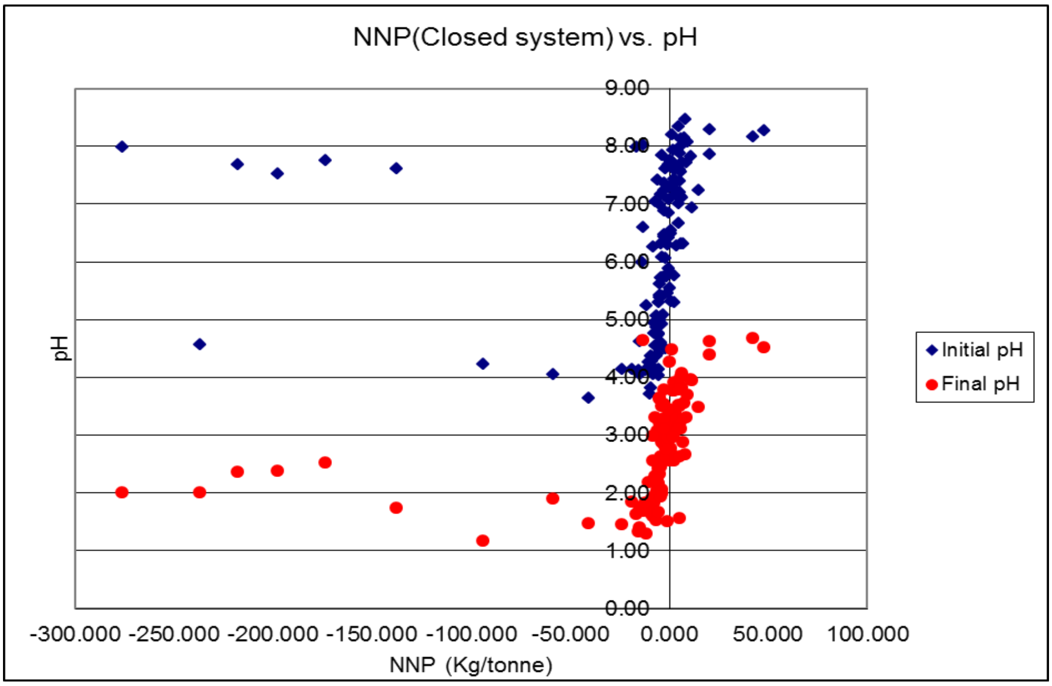


Figure 4-59 NNP results of all the investigated sites.

The majority of the samples (Figure 4-60) have a neutralising potential that is less than 50 kg/t and Acid generating potential lower than 50. Only a few closed- and 4 open systems show clearly that they will likely generate acidic conditions.

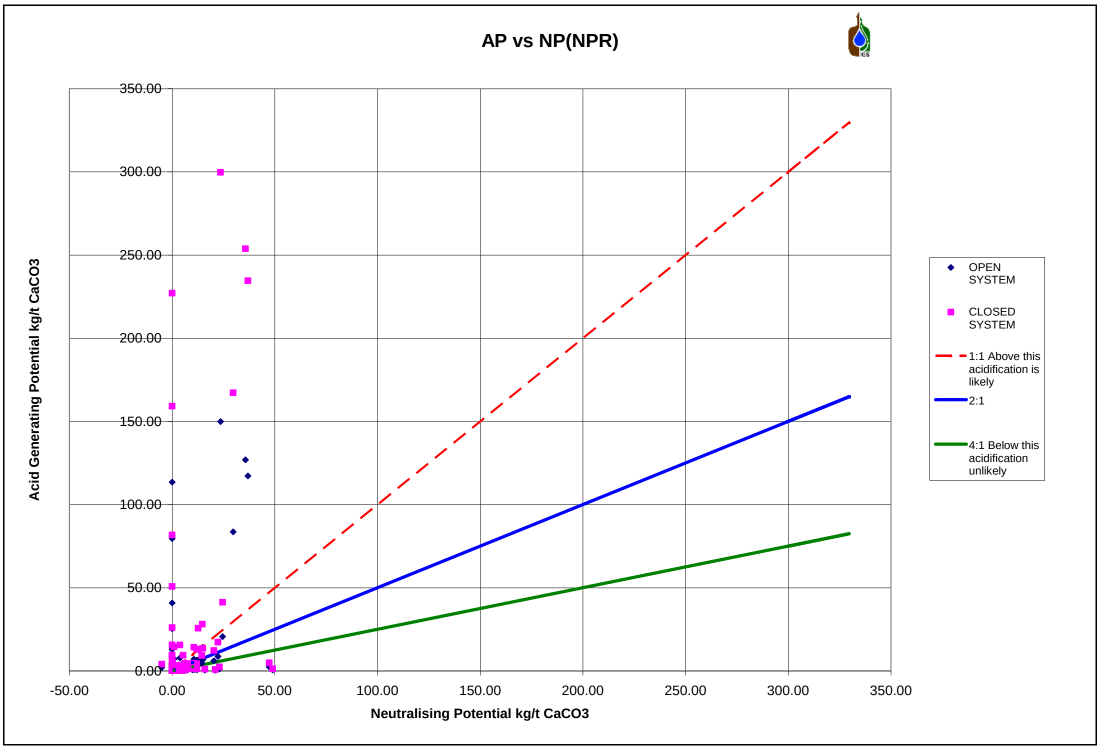


Figure 4-60 NPR results for all the investigated sites.

4.8.1 Static results versus Humidity cell pH

There are two important parameters that need to be considered in ABA. As already mentioned under the methodology section in this chapter, pH is the first parameter used to provide the actual acidity of the sample from the onset. It helps identify samples that need to be verified by other tests such as Kinetic tests. pH should also be taken during the first day of humidity cell testing because samples that are pulverised don't often have the same pH value as the chips.

The initial pH's of the humidity cells selected are summarised in Table 4-18 together with the initial static ABA done on the pulverized sample of the chips.

Table 4-18 Initial pH's of humidity cell samples vs paste pH (static ABA).

Samples	Lab number	Initial pH (static ABA)	Initial pH (chips) Humidity Cells
G1-1	M-1	3.65	2.40
G1-2	M-2	6.00	3.38
G2-3	M-5	6.66	3.72
G3-3	M-12	5.89	4.57
G3-6	M-15	6.59	2.75
G4-1	M-17	7.12	5.68
G5-3	M-23	7.75	5.68
G5-5	M-25	7.72	6.45
G5-6	M-26	7.42	6.43
G6-3	M-30	8.00	6.37
G7-2	M-32	6.08	5.65
G10-5	M-42	6.42	5.98
KN2-2	M-46	5.46	4.20
KN2-4	M-48	6.84	6.25
KN2-5	M-49	6.31	3.61

KN3-2	M-53	8.12	7.65
KS1-2	M-56	7.59	6.71
KS1-3	M-57	7.70	6.68
KS2-4	M-62	5.41	4.18
KS3-5	M-67	6.31	5.90
KS3-6	M-68	7.74	6.98
KS4-2	M-74	5.73	4.12
Slurry 2	M-84	8.02	6.52
Slurry 6	M-88	7.65	7.04
Slurry 9	M-91	8.47	7.31
Discard 4	M-96	4.14	2.88
Discard 5	M-97	7.69	3.33
H-16	H-16	7.30	6.35
H-17	H-17	7.21	6.38
H-23	H-23	7.17	6.37

The humidity cells that had an excess acid potential (AP) over neutralising potential had an initial pH that was not as low as the initial pH of the humidity cells. The pH's of some other humidity cell samples did not turned acidic after 20 weeks although the final pH (static ABA) indicates an acid producing sample upon oxidation. These cells are very important to consider. In the static testing section, it was shown that this was a potentially acid-generating portion, but the limitation was added that it was considered to have insufficient sulphide to generate long-term acidity. The pH recovery observed in these humidity cells is therefore of utmost importance since it suggests that these samples may generate acidity but only for a short period of time. The pH from the kinetic test is shown in Figure 4-61.

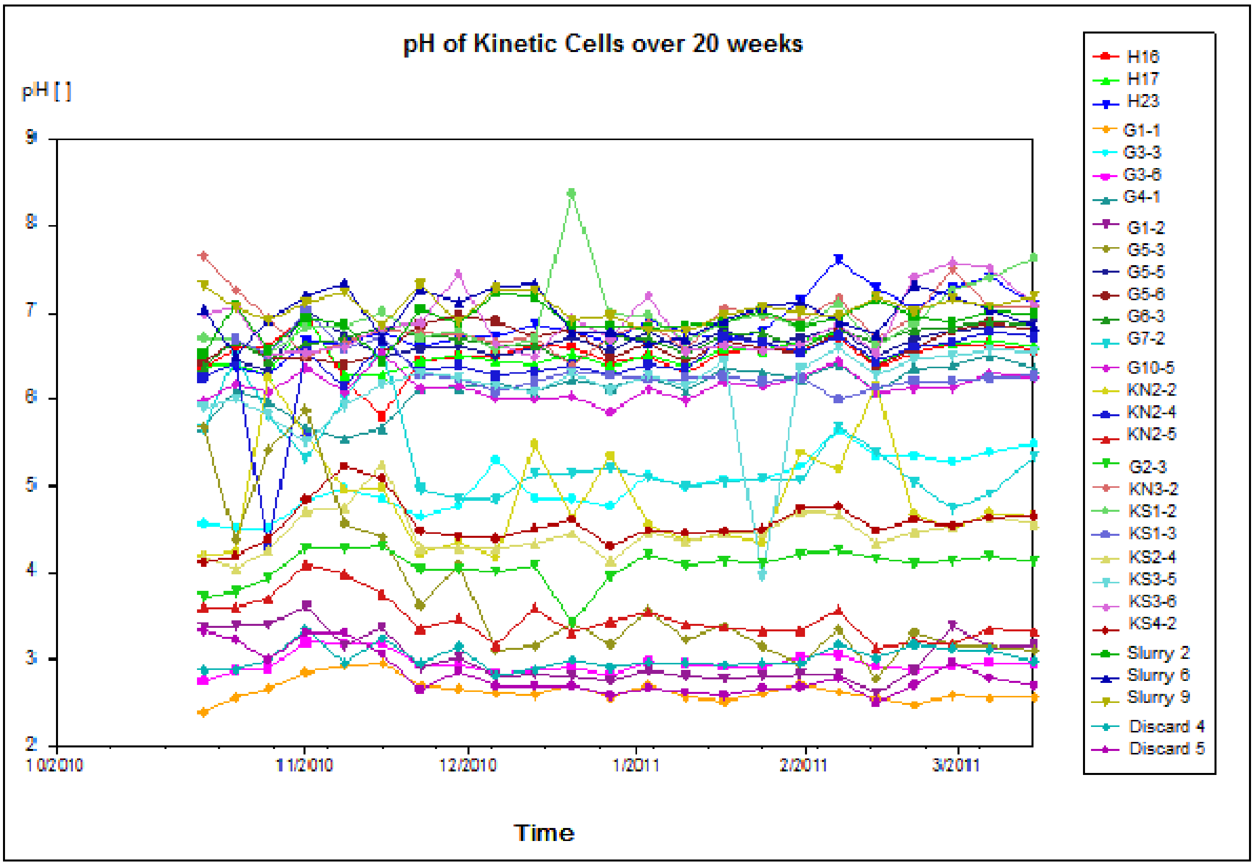


Figure 4-61 pH value over 20 weeks for each cell

pH and sulphate production often go hand in hand when it comes to samples turning acidic, so the next important parameter is SO_4. The cumulative mass of SO_4 produced (Figure 4-62) shows more clearly how the samples acidifying quicker, continue to produce sulphate at a greater rate than the other cells. The cumulative plot flattens over the course of the testing to provide a better spread of production rates. The gradient of the cure provides an indication of the relative rates, showing that the initially high sulphate production is temporal and reaches similar rates as the other cells.

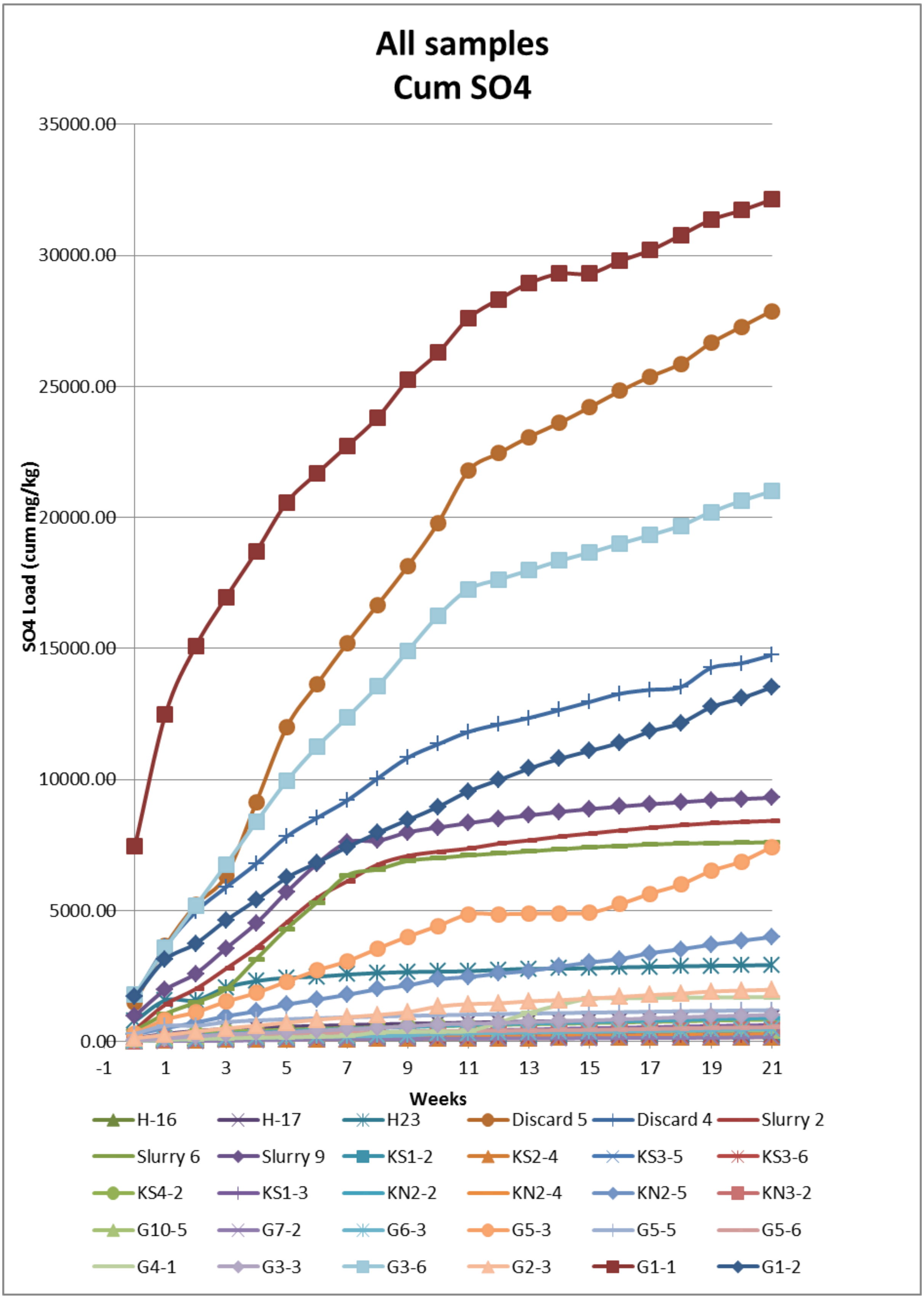


Figure 4-62 Cumulative sulphate production for each cell.

Figure 4-63 shows the cumulative values of calcium, magnesium and iron produced that gives an indication that the TDS load will go higher as oxidation occurs. The cumulative plot flattens over the course of the testing with the indication of relative rates.

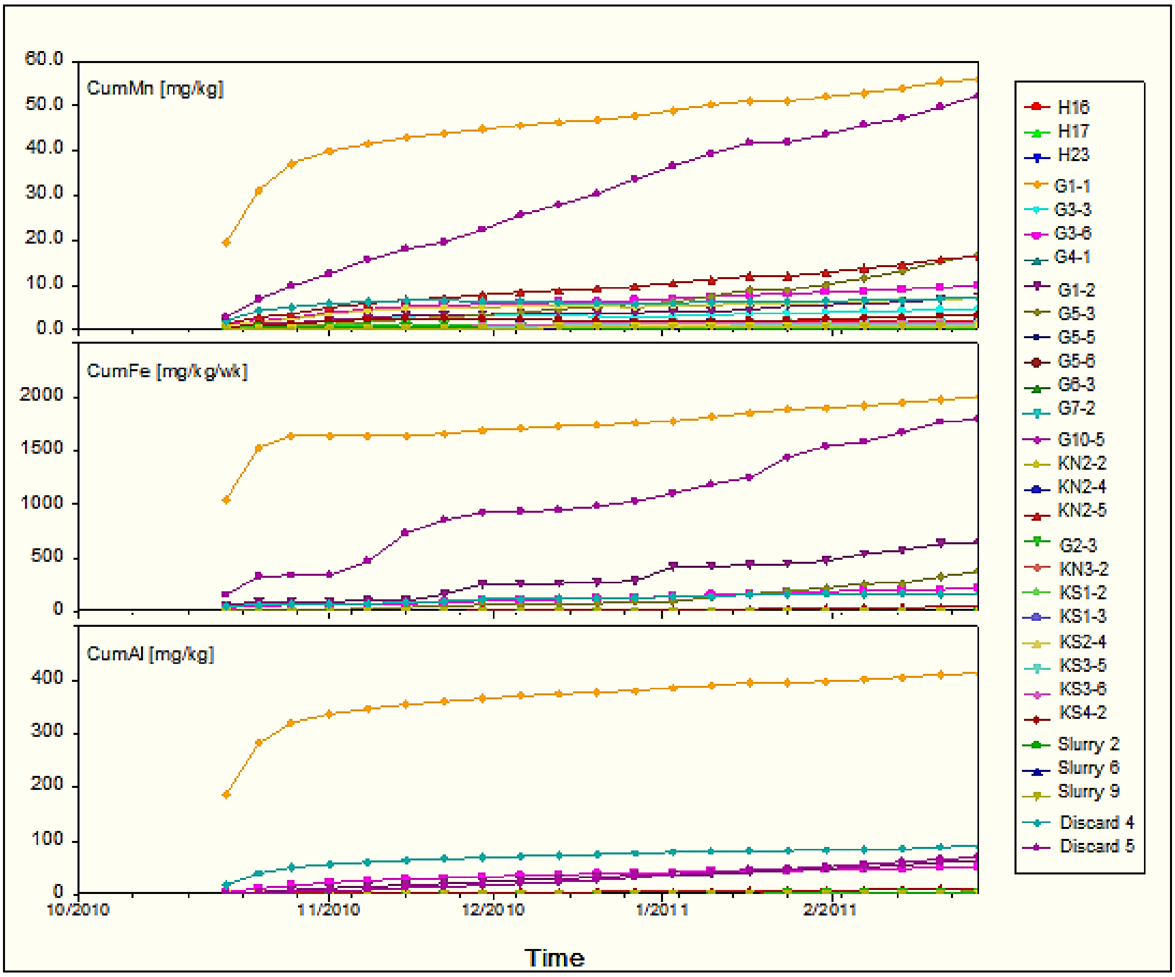


Figure 4-63 Cumulative Ca, Fe and Al.

According to the leachate analysis done during Kinetic testing, Discards have highest acid generating risk highest salt load and SO_4 concentration while Klipfontein North has the lowest results. The highest and lowest value for each facility is highlighted in red and green.

Table 4-19 Cumulative values of the major ions from the humidity cells after 20 weeks (mg/kg).

Klipfontein North											
Site name	**Lab Number**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO4**	**Al**	**Mn**	**Fe**	**Average**
KN2-2	**M-46**	137.1	68.2	48.7	30.6	29.2	828.3	0.0	7.2	0.0	127.7
KN2-4	**M-48**	71.9	42.9	34.1	37.9	17.8	281.7	0.0	0.0	0.0	54.0
KN2-5	**M-49**	498.4	118.3	45.3	27.0	27.4	3713.9	13.0	17.3	65.8	502.9
KN3-2	**M-53**	0.0	66.3	39.0	47.3	23.5	0.0	0.0	0.0	0.0	19.6
Average cumulative value		176.9	73.9	41.8	35.7	24.5	1206.0	3.2	6.1	16.5	176.1

Hartebeesfontein											
Site name	**Lab Number**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO4**	**Al**	**Mn**	**Fe**	**Average**
H-16	**H-16**	339.3	160.4	46.6	26.3	30.7	756.2	5.1	1.9	0.0	151.8
H-17	**H-17**	436.9	263.4	39.9	49.1	21.3	2138.8	0.0	0.0	0.0	327.7
H-23	**H-23**	140.3	45.6	43.0	59.7	17.6	1850.4	0.0	0.0	0.0	239.6
Average cumulative value		305.5	156.5	43.2	45.0	23.2	1581.8	1.7	0.6	0.0	239.7

Klipfontein South											
Site name	**Lab Number**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO4**	**Al**	**Mn**	**Fe**	**Average**
KS1-2	**M-56**	31.8	10.1	56.6	47.8	24.6	158.5	0.0	0.0	0.0	36.6
KS1-3	**M-57**	1951.7	169.3	35.2	56.2	15.1	638.8	0.0	0.0	638.8	389.5
KS2-4	**M-62**	62.4	44.9	40.7	30.8	25.7	318.8	0.0	0.0	0.0	58.1
KS3-5	**M-67**	73.1	54.7	35.1	30.0	16.8	220.3	0.0	0.0	0.0	47.8
KS3-6	**M-68**	147.9	70.5	36.7	36.0	22.9	748.3	0.0	0.0	0.0	118.0
KS4-2	**M-74**	2138.4	305.1	38.6	41.3	18.0	7969.6	0.0	0.0	0.0	1167.9

Average cumulative value		734.2	109.1	40.5	40.3	20.5	1675.7	0.0	0.0	106.5	303.0

Goedehoop

Site name	Lab Number	Ca	Mg	Na	K	Cl	SO4	Al	Mn	Fe	Average
G1-1	**M-1**	3132.1	649.3	53.6	13.6	93.1	32127.3	414.5	56.5	2023.7	4284.9
G1-2	**M-2**	1951.7	169.3	44.6	13.8	32.4	638.8	62.4	7.5	638.8	395.5
G2-3	**M-5**	140.3	45.6	39.8	28.8	18.5	1850.4	4.0	1.5	0.0	236.5
G3-3	**M-12**	119.8	58.1	38.3	30.7	18.9	979.8	0.0	4.8	0.0	138.9
G3-6	**M-15**	3133.7	141.2	37.9	11.7	54.4	19246.7	53.2	10.1	230.0	2546.5
G4-1	**M-17**	178.8	23.4	31.9	21.9	23.7	1672.0	0.0	0.0	0.0	216.9
G5-3	**M-23**	1609.6	466.6	54.0	37.1	20.9	7124.8	7.1	18.1	431.5	1085.5
G5-5	**M-25**	3132.1	649.3	42.5	43.9	15.5	32127.3	0.0	0.0	2023.7	4226.0
G5-6	**M-26**	88.8	58.9	34.1	38.5	18.4	481.7	0.0	0.0	0.0	80.0
G6-3	**M-30**	174.4	78.2	35.8	51.4	18.6	453.9	0.0	0.0	0.0	90.3
G7-2	**M-32**	32.9	19.6	43.9	35.4	30.9	169.7	0.0	0.0	0.0	36.9
G10-5	**M-42**	71.2	32.4	38.3	35.8	23.4	357.3	0.0	0.0	0.0	62.0
Average cumulative value		1147.1	199.3	41.2	30.2	30.7	8102.5	45.1	8.2	445.7	1116.7

Slurry

Site name	Lab Number	Ca	Mg	Na	K	Cl	SO4	Al	Mn	Fe	Average
Slurry 2	**M-84**	1782.2	337.6	51.2	30.6	42.7	7189.3	0.0	0.0	0.0	1048.2
Surry 6	**M-88**	2605.8	369.5	39.7	28.1	31.7	8311.5	0.0	0.0	0.0	1265.1
Slurry 9	**M-91**	2863.2	452.3	49.4	27.6	28.4	13090.4	0.0	0.0	184.3	1855.1
Average cumulative value		2417.0	386.5	46.8	28.8	34.3	9530.4	0.0	0.0	61.4	1389.5

Discards											
Site name	**Lab Number**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO4**	**Al**	**Mn**	**Fe**	**Average**
Discard 4	**M-96**	2459.7	1275.7	49.1	12.7	49.7	26535.1	91.4	7.3	1888.0	3596.5
Discard 5	**M-97**	285.4	39.5	50.9	19.6	53.4	354.5	72.6	53.7	0.1	103.3
Average cumulative value		1372.6	657.6	50.0	16.1	51.5	13444.8	82.0	30.5	944.0	1849.9

From the static and kinetic tests done on the samples from Middelburg North Mine, it is clear that acid mine drainage will be produced from most of the samples over the area upon oxidation and that there is very limited potential available to buffer the acid generated. The volume of the samples containing base potential as well as the distribution over the area will determine the actual potential of base that can be utilized to buffer the acid produced. Although some samples have a base potential, It is also clear that overall the acid production cannot be buffered by the small distribution of the base potential samples.

4.9 Conclusion and Recommendations on chapter 4

The mineralogy of the investigated area shows that most samples contain quartz and kaolinite and that calcite and dolomite was only detected in trace amounts. In contrast the presence of pyrite could be observed and it also disproved the ability of the samples to neutralise. Three principal components of the system are pyrite, calcite and dolomite. The absence of calcite and/or dolomite from the general mineralogy has a significant effect on sulphate load produced (i.e., Goedehoop, Klipfontein North). If calcite is present in the structure a lowering in sulphate load is observed due to the buffering capacity of the system (i.e., Klipfontein South). The Discards and Slurry systems have elevated levels of pyrite concentration in the structure which results in elevated sulphate loads in spite of a higher buffering capacity.

- Only 4.7% of the samples analysed in the static test method showed a net neutralizing potential while in the kinetic tests results only a handful of the samples shows a low salt load compared to the rest.

- Limited buffering capacity of the samples is available if any.
- The investigated collieries showed a high to medium risk of acid-generation upon oxidation. Summary of the investigated collieries are as follows:

  Hartebeesfontein:

  Most of the samples in this mine have the possibility of AMD production. There is potential available to buffer acid generated from some samples.

  Goedehoop Ramp 1 and 2:

  AMD will be produced upon oxidation and there is no buffering potential.

  Goedehoop Ramp 4:

  Most of the samples have potential for neutralization.

  Goedehoop Ramp 6:

  The samples have a possibility of might turn acidic.

  Goedehoop Ramp 3, 5, 7 and 10:

  Most of the samples will produce AMD because the buffering potential is very low.

  Klipfontein North:

  Most of the samples indicated that AMD can occur under certain conditions therefore most of the samples plotted within the grey (uncertain) zone and requires verification.

  Klipfontein South:

  Most of the samples show a low potential for AMD due to the base potential of some of the samples.

  Slurry and Discard dumps:

  High potential for acid mine drainage.

- With the prediction of AMD results, control measures can be put in place. The most primary objectives of acid mine drainage treatment is to remove metals (i.e. sulphides, hydroxides and carbonates) and raise the pH to alkalinity. Passive or Active treatments could be used.
- Deterioted water quality caused by the coal mining area could be remediated and released into the Upper Olifants river catchment. The recommended pH value is more than 6.0 when it comes to stabilising acid mine drainage, this pH is ideal because it can hydrolyse Fe_3^+ and Al^{3+} that will create mineral acidity.

CHAPTER 5

5. Overall conclusions and recommendations

This thesis investigated the South African and Australian ABA methodologies and extended the geochemical investigation of the Middelburg North Mines.

Chapter 1 discussed a basic overview of the thesis whereas chapter two included the literature research based on the processes/stages of AMD, the importance of microbiological influence and the oxidation and reduction of sulphate.

AMD occurs when the sulphide-bearing minerals are exposed by mining operations/constructions to oxygen and water. Leaching solution therefore affects the groundwater quality. AMD is a severe environmental pollutant that faces coal and other sulphide-containing ore mining operations because it generates a high salt load and acidity of the water that can have manifold environmental consequences.

This simple definition of AMD belies the complexity of reactions that give rise to the contaminated water.

The geochemical reactions that are related to AMD are

1) Oxidation of sulphide minerals
2) Dissolution of carbonates, oxyhydroxides and silicates
3) Precipitation of oxyhydroxides
4) Dissolution and precipitation of sulphate minerals

These geochemical reactions associated with AMD may/may not produce an alarming rate of pollution depending on the neutralising capacity of the system at equilibrium conditions. Some reactions may produce other metals (i.e. Al) that are soluble in the event of buffering and cause more damage to the environment.

Although bacterial analysis were not performed in this study it was important to emphasis the role of bacteria in the AMD process because the bacteria has the ability to accelerate the rate of oxidation by converting insoluble metal sulphate to water soluble metal sulphate.

In an acid medium, the rate of bioxidation is increased by 30 or more multiples compared to the pure chemical oxidation therefore bacterial analysis in the prediction, management and remediation of AMD should be considered.

A range of bacteriological species are present in the AMD but Cowan *et al*, 2007 proved that the dominant species found in AMD is *T. Ferrooxidans* and *L. Ferrooxidans*. They depend on CO_2 as their only carbon source.

Chapter 2 supported a developed understanding of the geochemistry/hydro-chemistry of AMD. Prediction and evaluation of AMD is therefore important in the mining industry since AMD is one of the great threats to the water resource in South Africa. To a certain degree, the prediction of AMD will assist the mining project from preparation of environmental impact assessments to get mine permits, mine layout, pollution control management and planning, financial planning of the remediation plan and closure of the mine. AMD if not predicted, prevented and managed could cost more than the bottom line of the operating mine.

The methodologies used to predict AMD are laboratory analysis referred to as Acid-Base Accounting (ABA). ABA is a procedure done in the laboratory to determine the existing and potential acidic generation.

Chapter 3 evaluated the South African and Australian ABA methodologies because South Africa uses the same laboratory guidelines as Europe and USA while Australia is the only country that has its own different laboratory guidelines for doing ABA. The Australian SPOCUS suite was used in order to compare the results with the South African ABA static results. SPOCUS suite is a self-contained ABA which also measures the residual acid soluble sulphur (S_{RAS}). Static tests are the analytical tests used as a screening criterion of the samples; used to determine the difference between the acid-generating capability and the acid-neutralising potential of the samples.

The Australian Actual Acidity method uses KCl which makes the sample less natural and stabilises the cations whereas the South African method uses only deionised water to determine the actual acidity of the sample as accurately as possible. More reagents are used in the Australian methods as compared to the South Africans therefore the South Africa's method gives an actual natural state of the sample.

The South Africa Actual Acidity method compared to the Australian showed that pH correlation was good even though the percentages of cations are not identical to each other but approximate. In 2011 %Ca had a low correlation as compared to the year 2010. %Ca consistency graphs seem to have erratic values because the samples subjected to NaOH titration yields half the values of the South African %Ca. When the pH is high and the sample is not subjected to NaOH titration, the %Ca values of the Australian methods are double the %Ca values of the South African methods therefore the Australian method might be misleading with the %Ca results. The range of %Mg is low whereas the range of %SO_4 is high

The Australian potential acidity method includes a total of 20 ml- 45 ml of hydrogen peroxide, hot steam bath, pH control methods such as carbonate modification, addition of other reagents, a longer period of time, and titration using a base (NaOH). However, carbonate modification has an advantage of dissolving excess carbonate using dilute HCl so that the efficiency of peroxide oxidation is not disturbed. South African methods on the other hand are fast, less expensive (less reagents) and a titration using a base is not required.

Australia's versus the South African peroxide method show a very good pH correlation but in the year 2010, the %Mg and %SO_4 correlation was poor. The South African methods show a higher correlation than the Australian method. It is unclear if the carbonate modification step has an influence on the result variance since in the year 2010 the South African samples that were subjected to carbonate modification showed more than double the amount of the South African value in the Australian methods with regards %SO_4 and %Mg. However, the 2011 samples that went through carbonate modification only have at least 2 units in variance.

The Australian Neutralising potential method includes reference samples of 0.100 AR grade $CaCO_3$, HCl and NaOH are used whereas South Africa uses H_2SO_4, NaOH and assume that all samples have reactive species available but not all samples lacking carbonates or a dunite composition have insufficient neutralising potential.

The Australian neutralising potential method is derived from lime analysis disciplines and can be an overestimate of the neutralising capacity. When the Australia's neutralising potential method was compared to the South African method, the hypothesis of methods and results can be compared or not was inconclusive.

Overall, both countries Actual Acidity methods and Peroxide methods are comparable however the Australian neutralising potential method is questionable since Australia methods overestimate/underestimates the sample's effective Acid Neutralising Capacity (ANC).

Since it is inconclusive to whether all the South African methods can be compared to the Australian methods or not, Only South African methods were used in Chapter 4.

In **Chapter 4**, the scope of investigation was the geochemical investigation and evaluation of the status quo at the Middleburg North mines by identification of soluble metals, mobile metals, prediction of the maximum metal concentration and the maximum metal loadings with respect to time. Kinetic tests and Static tests were used for laboratory analysis. A total of 127 samples were collected for potential AMD analysis at the Middelburg North Mines. Only 3 sites were discussed in chapter 4 but the rest of the samples are mentioned in Appendix 5.

- Water Quality:

  An indication of AMD was evident when the water voids showed that they were heavily contaminated. However this did not correspond to the groundwater quality from Goedehoop that indicated that the polluted water from the opencasts does not affect the water in the surrounding aquifer as yet. The groundwater at Hartebeesfontein indicated AMD with high sulphate and iron values but the H3 pit at Hartebeesfontein, situated to the west of the opencasts, is not polluted. This is an indication that water flow is down-gradient towards the north east and this is the reason for the polluted surface water dams down-gradient from the Hartebeesfontein opencasts. The EC time graph indicates that the water quality varies between sampling runs, but it basically remains in an increasing order over time.

- Mineralogy:

The mineralogy of the investigated area shows that most samples contain quartz and kaolinite and that calcite and dolomite was only detected in trace amounts. In contrast the presence of pyrite could be observed therefore the absence of buffering minerals (calcite and dolomite) suggested that the conversion of pyrite to depositional gypsum is already occurring.

Three principal components of the system are pyrite, calcite and dolomite. The absence of calcite and/or dolomite from the general mineralogy has a significant effect on sulphate load produced (i.e., Goedehoop, Klipfontein North). If calcite is present in the structure a lowering in sulphate load is observed due to the buffering capacity of the system (i.e., Klipfontein South). The Discards and Slurry systems have elevated levels of pyrite concentration in the structure which results in elevated sulphate loads in spite of a higher buffering capacity.

The data was used by senior personnel at the IGS to increase the confidence of results by doing additional geochemical modeling. The models confirmed that acidification of water leaching from the area will most likely contain high sulphate loads and that no significant buffering effect could be observed from the samples.

The average *XRF* results are summarised in Table 5-1. The major contributors to the base potential of the samples are the MgO and the CaO. This table emphasis on the open system's Net Neutralising potential (NNP). Values highlighted in red are of concern, the ones bolded in black show a fair NNP value. High levels of iron species correspond with low pH values.

Table 5-1 Static pH values, XRF and NNP results.

Samples	**Sample names**	**Initial pH Static method**	**Final pH**	**NNP (Open)**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MnO**	**MgO**	**CaO**	**K_2O**	**TiO_2**	**P_2O_5**
Discard	Average of all samples	5.75	1.91	-70.366	57.8	26.8	8.59	0.038	0.577	2.374	0.647	1.572	0.309
Highest (NNP Open)	Discard 4	4.14	1.66	-6.792	60.9	27.9	3.98	0.013	0.582	2.243	0.710	1.577	0.209

Samples	Sample names	Initial pH Static method	Final pH	NNP (Open)	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	TiO_2	P_2O_5
Lowest (NNP Open)	Discard 6	7.99	2.00	**-126.239**	55.8	24.7	12.23	0.043	0.784	2.885	0.693	1.378	0.288
Goedehoop	Average of all samples	5.48	2.67	-3.258	64.4	24.7	5.60	0.041	0.569	0.896	1.142	1.410	0.312
Highest (NNP Open)	G4-2	8.28	4.39	**20.621**	55.1	26.6	9.77	0.065	1.078	3.625	0.864	1.272	0.319
Lowest (NNP Open)	G5-3	7.75	2.52	**-94.183**	58.6	28.4	5.71	0.034	1.219	1.464	1.318	1.284	0.688
Slurry	Average of all samples	7.70	2.08	-0.265	55.7	24.5	9.32	0.065	0.970	5.005	0.843	1.735	0.611
Highest (NNP Open)	Slurry 9	8.47	2.67	**14.238**	55.6	24.2	7.26	0.061	1.640	6.191	0.821	1.690	0.627
Lowest (NNP Open)	Slurry 7	7.61	1.74	**-53.886**	61.2	19.6	9.36	0.077	0.641	5.229	0.642	1.226	0.347
Harties	Average of all samples	6.51	2.98	1.217	67.5	21.3	5.95	0.059	0.635	0.383	1.915	1.119	0.181
Highest (NNP Open)	H-12	8.27	4.52	**48.325**	63.1	21.0	8.31	0.097	1.509	2.256	2.523	1.110	0.179
Lowest (NNP Open)	H-20	4.13	1.33	**-10.847**	60.5	32.7	2.13	0.010	0.275	0.111	0.908	1.560	0.135
Klipfontien North	Average of all samples	6.53	2.91	2.115	63.4	26.1	4.59	0.051	0.720	0.608	1.892	1.198	0.446
Highest (NNP Open)	KN 3-3	7.71	3.30	**9.314**	58.4	30.4	4.18	0.051	0.476	1.195	1.471	1.339	1.206
Lowest (NNP Open)	KN 2-7	4.06	1.40	**-14.686**	67.1	24.8	2.38	0.010	0.335	0.662	1.337	1.468	0.106
Klipfontein South	Average of all samples	7.44	3.52	4.881	64.8	23.9	5.65	0.074	0.686	0.588	2.103	1.067	0.338
Highest (NNP Open)	KS 3-1	8.16	4.68	**44.906**	62.1	22.8	6.28	0.070	2.128	2.118	2.527	1.171	0.155
Lowest (NNP Open)	KS 2-3	4.17	2.98	**-7.641**	70.9	18.4	4.69	0.024	0.207	0.080	2.698	0.962	0.103

- Static and Kinetic tests:

  Only 4.7% of the Middelburg samples analysed in the static test method showed a net neutralizing potential while in the kinetic tests results only a handful of the samples shows a low salt load compared to the rest. Cumulative values from the kinetic tests indicate that the salt loads upon oxidation will significantly give higher TDS values to the receiving water bodies in the environment. As the pH lower over time, the NP of the samples will be depleted. This lower pH's will cause more heavy metals to go into solution.

The overall results show that acidic conditions will occur upon oxidation at most sites where the samples were taken. The investigated collieries showed a high to medium risk of acid-generation upon oxidation. In summary, the static tests indicate the following:

Hartebeesfontein:

Most of the samples in this mine have the possibility of AMD production. There is potential available to buffer acid generated from some samples.

Goedehoop Ramp 1 and 2:

AMD will be produced upon oxidation and there is no buffering potential.

Goedehoop Ramp 4:

Most of the samples have potential for neutralization.

Goedehoop Ramp 6:

The samples have a possibility of might turn acidic.

Goedehoop Ramp 3, 5, 7 and 10:

Most of the samples will produce AMD because the buffering potential is very low.

Klipfontein North:

Most of the samples indicated that AMD can occur under certain conditions therefore most of the samples plotted within the grey (uncertain) zone and requires verification.

Klipfontein South:

Most of the samples show a low potential for AMD due to the base potential of some of the samples.

Slurry and Discard dumps:

High potential for acid mine drainage.

Now that the prediction of AMD is done, control measures can be put in place. The most primary objectives of acid mine drainage treatment is to remove metals (i.e. sulphides, hydroxides and carbonates) and raise the pH to alkalinity. Passive or Active treatments could be used.

Affected water quality caused by the coal mining area could be remediated and released into the Upper Olifants river catchment. The recommended pH value is more than 6.0 when it comes to stabilising acid mine drainage, this pH is ideal because it can hydrolyse Fe_3^+ and Al^{3+} that will create mineral acidity.

Recommendations for further research

- To conclude whether the South African Neutralising potential methods can be compared to the Australians, tests should be performed on the same samples to verify if personal, analytical or instrumental error was significant and the same batch of samples to be tested.
- To omit re-occurring errors and to conclude whether the Australian methods and South African methods yield the same values, samples should be repeated by two different personnel and compared to the results in this chapter.

6. References

- (ASTM) American Society for Testing and Materials. (1996). Standard Test Method for Accelerated Weathering of Solid Material Using a Modified Humidity Cell. D5744-96 ASTM. West Conshohocken, Pa.

- Aston, J.J. (2000). Conceptual Overview of the Olifants River Basin's Groundwater, South Africa. An Occasional Paper for the International Water Management Institute (IWMI) in conjunction with the African Water Issues Research Unit (AWIRU). University of Pretoria, South Africa.

- Baker, B.J. and Banfield, J.F. (2003). Microbial communities in acid mine drainage. FEMS Microbiology Ecology. 44. 139 – 152.

- Berner, R.A. (1970). Sedimentary pyrite formation. American journal of Science, 268, 1-23.

- Bosch, C. (1990). Distribution and inhibition of iron-oxidising bacteria in relation to acid drainage from gold and coal mine dumps in the Southern Transvaal. Unpubl. M.Sc Thesis (unpublished). University of Stellenbosch, Stellenbosch, South Africa. 153pp.

- Botha, J.F., Verwey, J., Van der Voort, I., Vivier, J.J.P., Buys, J., Colliston, W.P. and Loock, J.C. (1998). Karoo Aquifers Their Geology, Geometry and Physical properties. Report to the Water Research Commission. WRC Report no: 4871/1/98.

- Claassen, M. (2011). How much water do we have?. Report no. CSIR/NRE/WR/IR/2011/0029/A. Council for Scientific and Indutrial Research, Pretoria.

- Council of Geoscience. (2011). Geological map of South Africa. http://www.geoscience.org.za/index.php?option=com_content&task=view&id=447 itemid=413. (accessed on the 27-05-2010).
- Cowan, D.A., Shitandi, A., Van Ijeperen, C., Kuhn, E., Musingarimi, W. and Petrik, L. (2007). The Microbiology of fly-ash-Acid Mine Drainage neutralization systems. Report for the Water Research Commission. WRC Report no 1549/1/07. 60pp.

- Cruywagen, L-M. (2010). Personal Communication. Institute of Groundwater Studies, University of the Free State.

- DLRA. (2011). Geology of Australia. http://www.dlra.org.au/ref-geological.htm (Accessed on the 27-05-2010).

- Eberhand, A. (2011). The Future of South African coal: Market, Investment and policy challenges. Working paper # 100.

- FDI. (2011). Geological map of South Africa. http://www.fdi.net/documents/WorldBank/databases/safrica/geoscience/Geologie%20van%20SA (accessed on the 27-05-2010).

- Fourie, P. J. (2007). The Description of phsyiso chemical processes in coal mine spoils and associated production of Acid Mine Drainage. M.Sc Thesis (unpublished), University of the Free State, Free State, South Africa, 153pp.

- García, I., Diez, M., Martín, F., Simón, M., Sánchez, J.A. and del Moral, F. (2007). Influence of CaCO3 on the aluminium toxicity in leachates of soils contaminated by acidic mine drainage. 14th International Symposium on Environmental Pollution and its Impact on Life in the Mediterranean Region (MESAEP), Sevilla, Spain, 10 – 14.

- Gavira, A. and Frances, P. (2008). Rocks and minerals: The Definitive visual guide. London. Dorling Kindersley limited, 360pp.

- Hines, M.E., Visscher, T.P. and Devereux, R. (2002). Sulfur cycling. In: Manual of environmental microbiology, Second Edition, Hurst, C.J.; Crawford, R.L.; Knudsen, G.R.; McInerney, M.J. and Stetzenbach (Eds.), New York Washington 427-438.

- Hobbs, P.J. and Kennedy, K. 2011. Acid Mine drainage: Addressing the problem in South Africa. Report no. CSIR/NRE/WR/IR/2011/0029/A. Council for Scientific and Indutrial Research, Pretoria.

- Hobbs, P.J., Oelofse, S.H.H. and Rascher, J. (2008). Management of environmental impacts from coal mining in the upper Olifants River catchment as a function of age and scale. International Journal of Water Resources Development, 24(3):417-431.

- Hodgson, F.D.I., Vermeulen, P D. Cruywagen L.M, and De Necker. E. (2007). The investigation of decant from the underground colliers in Mpumalanga with special emphasis on predictive tools and long term water quality management. Report for the Water Research Commission. WRC report no. 1263/1/07.

- Juszczak, A., Domka, F., Kozlowski, M. and Wachowska, H. (1995). Microbial desulfurization of coal with Thiobacillus Ferrooxidans Bacteria. Fuel. 74(5). 725-728.

- Kelly, M. (1988). Mining and the freshwater environment. Elsevier science publishers ltd New York 231pp.

- Lawrence, R. and Day, S. (1997). Chemical prediction techniques for ARD.Short Course #2. Fourth international conference of acid rock mine drainage. May 31-June 6, Vancouver, BC., pp449-464.

- Leroy, E. (2005). A study of the development of water resources in the Olifants catchment, South Africa: Application of the WEAP model. Published MSc thesis. Imperial College London. September 2005.

- McElnea, A.E. and Ahern, C.R. (2000). Issues associated with laboratory methods for assessing sulfate soil risk-particularly hydrogen peroxide-based methods.In “Proceedings of Workshop on remediation and assessment of Broadacre Acid Sulphate Soils”. (Ed. P Slavish) pp 1-15.

- McElnea, A.E., Ahern, C.R., Sullivan, L.A. (2004a). Procedure for predicting acid risk via the acid base account (ABA). In: Acid Sulfate Soils Laboratory Methods Guidelines.P Slavish (Eds) pp A2-1—A2-21.

- McElnea, A.E., Ahern, C.R., Sullivan, L.A. (2004b). Analytical methods for dried and ground ass samples. In: Acid Sulfate Soils Laboratory Method Guidelines. P Slavish (Ed.). pp B2-1—B4-1.

- Mey, W.S. and Van Niekerk, A.M. (2009). Evolution of mine water management in the Highveld coalfields. http://www.imwa.info/evolution.of.mine.water.management.in.the.highveld.coalfields/imwa2009_mey.pdf.(Accessed on the 07-07-2011).

- Mills, C. (2011). The Role of micro-organisms in Acid Rock Drainage. http://technology.infomine.com/enviromine/ard/microorganisms/roleof.htm (accessed on the 07-07-2011).

- Mine-water: The time to act is NOW. (2011). Acid Mine drainage, Red letter year for authorities to prevent mine-water catastrophe. In “The Water Wheel” magazine. South Africa 10(1).12-17.

- Mokoena, M.P. (2010). Comparison of the South African and Australian ABA methods. B.Sc (Hons) Case study (unpublished), University of the Free State, Free State, South Africa, 53pp.

- Näveke, R. (1986). Bacterial leaching of ores and other materials. InstitutfürMikrobiologie, TechnischeUniversität Braunschweig, http://www.spaceship-earth.de/REM/Naeveke.htm(accessed: 07-07-2011).

- Perry-Casteneda library Map collection. (2011). U.S Central intelligence Agency. http//www.lib.utexas.edu/maps/Africa/South_Africa_ind_1979.jpg. (accessed on the 27-05-2011).

- Price, W.A., Morin, K. and Hutt, N. (1997). Guidelines for the prediction of Acid Rock Drainage and Metal leaching for mines in British Columbia: Part 11. Recommended procedures for static and kinetic testing. In: Proceedings of the Fourth International Conference on Acid Rock Drainage. Vol. 1, May 31 – June 6, Vancouver, BC., pp. 15 – 30.

- Rawlings, D.E. (1989). Mining and the Growth of knowledge. Lecture Notes. University of Cape Town., Cape town, South Africa, 14pp.

- Rose, S. and Ghazi, A.M. (1997a). Release of sorbed sulphate from iron hydroxides precipitated from Acid Mine Drainage associated with coal mining. Environ. Sci. Technol., 31 (7). 2136 -2140.

- Saexplorer. (2011). Mpumalanga map. http://www.saexplorer.co.za/south-africa/map/mpumalanga_map.asp (assessed on the 07-07-2011).

- Saghafi, A., Pinetown, K.L., Grobler, P.G. and van Heerden, J.H.P. (2008). CO_2 storage potential of South African coals and gas entrapment enhancement due to igneous intrusions. International Journal of Coal Geology. 73(1):74–87.

- Schulze, R.E., Maharaj, M., Warburton, M.l., Gers, C.J., Horan, M.J.C., Kunz, R.P. and Clark, D.J. (2008). South African Atlas of Climatology and Agrohydrology. WRC Report No 1489/1/08. Water Research Commission, Pretoria, South Africa.

- South African Genealogy. (2011). South African map. http://home.global.co.za/~mercon/map.htm (assessed on the 07-07-2011).

- Steve Tshwete Municipal. (2005). Integrated Resource Information Report Mpumalanga Provincial Government. Department of Agriculture and Land Administration. South Africa.

- Steyl, G. (2010). Personal Communication. Institute of Groundwater Studies, University of the Free State.

- Steyl, G. (2012). Personal Communication. Institute of Groundwater Studies, University of the Free State.

- Thomas, B.P., Fitzpatrick, R.W., Merry, R.H., Hicks, W.S. (2003). Coastal sulphate Soil management Guidelines, Barker inland, SA. Acid Sulphate Soil technical Manual (1.2).CRISO land and water report.

- Usher, B.H. (2003). The development and evaluation of hydrogeochemical prediction techniqunues for South African Coalmines. Phd Thesis (unpublished), Universtity of the Free State, Free State, South Africa, 314pp.

- Usher, B.H., Cruywagen, L-M., Necker, de E., Hodgson, F.D.I. (2003). On-site and Laboratory inverstigations on spoil in opencast collieries and the development of Acid-Base Accounting Procedures.Water Research Commision. Report 1055/1/03.

- Van der leeden, F. (1975). Water resources of the world. Water Information Centre Inc., New York, 568.

- Vermeulen, D., Lukas, E. and Van Tonder, G. (2011). Groundwater assessment for Middelburg North Mines: Goedehoop, Hartebeesfontein, Bankfontein and Klipspruit. Report number: 2011/02/PDV.

- Whittington-Jones, K.J., Corbett, C.J. and Rose, P.D. (2002). The Rhodes Biosure process. Part 2: Enhanced Hydrolysis of organic carbon substrates-

Development of the recycling Sludge Bed Reactor. Report to the Water Research Commission. WRC report no TT 196/02(4). 97pp.

- Woodford, A.C., Chevallier, L. (2002). Hydrogeology of the main Karoo Basin: Current knowledge and Future Research Needs. Report for the Water Research Commission. WRC Report No TT179 / 02.

- World Trade Press. (2012). Precipitation Map of South Africa. http://www.bestcountryreports.com/Precipitation_Map_South%20Africa.php (Accessed on the 27-02-2012).

- Zajic, J.E. (1968). Microbial Biogeochemistry. Academic press. New york and London. 345pp.

7. Abstract

South Africa has several coal mines of which promised economic wealth since the 1700, however the exploitation of this commodity has a negative effect to the environment. Mining operations are a source of Acid Mine Drainage (AMD) in South Africa therefore salt loading and acidic conditions are of concern. Although lab methods such as Acid-Base Accounting (ABA) are used to predict the impact and effects of AMD, it is still difficult to predict its rate. The importance of laboratory analysis is to give the best and worst case scenario of the area, provided that the samples are representative of the area investigated.

This thesis is conducted to note the difference between South African and Australian Laboratory methods in determining the potential and existing acidity of the samples. Furthermore, AMD is predicted using ABA methods for the Middelburg area.

South Africa uses similar ABA laboratory guidelines as USA and Europe while Australia uses its own guidelines that are modified from time to time. After the comparisons of the methods were evaluated, the Australia's versus the South African results showed a very good correlation. However the Ca percentage from the ICP results had a lower correlation compared to other cations in the Actual Acidity Method. The KCl and NaOH used in the Australian Actual Acidity Method either displays the Ca as double or half of the South African ICP results. However, both countries' Actual and Potential Acidity Methods are comparable. The Australia's Neutralising Potential Method is derived from lime analysis disciples and can be an overestimate of the Neutralising Capacity. Whether the methods and results of Neutralising Capacity can be compared or not, is inconclusive. Other ABA tests have to be done on the same samples to verify if personal, analytical or instrumental error was significant.

To achieve another aim of this thesis, The IGS was approached by Middelburg mine services to update the 2006 groundwater model at Goedehoop, Hartebeesfontein, Bankfontein and Klipfontein Collieries. At a later stage, Acid-Base Accounting (ABA) methods were requested for AMD prediction. The aim of the project was to do groundwater assessment of the collieries and predict future impacts of AMD.

The locality of the investigated area is in the Middelburg, which falls in the central Highveld of the Mpumalanga province in South Africa. Open-cast coal mining is in operation at Klipfontein, Hartebeesfontein and Goedehoop. Klipfontein is along south of the Vaalbankspruit while Hartebeesfontein and Goedehoop spreads north of the Spookspruit. The area is in the Karoo Supergroup which underlines two thirds of the Republic of South Africa with typical rocks like sandstone, mudstone and shale.

About 4.7 % of the representative samples from the Middelburg Collieries showed a Net Neutralizing Potential in the Static test method whereas Kinetic tests results proved that only a handful of the samples had a low salt load and a limited buffering capacity. In conclusion, the representative samples showed the investigated Middelburg Collieries had high-medium risk of acid-generation upon oxidation.

With the prediction of AMD done, control measures can be put in place. The primary objective of AMD treatment is to remove metals (i.e. sulphides, hydroxides and carbonates) and raise the pH to alkalinity. Passive or Active treatments could be used to remedy the area. The deteriorated water quality caused by the coal mining area could be remediated and released into the Upper Olifants river catchment.

8. Opsomming

Suid-Afrika het verskeie steenkoolmyne wat sedert die 1700's ekonomiese welvaart belowe, maar die ontginning van hierdie kommoditeit het 'n negatiewe uitwerking op die omgewing. Mynboubedrywighede is 'n bron van suur myndreinering ("Acid Mine Drainage" - AMD) in Suid-Afrika, en daarom is sout- en suurtoestande van kommer. Hoewel laboratoriummetodes soos Suur-Basis-Rekening ("Acid-Base Accounting" - ABA) gebruik word om die impak en gevolge van AMD te voorspel, is dit steeds moeilik om die tempo te voorspel. Die belangrikheid van laboratorium-analise is om die beste en slegste scenario vir die gebied te verkaf, gegewe dat die monsters verteenwoordigend is van die gebied wat ondersoek word.

Hierdie ondersoek is onderneem om die verskil tussen Suid-Afrikaanse en Australiese laboratoriummetodes aan te dui in die bepaling van die potensiële en bestaande suurgehalte van die monsters. Verder is AMD voorspel deur gebruik te maak van ABA-metodes vir die Middelburg-omgewing.

Suid-Afrika gebruik soortgelyke ABA laboratoriumriglyne as die VSA en Europa, terwyl Australië sy eie riglyne gebruik wat van tyd tot tyd verander. Na afloop van die vergelykings van die metodes wat geëvalueer is, toon die Australiëse en Suid-Afrikaanse resultate 'n baie goeie korrelasie. Maar die Ca-persentasie van die ICP resultate het 'n laer korrelasie in vergelyking met ander katione in die Werklike Suurheidsmetode (Actual Acidity Method). Die KCl en NaOH wat gebruik is in die Australiese Werklike Suurheidsmetode gee óf die Ca as dubbel óf die helfte van die Suid-Afrikaanse ICP resultate weer. Maar, beide lande se werklike en potensiële suurheidsmetodes is vergelykbaar. Australië se Neutraliseringspotensiaalmetode is afgelei van die Kalk Analise Dissipline en kan die Neutraliseringsvermoë oorskat. Of die metodes en resultate van die Neutralisingskapasiteit vergelyk kan word of nie, is onoortuigend. Verdere ABA-toetse moet gedoen word op dieselfde monsters om te bepaal of persoonlike, analitiese of instrumentale fout van deurslaggewende belang was.

Om ‘n ander doel van hierdie ondersoek te bereik, is die IGS deur Middelburg myndienste genader om die 2006 grondwatermodel by Goedehoop, Hartebeesfontein, Bankfontein en Klipfontein Collieries, by te werk. Op 'n latere stadium is suur-basis-Rekening (ABA) metodes gevra vir AMD voorspelling. Die doel van die projek was om grondwaterassessering van die steenkoolmyne te doen en die toekomstige impak van AMD te voorspel.

Die ligging van die ondersoekgebied is Middelburg, wat in die sentrale Hoëveld van die Mpumalanga-provinsie in Suid-Afrika val. Sogenaamde “Open-cast” steenkoolmyning is in werking op Klipfontein, Hartebeesfontein en Goedehoop. Klipfontein strek langs die suide van die Vaalbankspruit terwyl Hartebeesfontein en Goedehoop noord van die Spookspruit geleë is. Die gebied is in die Karoo Supergroep, wat onderliggend is aan 2 / 3 van die Republiek van Suid-Afrika, met tipiese gesteentes soos sandsteen, modderklip en skalie.

Sowat 4,7% van die verteenwoordigende monsters van die Middelburg-Collieries toon 'n netto neutraliseringspotensiaal in die statiese toetsmetode, terwyl Kinetiese toetsresultate bewys het dat slegs 'n handjievol van die monsters 'n lae soutgehalte en 'n beperkte bufferkapasiteit het. Ten slotte, die verteenwoordigende monsters uit die ondersoekte Middelburg Collieries het getoon dat daar 'n hoë-medium risiko van suur-generasie tydens oksidasie is.

Met die voorspelling van AMD afgehandel, kan kontrolemaatreëls in plek gestel word. Die primêre doel van AMD behandeling is om metale te verwyder (m.a.w. sulfiede, hidroksiede en karbonate) en die pH na alkaliniteit te verhoog. Aktiewe of passiewe behandelings kan gebruik word om die gebied te herstel. Die besoedeling van die water wat veroorsaak word deur die steenkoolmyn-area kan herstel en vrygelaat word in die Bo-Olifantsrivier-opvanggebied.

9. Keywords

Coal

Acid Mine Drainage

Sulphur oxidation

Acidithiobacillus Ferrooxidans/ T. Ferroxidans

Acid-Base Accounting

Australian Spocus suite

South African static ABA methods

South African kinetic ABA methods

Middelburg North mines

Pyrite oxidation

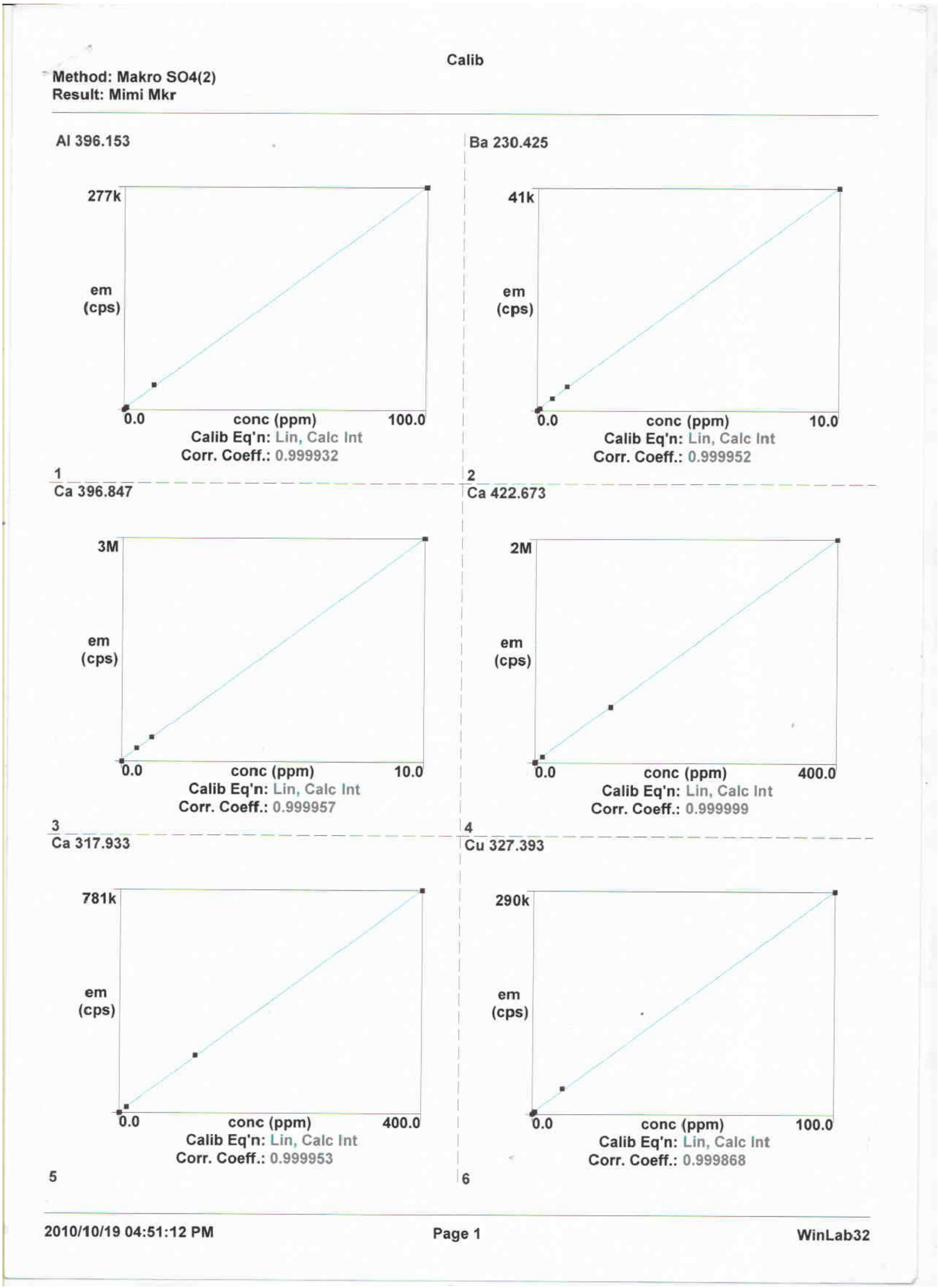
Appendix 1

GENERAL

EQUIPMENT USED

The experiments mentioned in chapter 3 and chapter 4 were performed in a batch configuration, using glass beakers with a volume that ranged from 50 ml to 100 ml with a magnetic stirrer. The pHwas measured by means of a Cyberscan 100 H1 1230 pH meter and an automatic Titronic T200 recording by Titrisoft 2.51, calibrated by using buffer solutions of pH 4 and 7. The Titrisoft 2.51 also provided the EC values and alkalinity methods. Electrical conductivity was measured at room temperature which then provided an approximate value for the TDS concentration, usually within ten-percent accuracy. Alkalinity was measured by the multi-titration system (Titrisoft 2.51) whereas the cation and anion concetrations were determined by ion chromatography (ICP).

The instrument was calibrated using a series of calibration standards containing known concentration. The instrument response is attached below to prove the accuracy of the readings. The graphs are plotted against known concentration of anion and cation in the standard in the solution against the instruments response (cps_Count per second). The correlation coefficient of the result is satisfactory with most fits being linear.



Calib

Method: Makro SO4(2)
Result: Mimi Mkr

Al 396.153

277k

em (cps)

0.0 conc (ppm) 100.0

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999932

1

Ba 230.425

41k

em (cps)

0.0 conc (ppm) 10.0

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999952

2

Ca 396.847

3M

em (cps)

0.0 conc (ppm) 10.0

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999957

3

Ca 422.673

2M

em (cps)

0.0 conc (ppm) 400.0

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999999

4

Ca 317.933

781k

em (cps)

0.0 conc (ppm) 400.0

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999953

5

Cu 327.393

290k

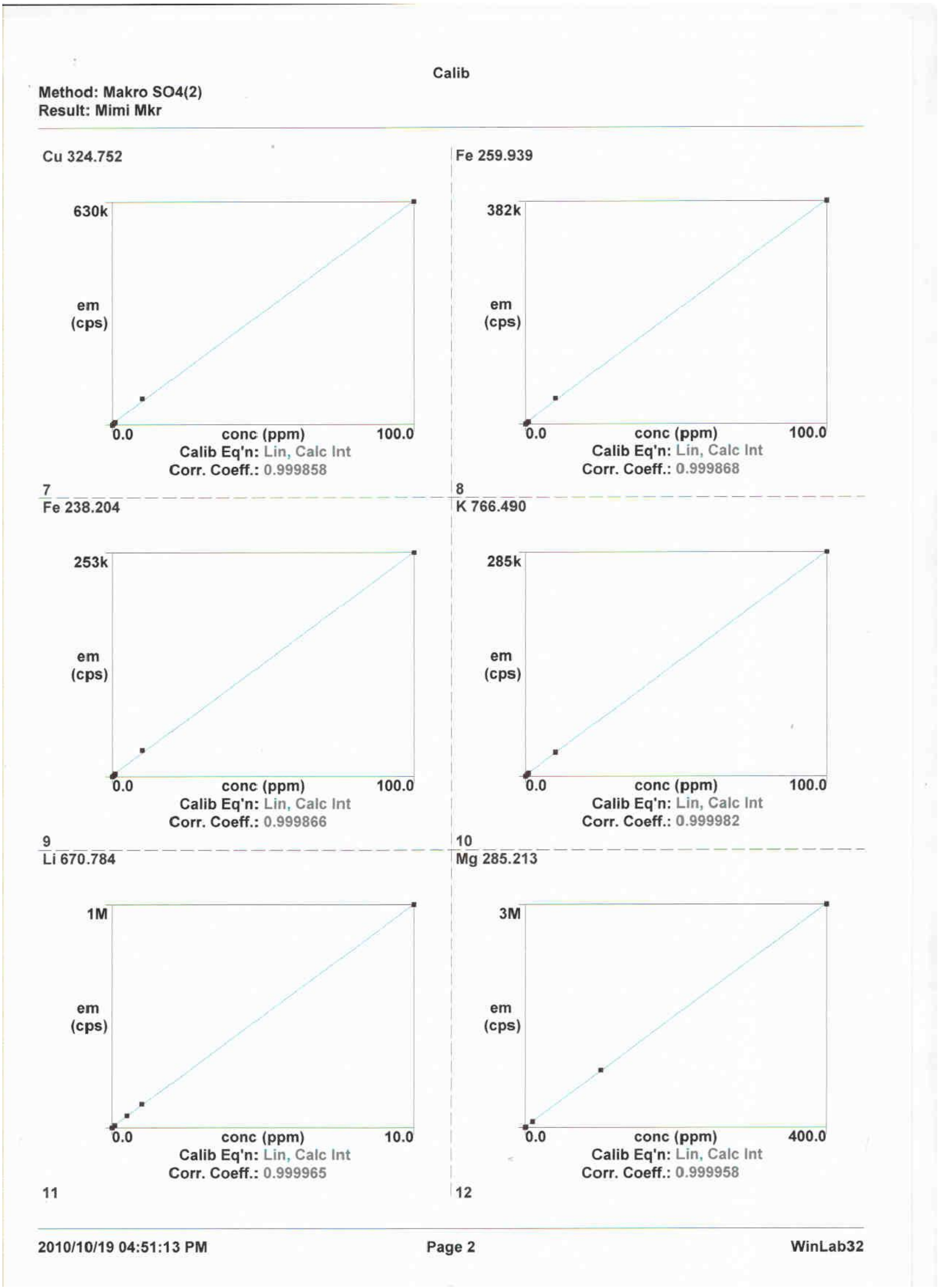
em (cps)

0.0 conc (ppm) 100.0

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999868

6

2010/10/19 04:51:12 PM Page 1 WinLab32



Calib

Method: Makro SO4(2)
Result: Mimi Mkr

Cu 324.752

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999858

7

Fe 259.939

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999868

8

Fe 238.204

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999866

9

K 766.490

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999982

10

Li 670.784

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999965

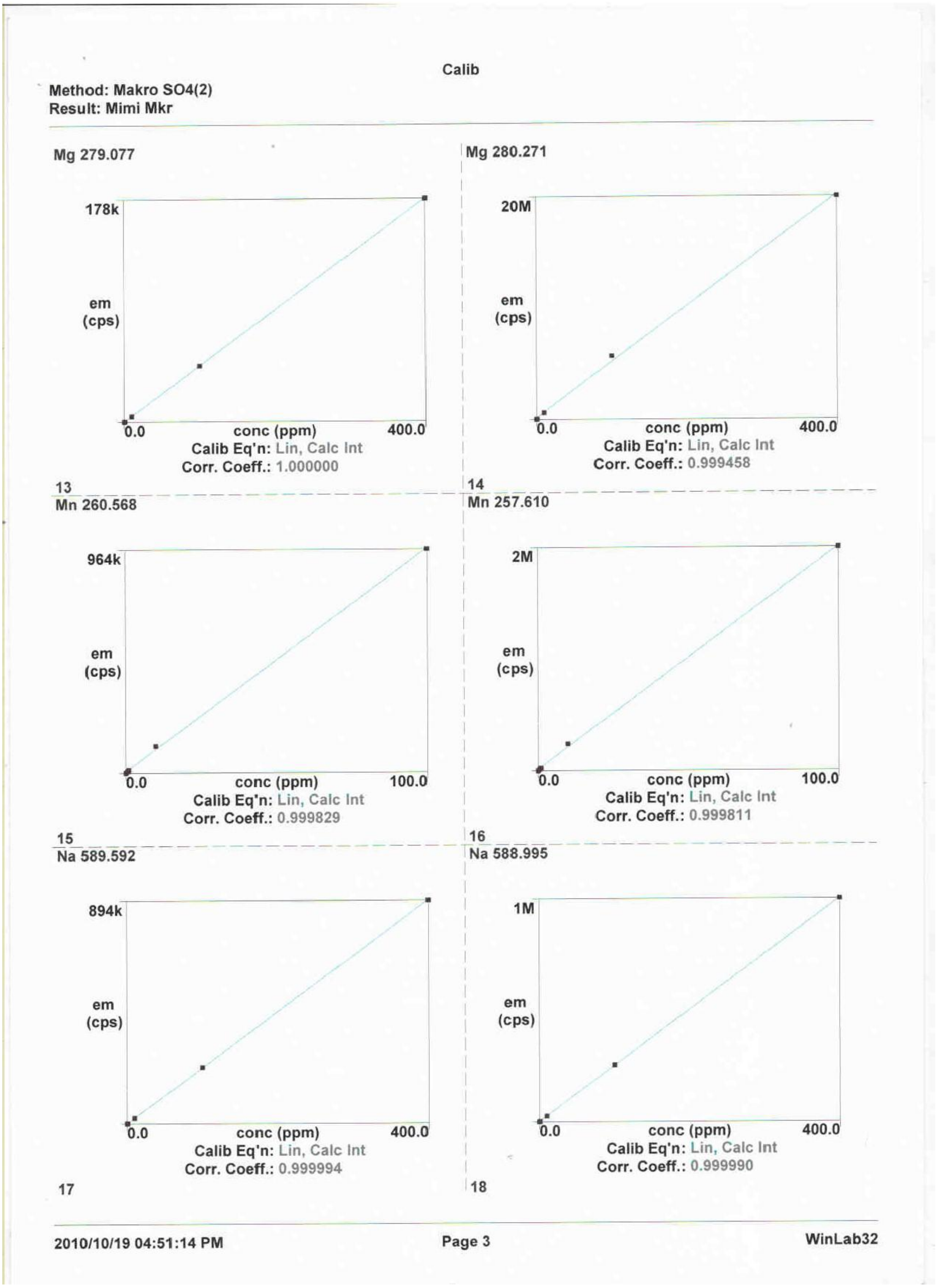
11

Mg 285.213

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999958

12

2010/10/19 04:51:13 PM Page 2 WinLab32



Calib

Method: Makro SO4(2)
Result: Mimi Mkr

Mg 279.077

178k

em (cps)

0.0 conc (ppm) 400.0

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 1.000000

13

Mg 280.271

20M

em (cps)

0.0 conc (ppm) 400.0

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999458

14

Mn 260.568

964k

em (cps)

0.0 conc (ppm) 100.0

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999829

15

Mn 257.610

2M

em (cps)

0.0 conc (ppm) 100.0

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999811

16

Na 589.592

894k

em (cps)

0.0 conc (ppm) 400.0

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999994

17

Na 588.995

1M

em (cps)

0.0 conc (ppm) 400.0

Calib Eq'n: Lin, Calc Int
Corr. Coeff.: 0.999990

18

2010/10/19 04:51:14 PM Page 3 WinLab32

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 CuKα-radiation and the PC-PDF2 computer programme for mineral identification.

Appendix 2

ABA METHODOLOGIES

Australian methods

Australia ABA includes the Chromium suite and SPOCUS suite, depending on the objective of the analysis the laboratory can choose to perform one or both of the Suites. The Chromium suite uses only required independent components of the ABA methods whereas the SPOCUS suite is a self-contained ABA with more steps and has measurements such as the residual acid soluble sulphur (S_{RAS}) unlike the Chromium reducible sulphur methods (S_{CR}) in the Chromium Suite (McElnea *et al.*, 2004a).

In this thesis a SPOCUS suite was used to achieve one of the aims of the study.

ACIDITY METHODS FOR AUSTRALIAN ABA

This involves direct determination of acidity by titration.

POTASSIUM CHLORIDE PH (PH_{KCL}) AND TITRATABLE ACTUAL ACIDITY (TAA)

- This is the first step of the SPOCUS suite
- 2grams of pulverised Australian and South African sample were weighed accurately and 1M of KCL(80ml) was added
- A blank containing 80ml KCL was done in 2011 and two in 2010.
- Sealed by a parafilm, the samples were mixed for 4 hours and left overnight(12-16 hours)
- pH was measured and recorded
- Determination of the actual acidity is necessary for sample samples with the pH of < 5.5. The samples were titrated to a pH of 6.5 using standardised NaOH. TAA is then calculated and expressed in mol H^+/t.
- Samples with the pH more than or equal to 6.5, TAA value is assumed to be zero.

1 M KCL EXTRACTABLE SULPHUR (S_{KCL}), CALCIUM (CA_{KCL}) AND MAGNESIUM (MG_{KCL})

- After the TAA was done, the suspensions were transferred to tarred beakers with deionised water. A final volume ranging from 200 - 403.5 grams plus the original sample was then weighed. For the approximate values of each sample please refer to the **Appendix 3.**
- Suspensions were mixed to homogenise, filtered through a medium speed high retention paper and the filtrate was used for analysis of S_{KCl},, $Ca_{KCl,}$ Mg_{KCl} by ICP.

PEROXIDE OXIDISED PH (PH_{OX}) AND TITRATABLE PEROXIDE ACIDITY (TPA)

- 2 grams of pulverised Australian and South African sample was weighed accurately.
- Two blanks were necessary so that the one blank could be subjected to carbonate modification should any of the samples need the same procedure.
- 10 ml of 30% Hydrogen peroxide was mixed with the weighed sample samples to oxidise sulphides such as pyrites and the production of SO_4 was expected.
  $FeS_2 + {}^{15}/_2\, H_2O_2 \rightarrow Fe(OH)_3 + 4\, H_2O + 2SO_4^{2-} + 4H^+$
- After half an hour, deionised water was added to make the volume of suspension in the beaker to be between 45-50 ml.
- The beakers with the suspension were placed in hot steam bath for a maximum of 30 minutes at 80-90 degree Celsius. Swirling of the beakers and the maintenance of the 45-50 ml volume was done periodically.
- The beakers were cooled to room temperature and 10 ml aliquot of H_2O_2 was added with a waiting period of 10 minutes before returning the beakers to the hot steam bath for a maximum of another 30 minutes.

- Cooled again to room temperature and maintenance of 45-50 ml of volume with deionised water was done.
- $pH_{(ox)}$ was recorded from the beakers and the beakers that had suspensions with high sulphide levels(pH equal or lower than 2) were repeated using a smaller weighed amount of sample. Beakers with suspensions that contained excess carbonates (pH higher than 6.5) were subjected to carbonate modification. The beakers with suspensions of pH higher than 2 and lower or equal to 6.5 were immediately subjected to peroxide decomposition.
- Carbonate modification was done by slowly titrating with a standardised 0.5 M HCl to a pH of 4, addition of 25 ml 30% hydrogen peroxide and for an hour, a certain period in a hot steam bath not forgetting to maintain the volume of 45-50ml. The suspensions could then be subjected to peroxide decomposition.
- To decompose any peroxide left, 1ml of 6.30 x 10^{-3} M $CuCl_2.2H_2O$ was added and the beakers were returned to the hot steam bath.
- Whether the effervescent bubbling has stopped or not after 30 min remove the beakers from the hot steam bath, maintain the 45-50 ml volume. If after the digest it was more than 50 ml, return to the hot steam bath until it has decreased to the volume of 45-50 ml.
- The beakers were cooled to room temperature and ~2.66 M KCl was added.
- Samples were titrated with NaOH to obtain TPA

PEROXIDE SULPHUR (S_P), PEROXIDE CALCIUM (CA_P) PEROXIDE MAGNESIUM (MG_P)

- After the TPA was done, the suspensions were transferred to tarred beakers with deionised water. Final volume ranging from 200 - 403.5 grams plus the original sample was then weighed. For the approximate values of each sample please refer to the **Appendix 3**

- Suspensions were mixed to homogenise, filtered through a medium speed high retention paper and the filtrate was used for analysis of $S_{p,}$ $Ca_{p,}$ $Mg_p$by ICP-AES.
- The filter paper was kept for the analysis of S_{ras} (Spocus residual acid soluble sulphur) mentioned below.

SPOCUS RESIDUAL ACID SOLUBLE SULPHUR (SRAS)

- The filter paper is washed with 2X10 ml aliquots of 1M KCl then 4X10 ml of deionised water.
- After the wash was completed, the filter paper was placed in a beaker with 80ml of 4M HCl for 16 hours on a shaker.
- When the reaction left overnight (16 hours) was complete, the contents of the beaker were filtered through a medium speed high retention paper and the filtrate was used for analysis of S_{RAS} or "jarositic" sulphur.

TITRATABLE SULPHURIC ACIDITY (TSA)

It is seldom to find this acidity rapidly realised into the environment in a short period however, the possibility of it taking place should not be dismissed. Titratable Sulphuric Acidity is defined as the difference between TPA (from the peroxide method) and TAA (from the KCL method).

TSA = TPA – TAA

The data for TSA and S_{Ras} detailed out in **Appendix 3**.

ACID NEUTRALISING CAPACITY (BACK TITRATION) METHOD

- 1 gram of pulverised samples was weighed and two blanks were made.
- Three 0.100 gram sample references of AR $CaCO_3$ were weighed.
- 50ml deionised water and 25 ml of standardised 0.1M HCl was added to all samples
- The samples were placed in a hot steam bath to boil and then cooled to room temperature.

    - pH was checked to see if the sample is acidic (pH<3). If the pH equal or >3, a further 25ml of 0.1M HCl until the ph<3.
    - Samples were titrated to the pH of 7 using standardised 0.1M NaOH

South African methods

South African methods used in this chapter are static methods that are inexpensive, simple analytical procedures and widely used across the world except for Australia. The methods are used to provide a possibility of acid mine drainage occurrence and sulphur content. The methodology followed in this chapter is adapted from Usher *et al.*, 2003.

ACIDITY METHODS OF SOUTH AFRICAN ABA

THE INITIAL PH

- 1 gram of pulverised Australian and South African sample was weighed accurately and 2 blanks in 2010 and one blank in 2011 were prepared.
- 50 ml of added of deionised water was added and the solution was left to stand for a 24 hour period.
- The pH was measured and recorded as initial pH or paste pH.
- For major ions the samples were filtered for ICP analysis.
- Micro ions were sampled by ion chromatograph

ACID POTENTIAL USING HYDROGEN PEROXIDE

From experience my supervisor (Cruywagen, 2010) suggested that we use 2 grams of the sample where the sample colour was dark and 4grams of the sample when it had a lighter colour.

It is has been proven that the darker the sample colour, the more of a violent reaction would occur as increments of hydrogen peroxide are added. This means that the oxidation will be incomplete due to higher sulphide content.

    - 80ml of 30% hydrogen peroxide was added to the samplein5 ml increments under the fume hood and covered with a watch glass.
    - Before the pH was recorded, the samples reaction should have ceased.

- The samples were filtered and the filtrate was used to analyse for Sulphur and associated cations

NEUTRALISING POTENTIAL METHOD

- 0.06 N of H_2SO_4 was added to 1gram of Australian and South African samples and 2 blanks in 2010 and 1 blank in 2011 were prepared.
- The normality of the Sulphuric acid does not have to be 0.06N as long as this is accounted for in the calculations.
- The pH of the samples after a 24 hour stand should be below or equal to 2.5 before the back titration to pH 7 is performed. To help lower the pH furthermore $H_2SO_4$was added and the sample was left for another 24 hour period so that a reaction takes place.
- Once the pH was below or equal to 2.5, the samples were titrated to pH of 7 with standardised NaOH to a pH value of 7.

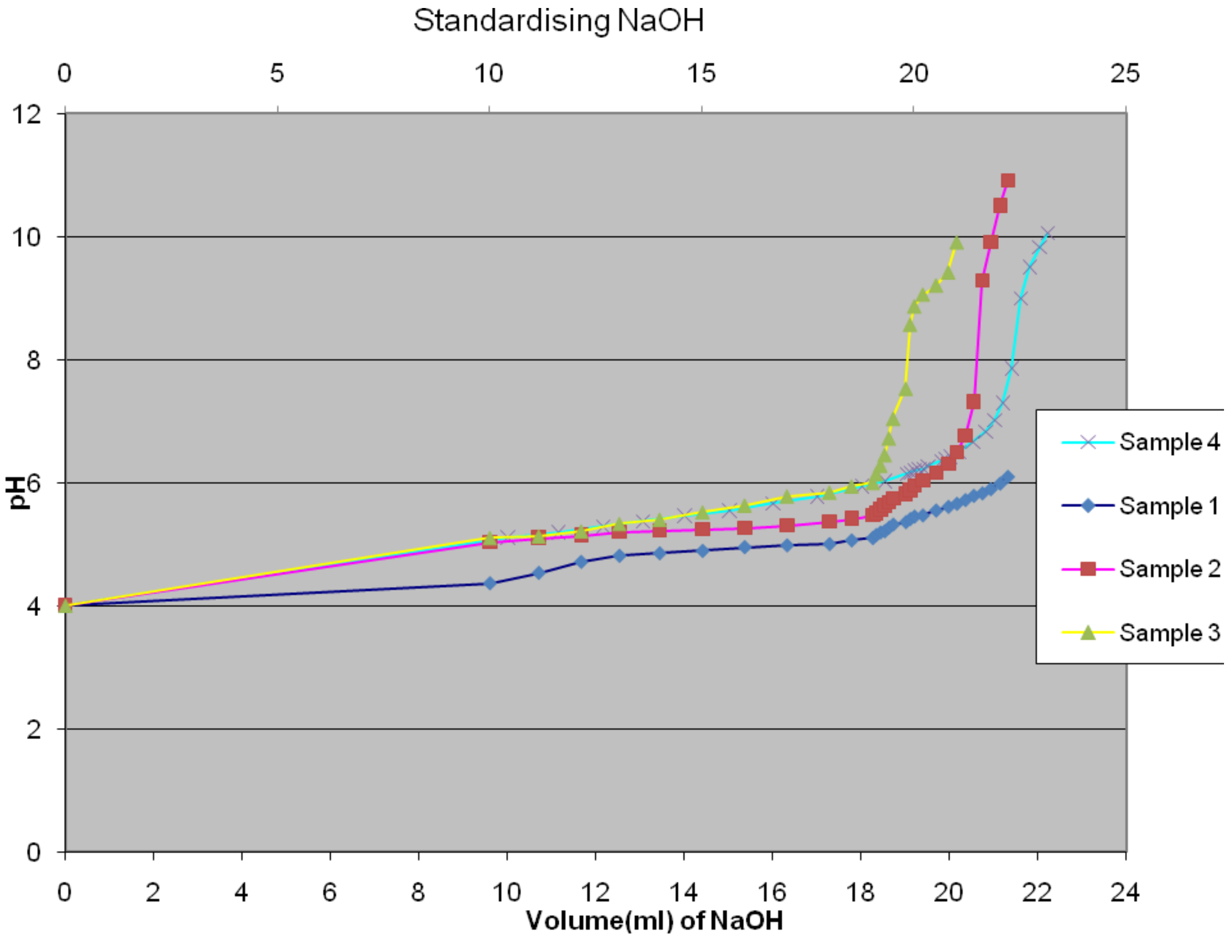
Appendix 3

AUSTRALIAN METHODS DATA

STANDARDISING FOR AUSTRALIAN METHODS

More than one sample was used for standardisation for more accurate results.

Summary of samples for standardising NaOH in 2010



Potassium Hydrogen phthalate ($C_6H_5O_4K$) was used to standardise NaOH. An average of 0.2500grams of $C_6H_5O_4K$ was weighed and dissolved in deionised water. The solution was titrated with NaOH. The average inflection point was 19.50 ml of NaOH.

$$C_6H_5O_4K + NaOH \rightarrow Na^+ + 3H_2O + K^+ + CO_2 + 5C^+$$

Balanced reaction for standardising NaOH in with Potassium Hydrogen phthalate 2010

$C_6H_5O_4K$ = B

NaOH = A

$C_A V_A b = C_B V_B a$

C_A (0.0195) *1 = m/Mr

C_A (0.0195) = 0.2485/180.1838

C_A = 0.001379/0.0195

C_A = 0.07 N

In the year 2011, standardisation was done using a known normality of H_2SO_4

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

Balanced reaction for standardising NaOH with H_2SO_4 in 2011

STANDARDISING NaOH in 2010

4 SAMPLES WERE USED FOR MORE ACCURACY

S1	
Vol NaOH	pH
0	4.01
2.5	4.36
4	4.53
5.51	4.71
6.54	4.81
7	4.85
7.5	4.89
8	4.95
8.5	4.98
9.01	5
9.5	5.06
10	5.1
10.5	5.15
11	5.19
11.5	5.21
12	5.27
12.54	5.32
13	5.36
13.5	5.41
14	5.45

S2	
Vol NaOH	pH
0	4.01
9	5.03
10	5.1
10.5	5.14
11.04	5.19
11.25	5.21
11.5	5.23
12	5.26
12.5	5.3
13	5.36
13.5	5.41
14	5.46
14.5	5.5
15	5.56
15.55	5.62
16	5.67
16.5	5.73
17.05	5.81
17.5	5.87
18	5.95

S3	
Vol NaOH	pH
0	4
10	5.1
11.01	5.13
12	5.21
13	5.33
14	5.4
15	5.52
16.04	5.63
17	5.78
17.5	5.84
18	5.94
18.5	6
19	6.14
19.5	6.28
20	6.45
20.53	6.72
20.92	7.04
21.2	7.53
21.4	8.57
21.45	8.87

S4	
Vol NaOH	pH
0	4
10	5.11
11.15	5.19
12.15	5.29
13.05	5.37
14	5.46
15.01	5.55
16	5.66
17	5.78
18	5.94
18.52	6.03
19.02	6.14
19.1	6.16
19.2	6.19
19.3	6.21
19.4	6.22
19.5	6.27
19.8	6.35
19.9	6.38
20	6.42

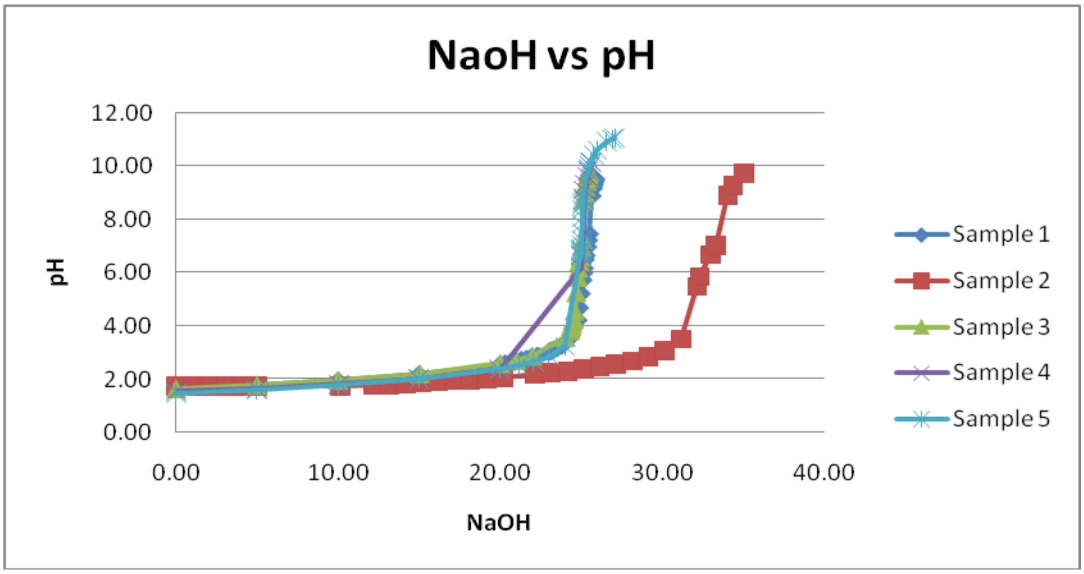
14.51	5.47
15.01	5.55
15.05	5.61
16.01	5.66
16.5	5.72
17	5.79
17.5	5.83
18	5.9
18.5	5.99
19.02	6.1
19.54	6.24
20	6.38
20.5	6.65
20.98	6.96
21	7.01
21.2	7.24
21.33	7.4
21.42	7.76
21.5	7.99
21.61	8.47
21.8	8.92
21.88	9.3
21.95	9.37
21.98	9.53
22	9.69
22.1	9.8
22.23	9.82
22.34	10.02
22.5	10.24

18.53	6.03
19	6.15
19.5	6.3
20	6.48
20.5	6.76
21	7.31
21.5	9.28
22.02	9.9
22.5	10.5
23.02	10.9
23.5	11.13

21.5	9.06
21.55	9.21
21.66	9.42
22	9.91

20.2	6.5
20.51	6.66
20.8	6.83
21	7.02
21.2	7.3
21.4	7.86
21.6	8.99
21.8	9.5
22.02	9.83
22.2	10.05

Standardising NaOH to 0.0656N in 2011



Sulphuric acid (H_2SO_4) was used to standardise NaOH. An average of 25ml of H_2SO_4 was pipetted into a beaker. The solution was titrated with NaOH. The average inflection point was 24.72 ml of NaOH.

H_2SO_4 = B

NaOH = A

$C_A V_A b = C_B V_B a$

C_a*24.72 *1 =0.0648648*25

C_B = 0.0648648*25*/24.72 =0.0656 N

Standardising NaOH with H2SO4 to 0.0656 in 2011

Sample 1	25ml H2SO4
NaoH	pH
0.00	1.68
5.00	1.78
10.00	1.94
15.00	2.18
20.00	2.55
20.30	2.59
20.60	2.62
20.92	2.66
21.30	2.72
21.61	2.76
21.90	2.81
22.30	2.88
23.02	3.03
23.15	3.07
23.30	3.11
23.51	3.17
23.80	3.27
24.00	3.37
24.32	3.56
24.80	4.22
24.90	4.69
25.00	5.22
25.10	5.74
25.15	6.00
25.20	6.18

Sample 2	25ml H2SO4
NaoH	pH
0.00	1.75
1.05	1.75
2.05	1.75
3.05	1.75
4.06	1.75
5.05	1.75
10.15	1.75
12.15	1.78
13.15	1.81
14.16	1.85
15.15	1.88
16.15	1.92
17.16	1.96
18.16	2.00
19.15	2.04
20.16	2.09
22.15	2.20
23.15	2.25
24.15	2.32
25.16	2.40
26.15	2.48
27.15	2.58
28.15	2.70
29.15	2.86
30.15	3.09

25.25	6.51
25.30	6.66
25.40	6.98
25.45	7.23
25.50	7.47
25.67	8.90
25.75	9.19
25.80	9.32
25.85	9.43
25.90	9.53

31.15	3.52
32.15	5.48
32.30	5.86
33.00	6.68
33.30	7.03
34.05	8.89
34.35	9.26
35.05	9.73

Sample 3 25ml H2SO4

NaoH	pH
0.00	1.63
5.00	1.76
10.00	1.95
15.04	2.20
20.00	2.58
21.00	2.70
22.00	2.86
24.04	3.55
24.30	3.82
24.35	3.91
24.40	3.98
24.45	4.10
24.50	4.20
24.55	4.26
24.60	4.56
24.70	5.25
24.80	5.83
24.85	6.16
24.90	6.42
24.96	6.60
25.05	6.98
25.10	7.25
25.20	8.73
25.25	8.99
25.30	9.25
25.35	9.43
25.40	9.58
25.45	9.69
25.50	9.79

Sample 4 25ml H2SO4

NaoH	pH
0.00	1.55
5.00	1.65
10.08	1.81
15.00	2.03
20.00	2.39
25.00	6.21
25.05	6.63
25.20	8.76
25.20	9.10
25.30	9.30
25.40	9.60
25.50	9.81
25.60	9.99
25.70	10.14

Sample 5 25ml H2SO4

NaoH	pH
0.00	1.47
5.00	1.62
10.04	1.80
15.02	2.02
20.00	2.38
21.16	2.52
22.08	2.67
23.04	2.87
24.03	3.24
25.00	6.65
25.01	6.71
25.02	6.80
25.03	6.84
25.04	6.91
25.05	7.04
25.06	7.24
25.07	7.51
25.08	7.82
25.09	8.09
25.10	8.38
25.11	8.54
25.12	8.63
25.13	8.74
25.14	8.84
25.40	9.81
25.45	9.92
25.60	10.17
25.80	10.42
26.00	10.60

Sample 1 10ml H2SO4

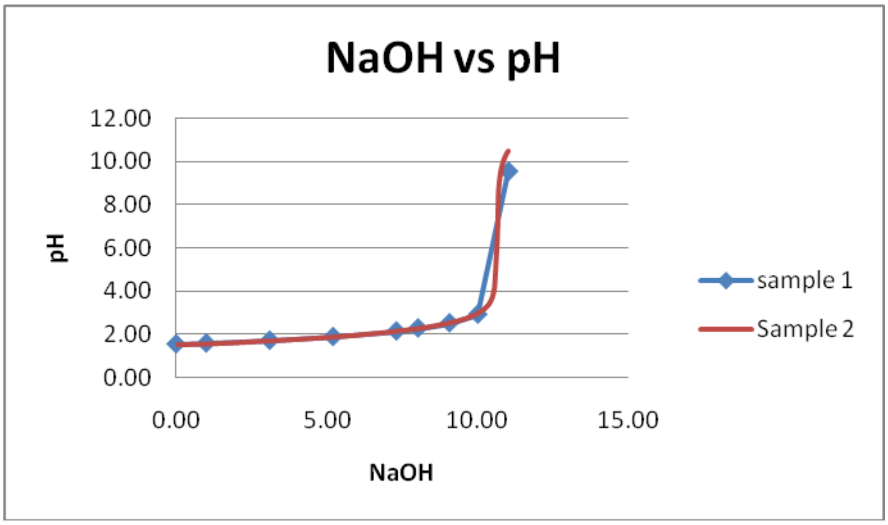
NaoH	pH
0.00	1.54
1.00	1.58
3.10	1.71
5.20	1.88
7.30	2.14
8.02	2.28
9.06	2.52
10.00	2.92
11.02	9.56

Sample 2 10ml H2SO4

NaoH	pH
0.00	1.54
1.02	1.58
2.00	1.64
3.00	1.72
4.00	1.79
5.01	1.88
6.01	1.99
7.00	2.12
8.00	2.29
9.00	2.53
9.05	2.55
9.10	2.57
9.15	2.58
9.20	2.60
9.25	2.62
9.30	2.64
9.35	2.66
9.40	2.68
9.45	2.70
9.50	2.72
9.60	2.76
9.65	2.79
9.70	2.82
9.75	2.84
9.80	2.87
9.85	2.91
9.95	2.97
10.00	3.01
10.05	3.05
10.10	3.10
10.15	3.14
10.20	3.20
10.25	3.26
10.30	3.33
10.35	3.41
10.40	3.52
10.45	3.67
10.50	3.89
10.55	4.32
10.60	5.56
10.61	5.81
10.62	6.07
10.63	6.28
10.64	6.75

Sample 2	10ml H2SO4
10.66	7.82
10.67	8.41

Standardising NaOH to 0.0678N in 2011



Sulphuric acid (H_2SO_4) was used to standardise NaOH. An average of 10 ml of H_2SO_4 was pipetted into a beaker. The solution was titrated with NaOH. The average inflection point was 10.65 ml of NaOH.

$H_2SO_4 = B$

NaOH = A

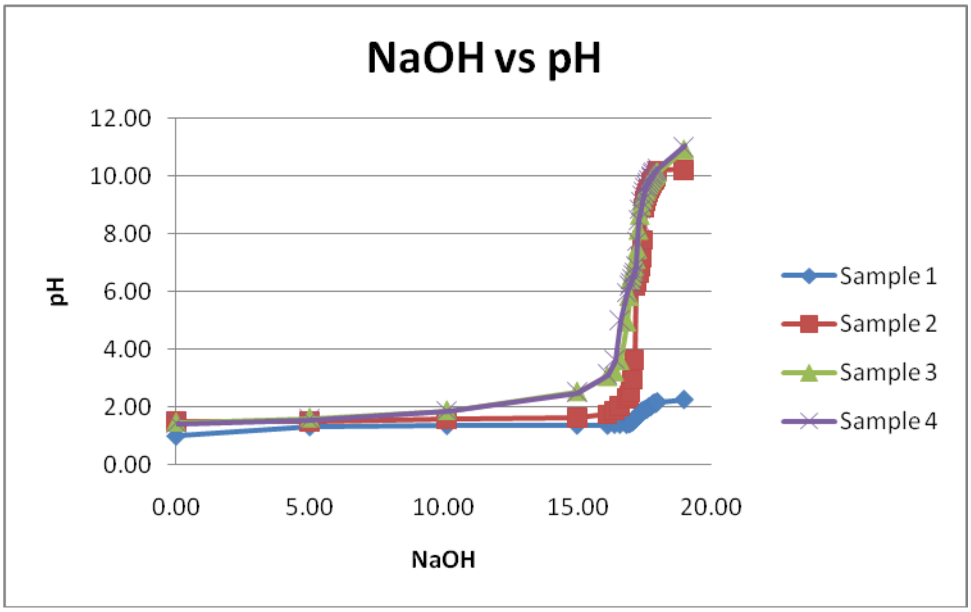
$C_A V_A b = C_B V_B a$

$C_a * 10.65 * 1 = 0.0722021 * 10$

$C_B = 0.0722021 * 10 / 10.65 = 0.0678N$

Standardising NaOH with H2SO4 to 0.067795

Summary of 4 Samples used to Standardise HCl in 2010



Hydrochloric acid (HCL) was used to standardise NaOH. An average of 10 ml of HCL was pipetted into a beaker. The solution was titrated with NaOH. The average inflection point was 16.50 ml of NaOH.

Balanced reaction for standardising HCl; $HCl + NaOH \rightarrow NaCl + H_2O$

HCl= B

NaOH = A

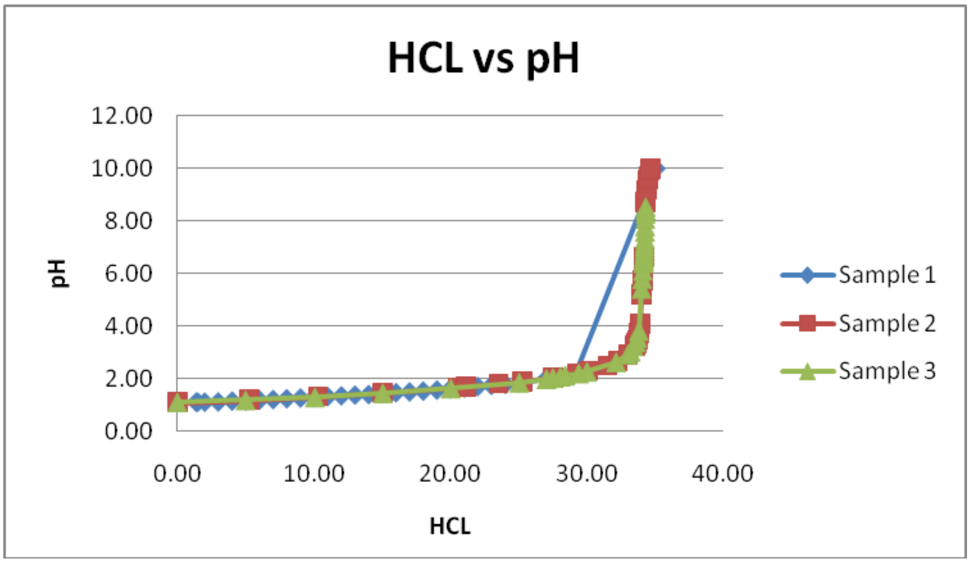
$C_A V_A b = C_B V_B a$

$16.50*0.07*1 = C_B*10*1$

$C_B = 1.155/10$

$C_A = 0.115$ N

Standardisation to 0.112173N HCL in 2011



Refer to the Balanced reaction for standardising HCl already discussed previously.

Hydrochloric acid (HCL) was used to standardise NaOH. An average of 20 ml of HCL was pipetted into a beaker. The solution was titrated with NaOH. The average inflection point was 34.22 ml of NaOH.

HCl= B

NaOH = A

$C_A V_A b = C_B V_B a$

$0.131199*34.22 *1 = C_B *20*1$

$C_B = 2.243462/20$

$C_A = 0.22448$ N

Standardasing HCL with 0.0655995N NaOH

Sample 1	20 ml HCL
NaOH	pH
0.00	1.11
1.38	1.12
1.50	1.12
2.00	1.12
3.00	1.13
4.02	1.16
5.02	1.17
6.02	1.20
7.02	1.22
8.02	1.25
9.03	1.28
10.02	1.30
11.02	1.33
12.02	1.36
13.02	1.39
14.02	1.41
15.02	1.44
16.02	1.48
17.02	1.51
18.02	1.54
19.02	1.58
20.02	1.63
21.06	1.66
22.02	1.71

Sample 2	20 ml HCL
NaOH	pH
0.00	1.09
5.25	1.20
10.30	1.33
15.00	1.47
20.50	1.67
21.10	1.70
23.50	1.81
25.25	1.89
27.50	2.04
29.30	2.21
30.10	2.29
31.50	2.49
32.25	2.66
33.00	2.92
33.50	3.25
33.60	3.35
33.70	3.48
33.81	3.73
33.90	4.08
34.00	5.21
34.05	5.74
34.10	6.16
34.15	6.63
34.27	8.73

Sample 3	20 ml HCL
NaOH	pH
0.00	1.13
5.00	1.21
10.07	1.32
15.05	1.47
20.03	1.66
25.04	1.88
27.03	2.01
27.50	2.06
28.05	2.10
28.40	2.14
29.40	2.22
30.00	2.29
32.14	2.65
33.00	2.94
33.20	3.05
33.40	3.25
33.60	3.40
33.70	3.57
33.80	3.83
34.00	5.42
34.05	5.80
34.10	6.10
34.15	6.39
34.16	6.44

23.02	1.76
24.04	1.80
25.02	1.86
27.02	2.00
28.09	2.08
29.04	2.15
35.08	9.98

34.35	9.20
34.40	9.43
34.45	9.59
34.50	9.71
34.60	9.95
34.65	10.01

34.17	6.51
34.18	6.61
34.19	6.65
34.20	6.77
34.21	6.90
34.22	7.02
34.23	7.15
34.24	7.31
34.25	7.57
34.26	7.78
34.27	8.06
34.28	8.26
34.29	8.40

MAJOR IONS XRD DATA

Sample name	Type	Application	Processing status	Meas. user	Meas. date/time	Sum	Result type	Na2O	P2O5	Al2O3	CaO	Fe2O3	K2O	MgO	MnO	SiO2	TiO2
		or Instrument monitor				of conc.		Na	P	Al1	Ca	Fe1	K	Mg	Mn	Si	Ti
		or Calibration update				(%)		(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
EAS61-11	R	Major Beads2	Finished	SuperQ	2011/10/06 09:19	98.518	Concentration	0.844	0.14	17.219	0.923	10.365	1.887	0.75	0.027	64.608	1.755
EAS62-11	R	Major Beads2	Finished	SuperQ	2011/10/06 09:31	98.745	Concentration	0.714	0.04	6.355	0.405	4.126	0.621	0.694	0.019	85.198	0.573
EAS63-11	R	Major Beads2	Finished	SuperQ	2011/10/07 12:45	98.776	Concentration	0.707	0.076	13.222	0.606	9.582	0.748	0.424	0.068	71.13	2.213
EAS64-11	R	Major Beads2	Finished	SuperQ	2011/10/06 09:44	94.758	Concentration	1.154	0.087	16.159	10.595	5.925	2.1	2.207	0.096	55.555	0.88
FEM-GCS	R	Major Beads2	Finished	SuperQ	2011/10/06 09:57	99.572	Concentration	0.518	0.05	29.161	0.434	1.396	1.991	0.297	0.016	64.319	1.39
FPK-GCS	R	Major Beads2	Finished	SuperQ	2011/10/06 10:10	98.7	Concentration	0.676	0.046	10.683	0.488	2.233	3.129	0.435	0.031	80.5	0.479

Crucible	Crucible + sample	Crucible+sample @ 110°C	Crucible+sample @ 980°C	Sample wt	Sample wt @ 110	Sample wt @ 980	H2O- wt	H2O-%	LOI wt	LOI wt%	TOTAL LO
2846810	3112930	3108000	3066500	266120	261190	219690	4930	1.852548	41500	15.88882	17.74136
1357000	1617290	1614330	1593220	260290	257330	236220	2960	1.137193	21110	8.203474	9.340667
1669790	1909780	1905660	1881810	239990	235870	212020	4120	1.716738	23850	10.1115	11.82824
1581090	1820600	1817590	1786020	239510	236500	204930	3010	1.256732	31570	13.34884	14.60557
2441680	2707820	2705510	2636150	266140	263830	194470	2310	0.867964	69360	26.28966	27.15762
1856240	2112550	2112250	2103740	256310	256010	247500	300	0.117046	8510	3.324089	3.441135

AN EXAMPLE OF HOW CALCULATIONS WERE DONE TO NORMALISE THE BACK THE SUM OF CONCENTRATION

TiO2				
Ti		%		
(%)		50	x 80%	40
		30	x 80%	24
1.755		20	x 80%	16
0.573				
2.213		100	x 80%	80
0.88				
1.39		20		20
0.479				
Sum less LOSS		80		
New sum of conc				100

TRACE IONS XRD DATA

Sample name	Type	Application	Processing status	Meas. use	Meas. date/time	Sum	Result type	CaO	Sc	TiO2	V	Cr	Fe2O3	Co
		or Instrument monitor				of conc.		Ca	Sc	Ti	V	Cr	Fe	Co
		or Calibration update				(%)		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
FPK-GCS	R	Traces	Finished	SuperQ	2011/10/06 17:55	2.581	Concentration	4061.584	4.981	4257.584	16.479	23.52	16343.24	4.783
FEM-GCS	R	Traces	Finished	SuperQ	2011/10/06 17:35	1.772	Concentration	1895.374	9.032	7776.731	63.785	104.192	6851.018	9.717
EAS-64-11	R	Traces	Finished	SuperQ	2011/10/06 17:15	13.605	Concentration	85180.82	-24.748	7243.721	45.728	55.188	42397.96	9.54
EAS-63-11	R	Traces	Finished	SuperQ	2011/10/06 16:54	11.746	Concentration	6654.213	14.788	25599.63	88.494	74.512	84269.43	38.981
EAS-62-11	R	Traces	Finished	SuperQ	2011/10/06 16:34	4.128	Concentration	3299.211	5.478	4886.527	33.503	272.659	32372.33	4.808
EAS-61-11	R	Traces	Finished	SuperQ	2011/10/06 16:14	11.095	Concentration	7240.33	11.226	15965.71	86.346	74.91	86752.7	6.448

TRACE IONS XRD DATAcont.

Sample name	Meas. date/time	Ni	Cu	Zn	As	Br	Rb	Sr	Y	Zr	Nb	Mo	Ag	Cd	Sn	Sb	Ba	Tl	Pb	Th	U
		Ni	Cu	Zn	As	Br	Rb	Sr	Y	Zr	Nb	Mo	Ag	Cd	Sn	Sb	Ba	Tl	Pb	Th	U
		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
FPK-GCS	2011/10/06 17:55	8.886	3.689	27.893	-21.56	-1.617	91.562	102.519	13.086	167.296	8.617	-0.338	0	2.813	19.869	1.143	652.547	-4.978	20.938	7.582	-2.476
FEM-GCS	2011/10/06 17:35	45.326	20.871	76.816	-19.117	-1.328	58.214	129.164	31.098	224.08	16.225	0.394	0	3.025	19.866	0.447	365.07	-4.392	25.262	13.253	0.885
EAS-64-11	2011/10/06 17:15	22.063	13.217	53.85	-6.768	58.276	94.428	406.846	23.619	183.498	10.676	1.824	0	1.349	21.508	7.298	221.737	-4.059	17.838	11.177	-1.131
EAS-63-11	2011/10/06 16:54	29.911	13.021	74.57	-15.941	3.953	21.543	115.281	11.771	177.517	18.338	1.695	0	-1.595	17.253	1.856	245.056	-3.916	7.984	5.347	-2.462
EAS-62-11	2011/10/06 16:34	15.574	7.247	25.217	-12.55	42.393	24.742	52.857	8.993	113.747	5.375	10.603	0	0.804	18.324	0.365	84.297	-3.321	6.563	3.801	-2.453
EAS-61-11	2011/10/06 16:14	17.525	13.46	55.566	2.647	34.135	59.196	124.423	12.321	184.637	14.977	8.652	0	-5.376	16.706	3.045	261.086	-3.946	11.405	5.254	-3.468

ACTUAL ACIDITY METHOD

pH (KCL) recordings in 2010

Sample name	pH	comment/action	recorded pH	Volume added(ml)	TAA
Blank	4.35	titrate till 6.50	10.16	0.39	-----------
EAS 1A	3.25	titrate till 6.50	6.49	9.38	2948.72
EAS 1B	3.66	titrate till 6.50	6.62	6.68	2191.04
EAS 2A	3.80	titrate till 6.50	6.51	5.46	1790.88
EAS 2B	3.34	titrate till 6.50	6.52	6.33	2076.24
EAS 3A	8.50	TAA is zero	0.00	0.00	0
EAS 3B	8.45	TAA is zero	0.00	0.00	0
EAS 4A	4.51	titrate till 6.50	6.51	2.96	970.88
EAS 4B	4.67	titrate till 6.50	6.50	1.79	587.12
SA:T5A	8.29	TAA is zero	0.00	0.00	0
SA:T5B	7.80	TAA is zero	0.00	0.00	0
SA:T28A	10.75	TAA is zero	0.00	0.00	0
SA:T28B	10.34	TAA is zero	0.00	0.00	0
SA:SB10B SAMPLE 1	9.44	TAA is zero	0.00	0.00	0
SA:SB10B SAMPLE 2	9.27	TAA is zero	0.00	0.00	0
SA:SB11A SAMPLE 1	9.30	TAA is zero	0.00	0.00	0
SA:SB11A SAMPLE 2	9.54	TAA is zero	0.00	0.00	0

2011 THE 1M KCL METHOD

Australian methods

	Soil		NaoH	NaOH normality	NaOH for blanks	diluted to volume	
Sample name	**G_M1**	**pH KCL**	**V1_TITRATION**	**C_NAOH(1 OR 2)**	**V2_TITRATE**	**SUS_V**	**TAA**
EAS 61-1 AUS	1.98	3.59	12.61	0.656	----	200.65	29249.60
EAS 61-2 AUS	2.00	3.6	11.99	0.656	----	230.82	27866.88
EAS 62-1 AUS	2.02	3.53	3.41	0.656	----	227.37	7456.49
EAS 62-2 AUS	2.08	3.53	3.85	0.656	----	254.66	8475.39
EAS 63-1 AUS	1.99	3.65	8.44	0.656	----	212.5	19753.80
EAS 63-2 AUS	2.00	3.66	8.47	0.656	----	234.24	19879.95
EAS 64-1 AUS	2.04	8.64	0.00	0.656	----	212.93	-1076.89
EAS 64-2 AUS	2.06	8.7	0.00	0.656	----	252.4	-1084.37
FKP 1 GCS	2.05	8.3	0.00	0.656	----	249.89	-1034.51
FKP 2 GCS	1.99	8.3	0.00	0.656	----	264.01	-1034.51
FEM 1 GCS	1.99	8.25	0.00	0.656	----	205.9	-1028.28
FEM 2 GCS	2.01	8.18	0.00	0.656	----	260.36	-1019.56
BLANK	----	5.86	----	0.656	0.19	201.31	

PEROXIDE DIGEST 2011

	Soil			NaoH	NaOH for blanks	NaOH normality		NaoH	NaOH for blanks	diluted to volume
Sample name	**G_M2**	**pH ox**	**pH TPA**	**V4/V5**	**V7**	**C2**	**V6**	**V8**	**V**	**V3**
EAS 61-1 AUS	2.02	2.41	2.62	18	----	0.067795	4.27	----	139.8	----
EAS 61-2 AUS	2.01	2.39	2.76	16.97	----	0.067795	5.85	----	113.01	----
EAS 62-1 AUS	2.01	2.21	2.32	14.68	----	0.067795	2.19	----	136.31	----
EAS 62-2 AUS	2.03	2.22	2.3	15.05	----	0.067795	2.06	----	131.65	----
EAS 63-1 AUS	1.02	1.99	sample lost	sample lost	sample lost	sample lost	sample lost	sample lost	sample lost	sample lost
EAS 63-2 AUS	1.01	1.99	2.06	30.88	----	0.067795	1.77	----	125.44	----
EAS 64-1 AUS	2.01	7.69	3.86	2.33	----	0.067795	1.26	----	104.81	9.3
EAS 64-2 AUS	2.02	7.72	3.77	3.6	----	0.067795	1.77	----	113.37	9.4
FKP 1 GCS	2.02	5.37	6.94	next step	----	0.067795	0.06	----	115.49	----
FKP 2 GCS	2	5.47	6.65	next step	----	0.067795	0	----	103.22	----
FEM 1 GCS	1.99	2.5	2.73	13.57	----	0.067795	4	----	153.09	----
FEM 2 GCS	2.01	2.47	3.57	6.36	----	0.067795	4.05	----	117.9	----
BLANK	----	3.3	3.65		0.99	0.067795	----	0.41	101	----
BLANK 2	----	3.28	3.97		0.49	0.067795	----	0.51	99.36	----

Repeated Samples in 2010

EAS 1A redo	1.88
EAS 1B redo	1.86
EAS 4A redo	1.84
EAS 4B redo	1.8

Carbonate modification samples in 2010

Sample name	Lab name	VOL OF 0.5 M HCL	pH
EAS 63-10	EAS 3A	1.25	4.08
EAS 63-10	EAS 3B	1.05	3.93
T28	SA:T28A	3.65	3.88
T28	SA:T28B	3.95	2.12
SB10B	SA:SB10B SAMPLE 1	0.6	2.67
SB10B	SA:SB10B SAMPLE 2	0.3	3.89
SB11A	SA:SB11A SAMPLE 1	0.7	4.06
SB11A	SA:SB11A SAMPLE 2	0.95	3.63

Carbonate modification samples in 2011

Sample name	Lab name	VOL OF 0.5 M HCL	pH
EAS 64-11	EAS 64-1 AUS	9.30	4.10
EAS 64-11	EAS 64-2 AUS	9.40	4.03

TPA without carbonate modification

Sample name	Lab name	pH	M2 mass of soil	pH recorded for 5.5 step	V5 Vol to 5.5	V6 Volume to 6.5	V7 Blank 5.5	V8 Blank 6.5	C2 stand NaoH	TPA (mol H^+/t)
EAS 61-10	EAS 1A redo	2.08	2.00	5.53	34.75	6.50	1.79	4.95	0.07	1207.85
EAS 61-10	EAS 1B redo	2.10	2.00	5.51	31.59	6.55	1.79	4.95	0.07	1098.90
EAS 64-10	EAS 4A redo	1.90	2.00	5.55	35.54	60.21	1.79	4.95	0.07	3115.35
EAS 64-10	EAS 4B redo	2.00	2.00	5.55	26.91	63.29	1.79	4.95	0.07	2921.10
EAS 62-10	EAS 2A	3.14	2.00	5.50	6.82	49.97	1.79	4.95	0.07	1751.75
EAS 62-10	EAS 2B	3.15	2.00	5.50	6.92	19.06	1.79	4.95	0.07	673.40
T5	SA:T5A	6.24	2.00	6.24	0.00	1.90	1.79	4.95	0.07	-169.40
T5	SA:T5B	4.92	2.00	5.50	1.70	19.05	1.79	4.95	0.07	490.35

TPA without Carbonate modification in 2011

Sample name	Lab name	M2 mass of soil	V5 Vol to 5.5	V6 Volume to 6.5	V7 Blank 5.5	V8 Blank 6.5	C2 stand NaoH	TPA
EAS 61-11	EAS 61-1 AUS	2.02	18.00	4.27	0.99	0.41	0.14	1400.9
EAS 61-11	EAS 61-2 AUS	2.01	16.97	5.85	0.99	0.41	0.14	1444.9
EAS 62-11	EAS 62-1 AUS	2.01	14.68	2.19	0.99	0.41	0.14	1043.6
EAS 62-11	EAS 62-2 AUS	2.03	15.05	2.06	0.99	0.41	0.14	1049.3
EAS 63-11	EAS 63-1 AUS	1.02	lost	lost	0.99	0.41	0.14	Sample lost
EAS 63-11	EAS 63-2 AUS	1.01	30.88	1.77	0.99	0.41	0.14	4195.2
FKP	FKP 1 GCS	2.02	0.00	0.06	0.99	0.41	0.14	-89.95
FKP	FKP 2 GCS	2.00	0.00	0.00	0.99	0.41	0.14	-94.91
FEM	FEM 1 GCS	1.99	13.57	4.00	0.99	0.41	0.14	1101.8
FEM	FEM 2 GCS	2.01	6.36	4.05	0.99	0.41	0.14	607.79

Titratable SulfidicAcidity(TSA)

TSA = TPA – TAA

TSA in 2010

Sample name	TPA	TAA	TSA
EAS 1A redo	1207.9	328.3	879.6
EAS 1B redo	3161.2	233.8	2927
EAS 2A	1751.8	0	1752
EAS 2B	673.4	221.6	451.9
EAS 3A	900.03	0	900
EAS 3B	595.61	0	595.6
EAS 4A redo	3115.4	103.6	3012
EAS 4B redo	2921.1	62.65	2858
SA:T5A	-169.4	0	-169.4
SA:T5B	490.35	0	490.4
SA:T28A	258.96	0	259
SA:T28B	983.08	0	983.1
SA:SB10B SAMPLE 1	33.10	0	33.1
SA:SB10B SAMPLE 2	220.29	0	220.3
SA:SB11A SAMPLE 1	534.29	0	534.3
SA:SB11A SAMPLE 2	617.87	0	617.9

TSA in 2011

Sample name	TPA	TAA	TSA
EAS 61-1 AUS	1400.87	798.4	602.47
EAS 61-2 AUS	1444.94	798.4	646.54
EAS 62-1 AUS	1043.57	220.16	823.41
EAS 62-2 AUS	1049.32	220.16	829.16
EAS 63-1 AUS	lost	-496.19	lost
EAS 63-2 AUS	4195.24	-496.19	4691.4
EAS 64-1 AUS	8055.66	0	8055.7
EAS 64-2 AUS	7559.46	0	7559.5
FKP 1 GCS	-89.9458	0	-89.946
FKP 2 GCS	-94.913	0	-94.913
FEM 1 GCS	1101.75	0	1101.8
FEM 2 GCS	607.794	0	607.79

SPOCUS residual acid soluble sulphur (S_{RAS})

This method was done to determine whether or not insoluble sulphur was present initially or formed during peroxide oxidation. It is not compulsory to do this method but it is recommended. In 2010 I did this method to calculate the sulphur that is retained after the peroxide oxidation. The results showed that no little or no residual acid soluble sulphur is present.

Residual acid soluble sulphur in 2010

Sample	lab name:	SO_4	S_{RAS}
Blank 1	Blank 1	6.19	0.00
Blank 2	Blank 2	1.95	0.00
EAS 61-10	EAS 1A	19.51	0.05
EAS 61-10	EAS 1B	51.55	0.18
EAS 62-10	EAS 2A	6.11	0.00
EAS 62-10	EAS 2B	7.05	0.00
EAS 63-10	EAS 3A	7.66	0.00
EAS 63-10	EAS 3B	7.65	0.01
EAS 64-10	EAS 4A	15.82	0.04
EAS 64-10	EAS 4B	25.82	0.07
T5	SA:T5A	7.25	0.00

T5	SA:T5B	10.71	0.02
T28	SA:T28A	33.25	0.10
T28	SA:T28B	43.09	0.15
SB10B	SA:SB10B SAMPLE 1	4.29	-0.01
SB10B	SA:SB10B SAMPLE 2	5.41	-0.00
SB11A	SA:SB11A SAMPLE 1	3.25	-0.01
SB11A	SA:SB11A SAMPLE 2	3.15	-0.01

ANC recordings in_2010

Sample	lab name:	Mass	pH	NaOH added	pH recorded
Blank 1	Blank 1	1.00	1.60	45.27	7.00
Blank 2	Blank 2	1.00	1.60	45.22	7.04
EAS 61-10	EAS 1A	1.00	1.60	47.86	7.06
EAS 61-10	EAS 1B	1.00	1.55	47.71	7.99
EAS 62-10	EAS 2A	1.00	1.47	46.58	6.98
EAS 62-10	EAS 2B	1.00	1.47	47.16	7.23
EAS 63-10	EAS 3A	1.00	1.53	36.29	6.99
EAS 63-10	EAS 3B	1.00	1.51	35.39	6.97
EAS 64-10	EAS 4A	1.00	1.57	45.42	7.04
EAS 64-10	EAS 4B	1.00	1.57	45.06	7.00
T5	SA:T5A	1.00	1.65	33.11	7.12
T5	SA:T5B	1.00	1.65	32.78	8.12
T28	SA:T28A	1.00	1.68	20.38	7.04
T28	SA:T28B	1.00	1.79	17.75	7.14
SB10B	SA:SB10B SAMPLE 1	1.00	1.48	37.00	6.98
SB10B	SA:SB10B SAMPLE 2	1.00	1.55	40.66	6.98
SB11A	SA:SB11A SAMPLE 1	1.00	1.60	40.06	7.26
SB11A	SA:SB11A SAMPLE 2	1.00	1.63	41.25	7.18
Ref sample	Ref sample 1	0.10	1.97	12.63	7.06
Ref sample	Ref sample 2	0.10	2.02	12.75	7.04
Ref sample	Ref sample 3	0.10	2.03	12.79	7.00

ANC recordings in_2010

NaOH

Sample name	**G_M**	**V_HCL**	**HCL normality C1**	**pH**	**NaOH normality C2**	**END POINT pH**	NaOH**V_B**	**Average M**	**Average pH**	**Average end point pH**	**Average V_B**
EAS 61-1 AUS	1.09	25	0.112173	1.48	0.0655995	7	49.15	1.065	1.495	7.01	48.98
EAS 61-2 AUS	1.04	25	0.112173	1.51	0.0655995	7.02	48.81				
EAS 62-1 AUS	1.03	25	0.112173	1.49	0.0655995	7.15	44.95	1.01	1.51	7.17	44.905
EAS 62-2 AUS	0.99	25	0.112173	1.53	0.0655995	7.19	44.86				
EAS 63-1 AUS	1.01	25	0.112173	1.55	0.0655995	8.19	46	1.01	1.56	7.61	45.975
EAS 63-2 AUS	1.01	25	0.112173	1.57	0.0655995	7.03	45.95				
EAS 64-1 AUS	1.04	25	0.112173	1.76	0.0655995	7.01	39.58	1.03	1.705	7.03	42.58
EAS 64-2 AUS	1.02	25	0.112173	1.65	0.0655995	7.05	45.58				
FKP 1 GCS	1.01	25	0.112173	1.68	0.0655995	7.09	40.75	1.005	1.68	7.045	40.35
FKP 2 GCS	1	25	0.112173	1.68	0.0655995	7	39.95				
FEM 1 GCS	1.01	25	0.112173	1.63	0.0655995	7.64	41.31	1.01	1.805	7.913333333	41.4
FEM 2 GCS	1.01	25	0.112173	1.6	0.0655995	7.84	41.49				
REF 1	0.1	25	0.112173	2.01	0.0655995	8.26	13.33	0.0987	2.073333333	7.47	13.74333333
REF 2	0.1	25	0.112173	2.15	0.0655995	7.02	12.16				

REF 3	0.1	25	0.112173	2.06	0.0655995	7.13	15.74				
BLANK	----	25	0.112173	1.55	0.0655995	10.69	45.58		1.54	9.32	44.51
BLANK 2	----	25	0.112173	1.53	0.0655995	7.95	43.44				

Table 0-1 pH (KCL) recordings in 2011

Sample name	Lab name	pH	comment/action	recorded pH	Volume added(ml)	TAA (mol H^+/t)
Blank	BLANK	5.86	titrate till 6.5	9.75	0.19	
EAS 61-11	EAS 61-1 AUS	3.59	titrate till 6.5	6.65	12.61	29249.60
EAS 61-11	EAS 61-2 AUS	3.60	titrate till 6.5	6.50	11.99	27866.88
EAS 62-11	EAS 62-1 AUS	3.53	titrate till 6.5	6.54	3.41	7456.49
EAS 62-11	EAS 62-2 AUS	3.53	titrate till 6.5	6.79	3.85	8475.39
EAS 63-11	EAS 63-1 AUS	3.65	titrate till 6.5	6.48	8.44	19753.80
EAS 63-11	EAS 63-2 AUS	3.66	titrate till 6.5	6.52	8.47	19879.95
EAS 64-11	EAS 64-1 AUS	8.64	TAA is zero	-	TAA is zero	0
EAS 64-11	EAS 64-2 AUS	8.70	TAA is zero	-	TAA is zero	0
FKP	FKP 1 GCS	8.30	TAA is zero	-	TAA is zero	0
FKP	FKP 2 GCS	8.30	TAA is zero	-	TAA is zero	0
FEM	FEM 1 GCS	8.25	TAA is zero	-	TAA is zero	0
FEM	FEM 2 GCS	8.18	TAA is zero	-	TAA is zero	0

1M KCL EXTRACTABLE SULPHUR (S_{KCL}), CALCIUM (CA_{KCL}) AND MAGNESIUM (MG_{KCL})

The % of all the main cations were calculated using the equations

S% =(S (ICP result)-S (ICP Blank1 result)*(Vol/mass of sample))/10000

Ca% = (Ca (ICP result)-Ca (ICP Blank1 result)*(Vol/mass of sample))/10000

Fe% =(S (ICP result)-S (ICP Blank1 result)*(Vol/mass of sample))/10000

SO_4% = (SO_4 (ICP result)-SO_4 (ICP Blank1 result)*(Vol/mass of sample))/10000

The above equations will now be referred to as the following equation for the rest of this chapter:

Cation % = (Cation (ICP result)-Cation (ICP Blank1 result)*(Vol/mass of sample))/10000

Equation 0-1 Cation %

Equation 0-1 is used to calculate the percentages and samples that have a high value compared to others in table are highlighted with a specific colour (i.e. High Mg with the colour yellow).

Table 0-2 KCL extractable (Mg, S and Ca results in 2010)

Sample	lab name:	Mg(mg/l)	%Mg	SO4(mg/l)	%SO4	Ca(mg/l)	%Ca
EAS 61-10	EAS 1A	4.39	0.03	60.94	0.61	5.39	0.02
EAS 61-10	EAS 1B	4.24	0.03	50.01	0.50	5.64	0.02
EAS 62-10	EAS 2A	1.48	0.00	16.27	0.16	4.26	0.01
EAS 62-10	EAS 2B	1.34	0.00	22.48	0.22	2.67	0.01
EAS 63-10	EAS 3A	16.26	0.15	33.92	0.34	34.70	0.31
EAS 63-10	EAS 3B	16.22	0.15	35.23	0.35	36.34	0.33
EAS 64-10	EAS 4A	37.86	0.37	126.27	1.28	24.76	0.21
EAS 64-10	EAS 4B	37.76	0.37	129.47	1.29	24.37	0.21
T5	SA:T5A	4.70	0.04	88.00	0.88	59.79	0.56
T5	SA:T5B	5.09	0.04	90.12	0.90	71.11	0.67
T28	SA:T28A	4.83	0.03	22.96	0.17	12.65	0.07
T28	SA:T28B	5.08	0.03	23.26	0.18	13.78	0.08
SB10B	SA:SB10B SAMPLE 1	2.18	0.01	2.60	0.03	9.80	0.07
SB10B	SA:SB10B SAMPLE 2	1.91	0.01	1.73	0.02	8.18	0.05
SB11A	SA:SB11A SAMPLE 1	2.42	0.01	1.88	0.02	20.02	0.16
SB11A	SA:SB11A SAMPLE 2	2.32	0.02	1.79	0.02	20.56	0.20

Table 0-3 KCL extractable (Mg, S and Ca results n 2011)

Sample	lab name:	Mg(mg/l)	%Mg	SO4(mg/l)	%SO4	Ca(mg/l)	%Ca
EAS 61-11	EAS 61-1 AUS	5.800	0.055	87.429	0.880	10.533	0.095
EAS 61-11	EAS 61-2 AUS	4.800	0.051	73.000	0.836	8.180	0.081
EAS 62-11	EAS 62-1 AUS	11.500	0.126	55.000	0.613	10.574	0.106
EAS 62-11	EAS 62-2 AUS	10.600	0.125	51.000	0.618	10.040	0.109

EAS 63-11	EAS 63-1 AUS	4.800	0.048	64.000	0.677	8.649	0.080
EAS 63-11	EAS 63-2 AUS	5.400	0.059	64.000	0.743	10.116	0.105
EAS 64-11	EAS 64-1 AUS	7.000	0.069	60.000	0.620	47.250	0.481
EAS 64-11	EAS 64-2 AUS	7.000	0.081	55.000	0.667	43.653	0.521
FKP	FKP 1 GCS	1.412	0.011	7.036	0.067	11.270	0.105
FKP	FKP 2 GCS	1.038	0.009	4.733	0.054	10.015	0.115
FEM	FEM 1 GCS	1.525	0.014	6.315	0.070	16.830	0.191
FEM	FEM 2 GCS	1.168	0.011	6.231	0.075	14.829	0.182

- ✓ The EAS 62-11 duplicates have a high Mg content whereas EAS 64-11 duplicates has a high Ca content relative to the others.
- ✓ South African samples have the lowest SO_4 content; Conversely EAS 61-11 duplicates have a high content of SO_4.

MINERALOGICAL ANALYSIS OF THE 2011 SAMPLES

To verify the mineralogical content of the samples, XRD and XRF analyses were performed at the Department of Geology at the University of the Free State in 2011. **Appendix 1** details the methodology of these analyses.

Mineralogical results of the 2011 samples (major elements %)-XRF

	Na2O **Na** (%)	Al2O3 **Al1** (%)	CaO **Ca** (%)	Fe2O3 **Fe1** (%)	K2O **K** (%)	MgO **Mg** (%)	MnO **Mn** (%)	SiO2 **Si** (%)
EAS61-11	**0.84**	**17.22**	**0.92**	**10.37**	**1.89**	**0.75**	**0.03**	**64.61**
EAS62-11	0.71	6.36	0.41	4.13	0.62	0.69	0.02	85.20
EAS63-11	**0.71**	**13.22**	**0.61**	**9.58**	**0.75**	**0.42**	**0.07**	**71.13**
EAS64-11	1.15	16.16	10.60	5.93	2.10	2.21	0.10	55.56
FPK GCS	**0.68**	**10.68**	**0.49**	**2.23**	**3.13**	**0.44**	**0.03**	**80.50**
FEM GCS	0.52	29.16	0.43	1.40	1.99	0.30	0.02	64.32

The highest values are highlighted with red in **Error! Reference source not found.** The loss of water (at 110^0C) and the loss of ignition (at 980^0C) were accounted for in the calculations done to normalise the values back to the sum of concentration by including them in the total. The sum of concentration did not add to a 100% even after the trace ions were converted to percentages and added to the total. In fact, some samples (i.e. EAS 64-11) showed a relatively large discrepancy due to typical theoretical reasons such as the content of SiO_2 (depending on the abundance) and significant halite and pyrite. A variance of up to 2 was evident in such cases.

Assumptions of minerals from the XRD results

	EAS61-11	EAS62-11	EAS63-11	EAS64-11	FPK GCS	FEM GCS
Dominant mineral (>50%)	-	Quartz	Quartz	-	Quartz	-
Major minerals (20-50%)	Quartz	-	-	Quartz	-	Quartz, Kaolinite
Minor minerals (10-20%)	Natrojarosite	-	-	Halite	Feldspar, Kaolinite	Mica
Accessory minerals (2-10%)	Feldspar, Kaolinite	Feldspar, Halite, Pyrite	Feldspar, Pyrite, Kaolinite	Pyrite, Feldspar, Mica, Kaolinite	Mica	Feldspar
Rare minerals (<2%)	-	-	Ilmenite	Aragonite	-	-

Brief description of minerals found in Table above

Aragonite $CaCO_3$

- Calcium Carbonate mineral that is formed in low temperatures near the surface of the earth.
- Found in the oxidation zone of ore deposits, hot springs, caves and in mineral veins.
- In iron-ore deposits it associated with siderite (Gavira and Frances, 2008).

Feldspar

- Aluminosilicate mineral group that contain Calcium (Ca), Sodium (Na) or Potassium (K).
- Have two groups, namely Alkali and plagioclase (Gavira and Frances, 2008).
- In this chapter no specific mineral formula will be mentioned in relation to the feldspar mineral since there are two groups and the formation of them both is unknown.

Halite NaCl

- A sodium chloride mineral that is often accompanied by gypsum, anhydrite and slyvite.
- Widely spread in large saline(i.e. sea water) evaporates (Gavira and Frances, 2008

Ilmenite $FeTiO_3$

- Distributed widely as an accessory mineral in igneous rocks.
- With relevance to the samples studied in this chapter, ilmenite is also found in the Western Australia amongst other places.(Gavira and Frances, 2008

Kaolinite $Al_2Si_2O_5(OH)_4$

- An aluminium silicate hydrate mineral
- Under the influence of water it is a natural product of the alteration of mica and plagioclase and alkali feldspars. (Gavira and Frances, 2008).

Mica

- Is a sheet structure silicate (phyllsosilicate) mineral group.
- It is a potassium aluminosilicate hydrates with sodium, lithium, magnesium or iron in certain varieties (Gavira and Frances, 2008).
- Due to a variety of this group and unknown origins of the Australian samples, no mica mineral composition will be mentioned in this chapter.

Natrojarosite $NaFe_3 (SO_4)_2 (OH)_6$

- Ahydroxy sulphate mineral that is readily insoluble and stable at a pH values between3-4.
- An acidic by-product of ASS oxidation(Thomas et al., 2003)

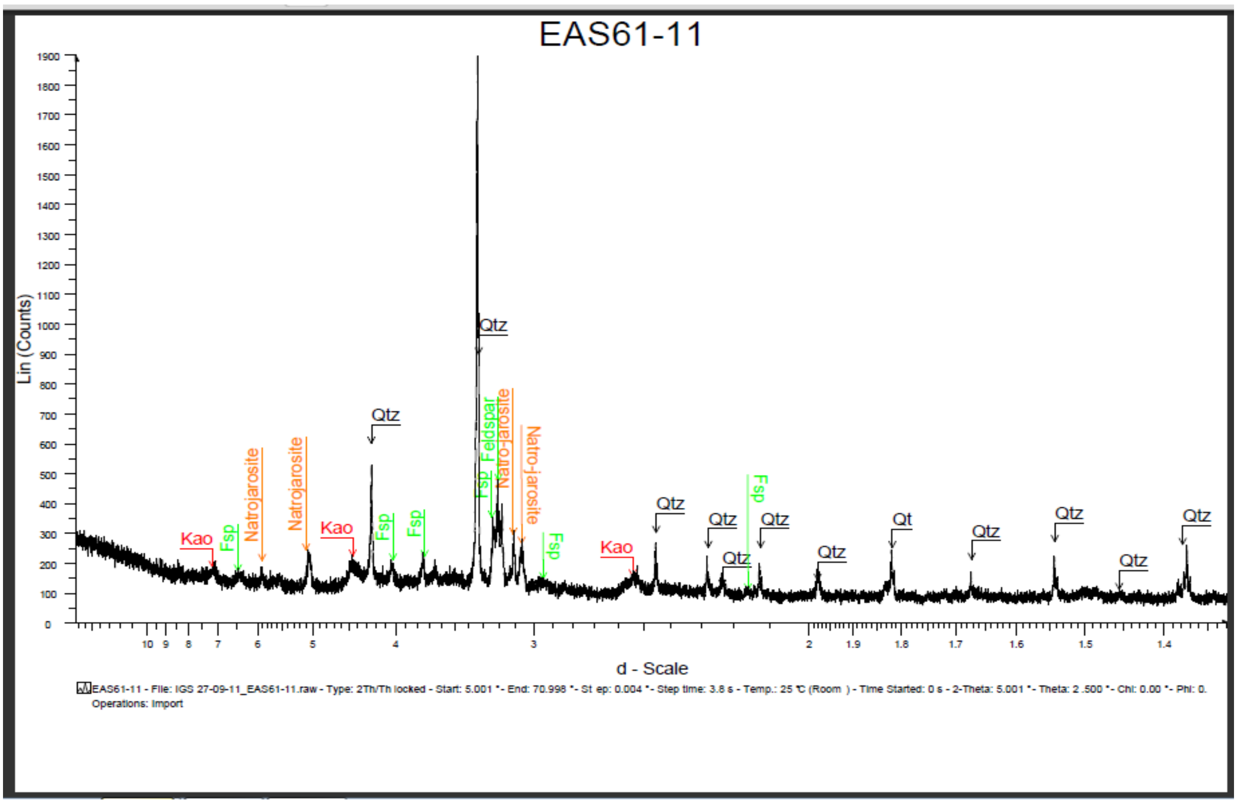
Pyrite FeS_2

- A widely spread sulphide mineral that is the primary source of AMD in the South African mines or a source of acidic conditions in other environments.

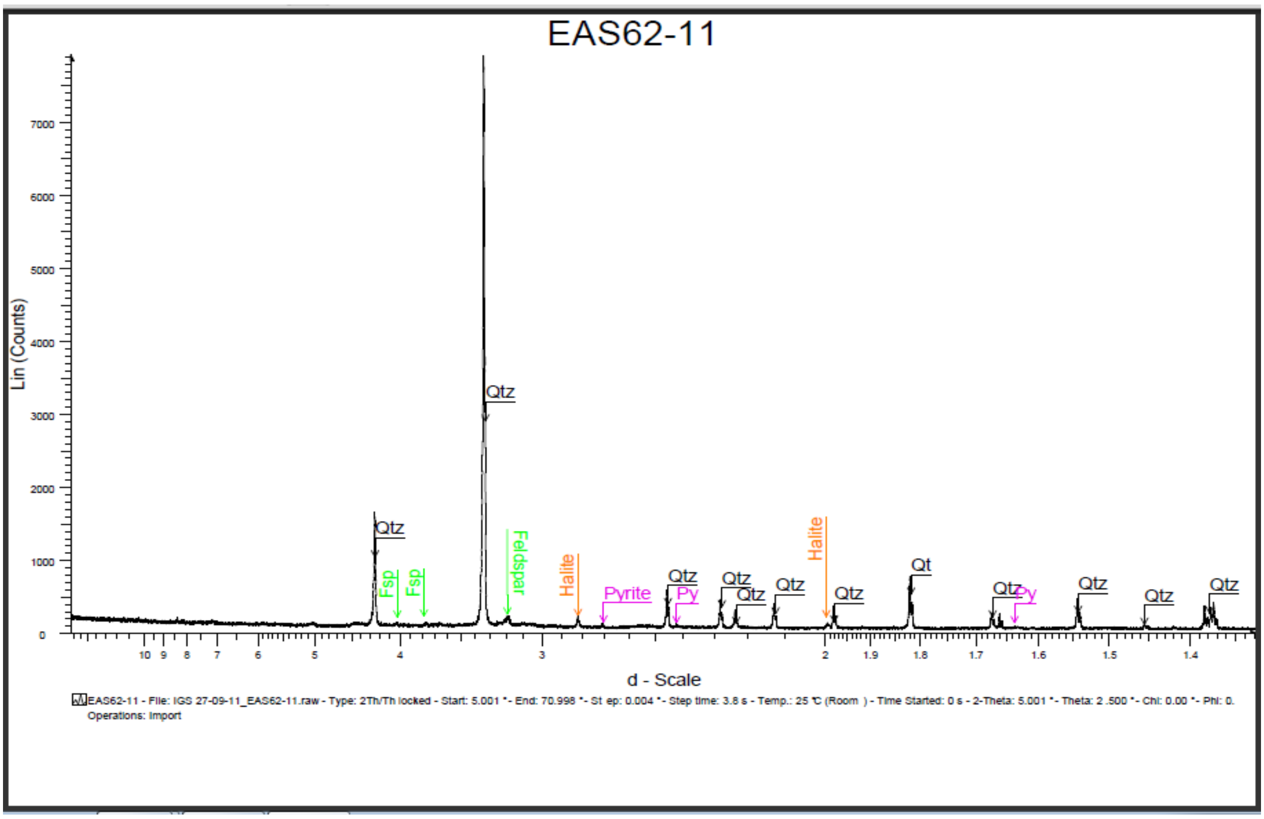
Quartz SiO_2

- A silicon dioxide mineral that is common in the earth’s crust.

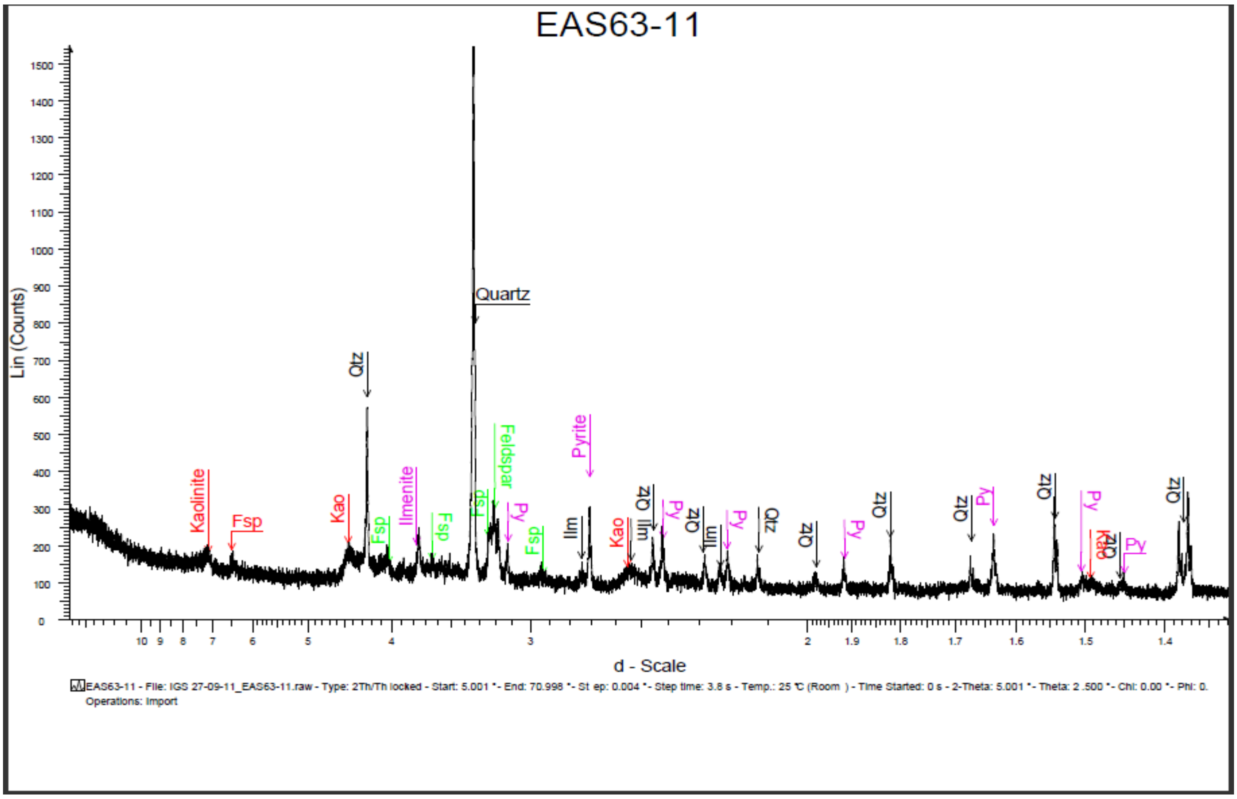
XRD RESULTS DONE ON THE 2011 SAMPLES



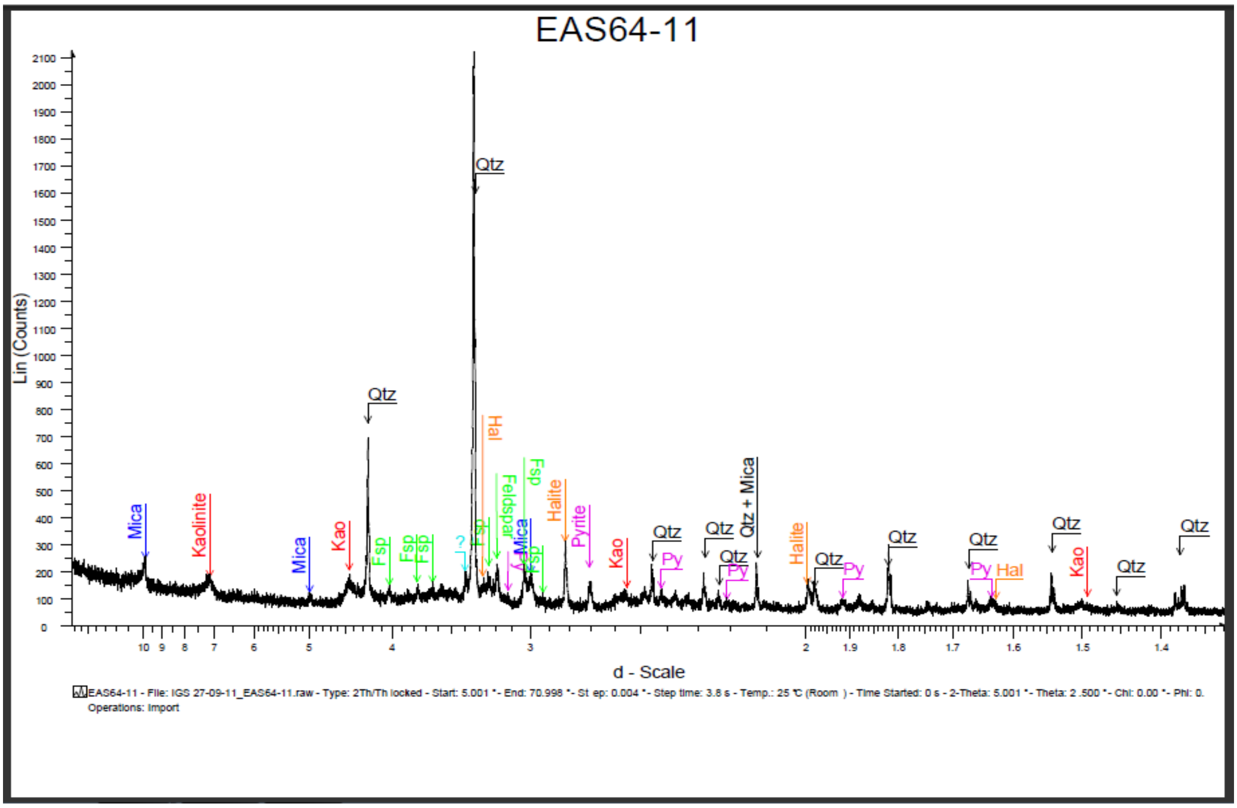
EAS 61-11 XRD OUTPUT GRAPH



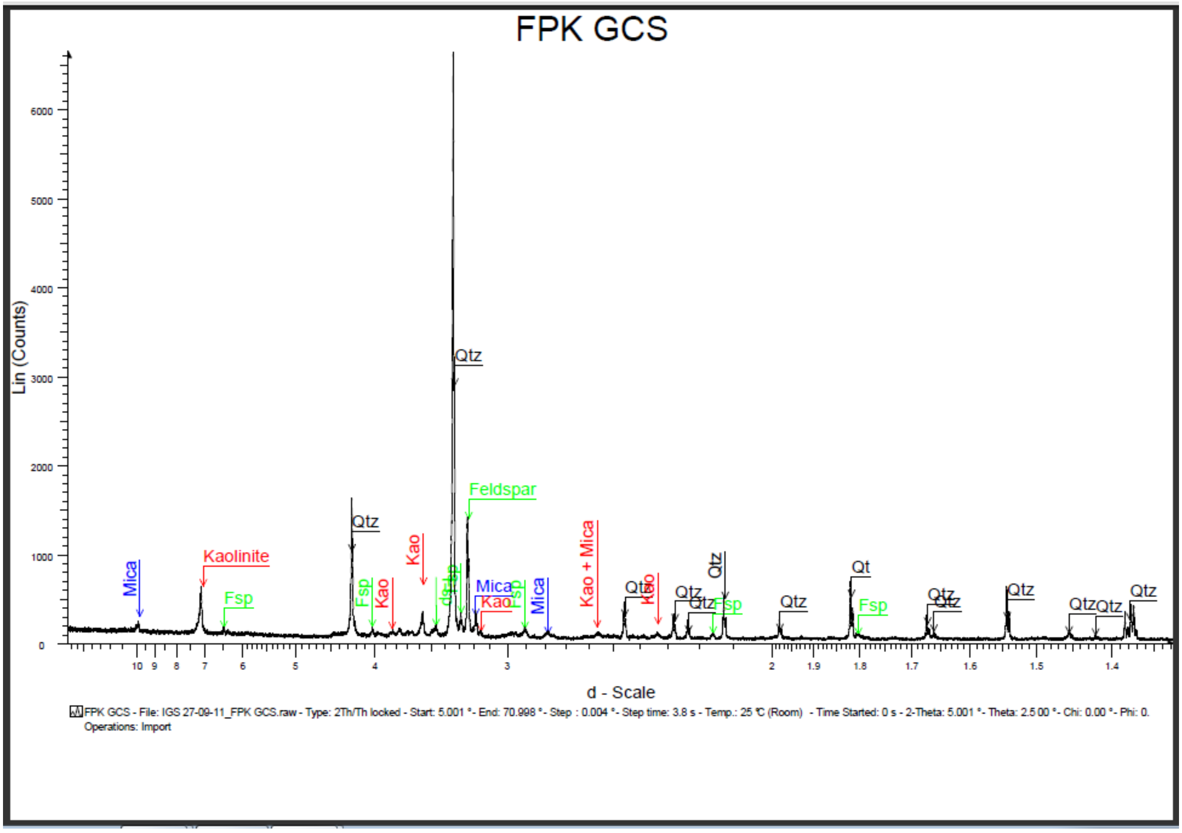
EAS 62-11 XRD OUTPUT GRAPH



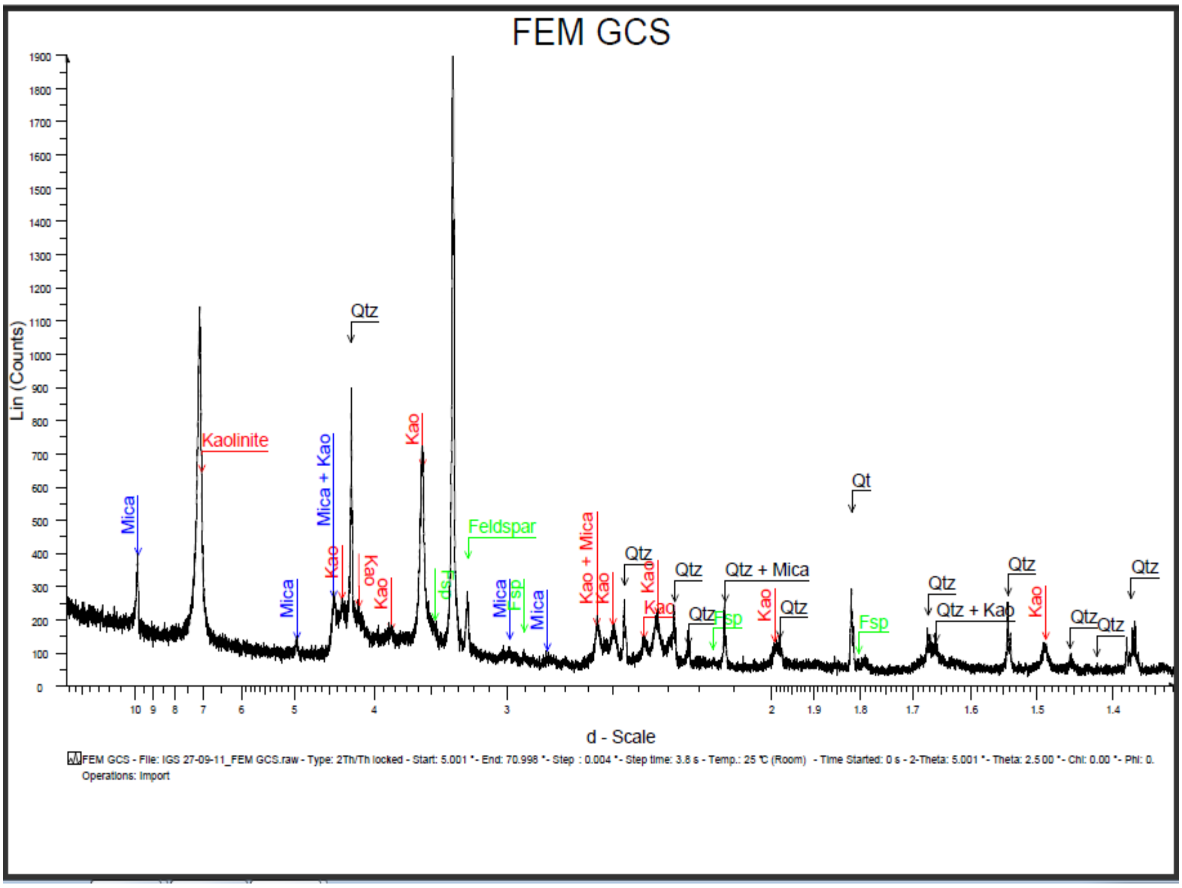
EAS 63-11 XRD OUTPUT GRAPH



EAS 64-11 XRD OUTPUT GRAPH



FKP GCS XRD OUTPUT GRAPH



FKP GCS XRD OUTPUT GRAPH

SUMMARY OF THE RESULTS FROM THE XRD, XRF AND ICP ANALYSIS -2011

Please take note that only the 3 ions of the ICP results are discussed and that the ICP results are derived from the samples that had undergone the Australian KCl method (analysis of the initial state of the sample). Since quartz is the most common mineral in the earth's crust it is practical that the content of it in the EAS 61-11 duplicates has a high percentage of it

- ✓ The average TAA is 28558.24mol H^+/t therefore verifies the presence of by-product of oxidation (Natrojarosite) and the high ICP value of SO_4.
- ✓ Quartz is a dominant mineral in sample EAS 62-11 duplicate because it is the most common mineral in the earth's crust.

SUMMARY OF XRD, XRF AND ICP RESULTS FOR EAS 61-11 (AUSTRALIAN METHODS)

EAS 61-11 duplicate XRD results	EAS 61-11 duplicateaverageICP results

SiO$_2$ (Si)__64.61%	**Major minerals (20-50%)** Quartz: SiO$_2$	
Na$_2$O (Na)__0.84% Fe$_2$O$_3$ (Fe)__10.37 %	**Minor minerals (10-20%)** Natrojarosite: NaFe$_3$ (SO$_4$)$_2$ (OH)$_6$	SO$_4$___0.858%
CaO (Ca)__0.92 % Al$_2$O$_3$(Al) __17.22 % K$_2$O(K)__1.89 % MgO(Mg)__0.75%	**Accessory minerals (2-10%)** Feldspar: Aluminosilicate mineral group with Calcium (Ca), Sodium (Na) or Potassium (K). Kaolinite:Al$_2$ Si$_2$ O$_5$ (OH)$_4$	Ca___0.088% Mg___0.053%

- ✓ The high Fe content from the XRD results and SO$_4$ relate well to the TAA (Average 7965.94 mol H$^+$/t) of the sample. The results show the oxidation had taken place and the sample is already acidic. Further acidity of the sample may also occur.
- ✓ With the buffering capacity (Ca and Mg %) lower than the SO$_4$%, self-remediation of the sample area does not seem to be a reliable option for remediation of acidity.

SUMMARY OF XRD, XRF AND ICP RESULTS FOR EAS 62-11 (AUSTRALIAN METHODS)

EAS 62-11 duplicate XRF results	XRD results	EAS 62-11 duplicate average ICP results
SiO$_2$ (Si)__ 85.20 %	**Dominant minerals (>50%)** **Quartz:**	

	SiO_2	
CaO (Ca)__ 0.41% Al_2O_3(Al) __6.36% K_2O(K)__ 0.62% MgO(Mg)__0.69% Na_2O(Na)__ 0.71% Fe_2O_3(Fe)___4.13%	**Accessory minerals (2-10%)** Feldspar: Aluminosilicate mineral group with Calcium (Ca), Sodium (Na) or Potassium (K). Halite: NaCl Pyrite: FeS_2	Ca___0.1075% Mg___0.1255% SO_4____0.616%

- ✓ The average TAA is 19816.875mol H+/t therefore it verifies the presence of the high Fe and SO4 content.

SUMMARY OF XRD, XRF AND ICP RESULTS FOR EAS 63-11 (AUSTRALIAN METHODS)

EAS 63-11 duplicate XRF results	XRD results	EAS 63-11 duplicate average ICP results
SiO_2 (Si)__ 71.13%	**Dominant Mineral (>50%) Quartz:** SiO_2	
CaO (Ca)__0.61% Al_2O_3(Al) __13.22% K_2O(K)__0.75% MgO(Mg)__0.42% Na_2O(Na)__0.71%	**Accessory minerals (2-10%)** Feldspar: Aluminosilicate mineral group with Calcium (Ca), Sodium (Na) or Potassium (K). Kaolinite: $Al_2 Si_2 O_5 (OH)_4$ Pyrite: FeS_2	Ca___0.09% Mg___0.407% SO_4____0.710%

Fe_2O_3(Fe)___9.58%	

- ✓ The TAA of this sample is zero but the ICP show high values of SO_4 and Ca.
- ✓ Both the ICP and XRD results show high Ca values as compared to the rest of the samples. This might help with self-remediation of the sample since Mg and Na also have high XRD values with the assumption that the SO_4 can be depleted or equilibrium is reached.
- ✓ An assumption that there is potential acidity of the sample is made since there is high SO_4 ICP value but a TAA value of zero. This assumption will be verified by the TPA method that is discussed further in the chapter.
- ✓ The sum of concentration from the XRD results did not add up to 100%, having the largest discrepancy of all the samples analysed because of halite (very soluble) and pyrite (loss of sulphur on ignition) in the EAS 64-11 sample.

SUMMARY OF XRD, XRF AND ICP RESULTS FOR EAS 64-11 (AUSTRALIAN METHODS)

EAS 64-11 duplicate XRF results	XRD results	EAS 64-11 duplicate average ICP results
SiO_2 (Si)__ 55.56%	**Major minerals (20-50%)** Quartz: SiO_2	
Na2O(Na)__ 1.15%	**Minor minerals (10-20%):** Halite	

CaO (Ca)__10.60% Al_2O_3(Al) __16.16% K_2O(K)__2.10% MgO(Mg)__2.21%	**Accessory minerals (2-10%):** Feldspar: Aluminosilicate mineral group with Calcium (Ca), Sodium (Na) or Potassium (K). Pyrite: FeS_2 Mica: Potassium Aluminosilicate hydrates with sodium, lithium, magnesium or iron in certain varieties Kaolinite: $Al_2 Si_2 O_5 (OH)_4$	Ca___0.501% Mg___0.075% SO_4___0.644%

- ✓ The Average TAA value is zero, with the samples pH around 8.
- ✓ There is a low SO_4 content in this FKP GCS sample showing that non-acidic conditions prevail.
- ✓ The aluminium percentage followed by the potassium is evidently high compared to the others due to the Accessory and Minor minerals being Aluminosilicate minerals with potassium.

SUMMARY OF XRD, XRF AND ICP RESULTS FOR FKP GCS (AUSTRALIAN METHODS)

FKP GCS duplicate XRF results	XRD results	FKP GCS duplicate average ICP results
SiO_2 (Si)__80.50%	**Dominant minerals (>50%)** Quartz: SiO_2	

CaO (Ca)__0.49 % Al_2O_3(Al) __10.68% K_2O(K)__ 3.13% MgO(Mg)__ 0.44% Na2O(Na)__0.68 % Fe_2O_3(Fe)___2.23%	**Minor minerals (10-20%):** Feldspar, Aluminosilicate mineral group with Calcium (Ca), Sodium (Na) or Potassium (K). Kaolinite: $Al_2 Si_2 O_5 (OH)_4$ **Accessory minerals (2-10%):** Mica: Potassium Aluminosilicate hydrates with sodium, lithium, magnesium or iron in certain varieties.	Ca___0.148% Mg___0.010% SO_4___0.060%

- ✓ The average pH of the FEM GCS sample was 8.22 showing alkaline conditions which resulted in the TAA being zero.
- ✓ The Sulphate percentage of this sample is low compared to the Australian results.
- ✓ FEM GCS sample has the highest aluminium percentage compared to the rest of the samples analysed by the mineralogical analysis. Kaolinite is a major mineral together with Quartz which might be the reason for high aluminium percentage in the mineral.

SUMMARY OF XRD, XRF AND ICP RESULTS FOR FEM GCS (AUSTRALIAN METHODS)

FEM GCS duplicate XRF results	XRD results	FEM GCS duplicate average ICP results
SiO_2 (Si)__64.32%	**Dominant minerals (>50%)** Quartz: SiO_2	

CaO (Ca)__ 0.43%	**Minor minerals (10-20%):**	Ca___0.187%
	Kaolinite: $Al_2 Si_2 O_5 (OH)_4$	
Al_2O_3(Al) __29.16%		
K_2O(K)__ 1.99%	Mica: Potassium Aluminosilicate hydrates with sodium, lithium, magnesium or iron in certain varieties	Mg___0.013%
MgO(Mg)__ 0.30%		SO_4___0.073%
	Accessory minerals (2-10%):	
Na2O(Na)__ 0.52%	Feldspar, Aluminosilicate mineral group with Calcium (Ca), Sodium (Na) or Potassium (K).	

The ratio between the XRF/XRD of cations and ICP values is large in all the samples. The ratio might be a resultant of the different sample states analysed with different methods. The mineralogical analysis was done on a sample in its “natural” pulverised state whereas the ICP analysis was done on the in sample that had been mixed with KCL according to the Australian methods. Therefore one state of the sample is in analysed in a solid form while the other is in a water soluble state. Another environmental problem would be prevalent if the Aluminium content has highest percentage and could leach into the groundwater, vegetation or soil.

PEROXIDE OXIDISED PH (PH$_{OX}$) AND TITRATABLE PEROXIDE ACIDITY (TPA)

pH (ox) recorded in 2010

Sample name	name of sample:	Mass(g)	pH recorded	action taken
Blank 1	Blank 1	2 .00	3.23	
Blank 2	Blank 2	2 .00	3.18	
EAS 61-10	EAS 1A	2 .00	1.79	repeated using only 1 gram of sample

EAS 61-10	EAS 1B	2 .00	1.77	repeated using only 1 gram of sample
EAS 62-10	EAS 2A	2 .00	2.78	
EAS 62-10	EAS 2B	2 .00	2.77	
EAS 63-10	EAS 3A	2 .00	7.2	carbonate modification
EAS 63-10	EAS 3B	2.00	7.16	carbonate modification
EAS 64-10	EAS 4A	2 .00	------------------	----------------
EAS 64-10	EAS 4A TRY 3	1.67	1.86	repeated using only 1 gram of sample
EAS 64-10	EAS 4B	2 .00	1.76	repeated using only 1 gram of sample
T5	SA:T5A	2 .00	5.85	
T5	SA:T5B	2.00	5.11	
T28	SA:T28A	2.00	7.42	carbonate modification
T28	SA:T28B	2.00	7.46	carbonate modification
SB10B	SA:SB10B SAMPLE 1	2 .00	6.62	carbonate modification
SB10B	SA:SB10B SAMPLE 2	2 .00	6.54	carbonate modification
SB11A	SA:SB11A SAMPLE 1	2 .00	6.67	carbonate modification
SB11A	SA:SB11A SAMPLE 2	2 .00	6.74	carbonate modification

pH (ox) recorded in 2011

Sample name	Lab name	Mass(g)	pH recorded	action taken/comment
Blank	BLANK	----	3.30	
Blank 2	BLANK 2	----	3.28	
EAS 61-11	EAS 61-1 AUS	2.02	2.41	
EAS 61-11	EAS 61-2 AUS	2.01	2.39	
EAS 62-11	EAS 62-1 AUS	2.01	2.21	
EAS 62-11	EAS 62-2 AUS	2.03	2.22	
EAS 63-11	EAS 63-1 AUS	1.02	1.99	Violent reaction with 2 gram.
EAS 63-11	EAS 63-2 AUS	1.01	1.99	violent reaction with 2 gram

EAS 64-11	EAS 64-1 AUS	2.01	7.69	carbonate modification
EAS 64-11	EAS 64-2 AUS	2.02	7.72	carbonate modification
FKP	FKP 1 GCS	2.02	5.37	
FKP	FKP 2 GCS	2.00	5.47	
FEM	FEM 1 GCS	1.99	2.5	
FEM	FEM 2 GCS	2.01	2.47	

2 grams of EAS 63-1 AUS and EAS 63-2 AUS reacted violently when increments of peroxide were added; the violent reaction caused some of the sample to be lost so the sample was repeated with a lesser amount of sample. 1 gram of EAS 63-1 AUS and EAS 63-2 AUS sample was then used but the violent reaction did not seem to decrease. The pH was not less than 2 indicating high sulphide content in the EAS 63-11 sample. EAS 64-11 was the only sample that had to be subjected to carbonate modification.

TPA CALCULATION FOR SAMPLES WITHOUT CARBONATE MODIFICATION

$$\text{TPA (mol } H^{+}/t) = [(v_5 + v_6 - v_7 - v_8) * C_2] * (1000/m_2) \ldots\ldots\ldots\ldots(2)$$

TPA without carbonate modification

The samples that had a pH value lower than 6.5 after peroxide digestion did not have to go through carbonate modification; Equation 0-1 was used to calculate the samples TPA in mol H^{+}/t.

TPA without Carbonate Modification in 2010

Sample name	Lab name	pH	M2	pH recorded for 5.5 step	V5	V6	V7	V8	C2	TPA (mol H^{+}/t)
EAS 61-10	EAS 1A redo	2.08	1.00	5.53	34.75	60.50	1.79	4.95	0.07	6195.70
EAS 61-10	EAS 1B redo	2.10	1.00	5.51	31.59	64.55	1.79	4.95	0.07	6257.79
EAS 64-10	EAS 4A redo	1.90	1.00	5.55	35.54	60.21	1.79	4.95	0.07	6230.70
EAS 64-10	EAS 4B redo	2.00	1.00	5.55	26.91	63.29	1.79	4.95	0.07	5842.20
EAS 62-10	EAS 2A	3.14	2.00	5.50	6.82	49.97	1.79	4.95	0.07	1751.75
EAS 62-10	EAS 2B	3.15	2.00	5.50	6.92	49.06	1.79	4.95	0.07	1723.40
T5	SA:T5A	6.24	2.00	6.24	0.00	19.00	1.79	4.95	0.07	429.10
T5	SA:T5B	4.92	2.00	5.50	1.70	19.05	1.79	4.95	0.07	490.35

TPA without Carbonate modification in 2011

Sample name	Lab name	pH	M2	pH recorded for 5.5 step	V5	V6	V7	V8	C2	TPA (mol H^+/t)
EAS 61-11	EAS 61-1 AUS	2.62	2.02	5.50	18.00	4.27	0.99	0.41	0.14	1400.9
EAS 61-11	EAS 61-2 AUS	2.76	2.01	5.50	16.97	5.85	0.99	0.41	0.14	1444.9
EAS 62-11	EAS 62-1 AUS	2.32	2.01	5.59	14.68	2.19	0.99	0.41	0.14	1043.6
EAS 62-11	EAS 62-2 AUS	2.30	2.03	5.63	15.05	2.06	0.99	0.41	0.14	1049.3
EAS 63-11	EAS 63-1 AUS	lost	1.02	lost	Lost	lost	0.99	0.41	0.14	Sample lost
EAS 63-11	EAS 63-2 AUS	2.06	1.01	5.50	30.88	1.77	0.99	0.41	0.14	4195.2
FKP	FKP 1 GCS	6.94	2.02	6.94	0.00	0.06	0.99	0.41	0.14	-89.95
FKP	FKP 2 GCS	6.65	2.00	6.65	0.00	0.00	0.99	0.41	0.14	-94.91
FEM	FEM 1 GCS	**2.73**	1.99	5.51	**13.57**	4.00	0.99	0.41	0.14	**1101.8**
FEM	FEM 2 GCS	**3.57**	2.01	5.51	**6.36**	4.05	0.99	0.41	0.14	**607.79**

In 2011, the samples (**Error! Reference source not found.**) values were more approximate to their duplicates except in the case of FEM duplicates. The difference in the pH values of FEM samples resulted in the difference of NaOH volumes needed to standardise to a pH of 5.5 (highlighted in green, **Error! Reference source not found.**) which lead to the difference of TPA values.

One of the EAS 63-11 duplicates got knocked over due to personal error in the lab. The TPA of this sample was the highest which also validates why the mass of the sample had to be decreased due to the violent reaction when peroxide was added. However, the value is not conclusive since the duplicate was lost.

CARBONATE MODIFICATION OF SAMPLES

Samples with pH values that are higher or equal to 6.5 are subjected to the carbonate modification. This process is done as part of the Australian potential acidity method to dissolve excess carbon content that could interfere with the efficiency of the peroxide oxidation. Carbonate Modification could also be used to determine the excess acid neutralising capacity of the sample.

To ensure there is maximum recovery of the carbonate, a slow titration is necessary. It became very difficult to standardise and be consistent without the use of an auto-titrator.

TPA CALCULATION FOR SAMPLES WITH CARBONATE MODIFICATION

$$\text{TPA} = \text{HCl titration} - \text{a-ANCe} \ldots\ldots\ldots (1)$$

$$\text{HCl titration (mol H}^+\text{/t)} = V_3{*}C_3{*}(1000/m2) \ldots\ldots\ldots\ldots (2)$$

$$\text{a-ANCe (mol H}^+\text{/t} = [V_3{*}C_3{*}(1000/m2)] - [(V_4{*}C_1) - (V_7{*}C_2) + (V_6{*}C_8) {*}C_2]{*} (1000/m2) \ldots\ldots\ldots (3)$$

Equation 0-2 Calculation of a-ANCe (1) – (3)

a-ANCe is a calculation of excess acid neutralising capacity of the sample, it gives an indication of how much acid neutralising components exceed acid generation caused by oxidation of sulphides. The conventional way to report ANC is by converting it to the percentage calcium carbonate equivalence by calculating it as follows:

$$\%CaCO_3\text{: ANCe= a-ANCe /199.8}\ldots (4)$$

Equation 0-3 Calculation of %CaCO3 equivalence

The calculation of excess acid neutralising capacity (a-ANCe) is always required because the reaction is not completed at near-neutral or alkaline pH values due to the equilibrium with bicarbonate ions (McElnea *et al.,* 2000).

Table 0-4 TPA calculations for samples that went through Carbonate Modification in 2010

	v3	v4	v7	c1/c2	v6	c3	v8	m2			
	VOL	Vol	Blank	Stand	Vol	conc	Blank	mass soil	HCl	a-ANCe	TPA
Sample name	HCL	5.5	5.5	NaOH	6.5	HCl	6.5	g	titr		
EAS 64-1 AUS	9.3	2.33	0.49	0.1	1.26	0.49	0.51	2	9158	8027	1131
EAS 64-2 AUS	9.4	3.6	0.49	0.1	1.77	0.49	0.51	2	9302	7540	1762
EAS 3A	1.25	0	1.72	0.07	1.74	0.5	4.53	2	1250	1069	180.7
EAS 3B	1.05	0	1.72	0.07	2.08	0.5	4.53	2	1050	815.4	234.6
SA:T28A	3.65	1.5	1.72	0.07	9.2	0.5	4.53	2	3650	1537	2113
SA:T28B	3.95	1.18	1.72	0.07	8.34	0.5	4.53	2	3950	2133	1817
SA:SB10B SAMPLE 1	0.3	0.44	1.72	0.07	0.73	0.5	4.53	2	300	59.46	240.5

SA:SB10B SAMPLE 2	0.3	0.44	1.72	0.07	0.86	0.5	4.53	2	300	38.85	261.2
SA:SB11A SAMPLE 1	0.96	0.21	1.72	0.07	1.14	0.5	4.53	2	960	769.5	190.5
SA:SB11A SAMPLE 2	0.95	0.21	1.72	0.07	1.34	0.5	4.53	2	950	727.7	222.3

Erratic values (highlighted in green) are evident in

	v3	v4	v7	c1/c2	v6	c3	v8	m2			
	VOL	Vol	Blank	Stand	Vol	conc	Blank	mass soil	HCl		
Sample name	HCL	5.5	5.5	NaOH	6.5	HCl	6.5	g	titr	a-ANCe	TPA
EAS 64-1 AUS	9.3	2.33	0.49	0.1	1.26	0.49	0.51	2	9158	8027	1131
EAS 64-2 AUS	9.4	3.6	0.49	0.1	1.77	0.49	0.51	2	9302	7540	1762
EAS 3A	1.25	0	1.72	0.07	1.74	0.5	4.53	2	1250	1069	180.7
EAS 3B	1.05	0	1.72	0.07	2.08	0.5	4.53	2	1050	815.4	234.6
SA:T28A	3.65	1.5	1.72	0.07	9.2	0.5	4.53	2	3650	1537	2113
SA:T28B	3.95	1.18	1.72	0.07	8.34	0.5	4.53	2	3950	2133	1817
SA:SB10B SAMPLE 1	0.3	0.44	1.72	0.07	0.73	0.5	4.53	2	300	59.46	240.5
SA:SB10B SAMPLE 2	0.3	0.44	1.72	0.07	0.86	0.5	4.53	2	300	38.85	261.2
SA:SB11A SAMPLE 1	0.96	0.21	1.72	0.07	1.14	0.5	4.53	2	960	769.5	190.5
SA:SB11A SAMPLE 2	0.95	0.21	1.72	0.07	1.34	0.5	4.53	2	950	727.7	222.3

, the source of the errors might be at the slow titration of HCL (V3) during the carbonate modification step. The outcome large variance of the V4, HCl titr and TPA values between the duplicates themselves is evident. Regardless of the inconsistent values, the a-ANCe/ANCe values are not as erratic at all.

Table 0-5 TPA calculations for samples that went through Carbonate Modification in 2011

Sample name	v3	v4	v7	c1/c2	v6	c3	v8	m2	HCltitr (mol H^+/t)	a-ANCe (mol H^+/t)	TPA (mol H^+/t)	ANCe (%$CaCO_3$)
EAS 64-1 AUS	9.30	2.33	0.49	0.07	1.26	0.49	0.51	2.01	9157.70	8056	1131	40.32
EAS 64-2 AUS	9.40	3.6	0.49	0.07	1.77	0.49	0.51	2.02	9302.20	7559	1762	37.83

The results (Table 0-5) in 2011 are more reliable since the values are more approximate.

PEROXIDE SULPHUR (S_P), PEROXIDE CALCIUM (CA_P) PEROXIDE MAGNESIUM (MG_P)

The % of all the main cations were calculated using Equation 0-1 and the samples that have high values compared to others in the tables to follow are highlighted with a specific colour (i.e. High Mg with the colour yellow).

Table 0-6 Peroxide digest Mg, S, and Ca results in 2010

Sample name	Lab name:	Mg(mg/l)	%Mg	SO4(mg/l)	%SO4	Ca(mg/l)	%Ca
EAS 61-10	EAS 1A	5.20	0.08	619.43	12.32	13.66	0.21
EAS 61-10	EAS 1B	3.69	0.05	583.40	11.59	5.83	0.05
EAS 62-10	EAS 2A	2.24	0.02	50.19	0.93	5.61	0.05
EAS 62-10	EAS 2B	2.50	0.03	49.14	0.92	6.59	0.06
EAS 63-10	EAS 3A	38.29	0.74	161.46	3.16	115.37	2.25
EAS 63-10	EAS 3B	39.05	0.76	158.44	3.09	117.46	2.28
EAS 64-10	EAS 4A	27.33	0.53	607.34	12.08	22.11	0.38
EAS 64-10	EAS 4B	27.09	0.52	609.19	12.11	22.02	0.38
T5	SA:T5A	21.26	0.40	193.83	3.80	152.91	3.00
T5	SA:T5B	25.73	0.49	194.59	3.82	160.33	3.14
T28	SA:T28A	56.82	1.12	755.80	15.05	311.42	6.17
T28	SA:T28B	56.53	1.11	628.77	12.50	315.73	6.25
SB10B	SA:SB10B SAMPLE 1	12.54	0.23	10.62	0.14	29.64	0.53
SB10B	SA:SB10B SAMPLE 2	10.04	0.18	7.51	0.08	23.99	0.42
SB11A	SA:SB11A SAMPLE 1	7.15	0.12	2.61	-0.02	49.41	0.92
SB11A	SA:SB11A SAMPLE 2	8.46	0.15	2.55	-0.02	54.18	1.02

- ✓ T28A and T28B have the highest percentages in all three major cations.
- ✓ There is no trend that is evident in terms of the difference between the sample batches from South Africa and Australia.

Table 0-7 Peroxide digest Mg, S, Ca results in 2011

Sample name	Lab name:	Mg(mg/l)	%Mg	SO4(mg/l)	%SO4	Ca(mg/l)	%Ca
EAS 61-11	EAS 61-1 AUS	6.50	0.04	184.71	1.28	9.11	0.05

EAS 61-11	EAS 61-2 AUS	7.60	0.04	210.57	1.18	9.25	0.04
EAS 62-11	EAS 62-1 AUS	16.00	0.11	409.03	2.77	11.99	0.07
EAS 62-11	EAS 62-2 AUS	17.03	0.11	310.78	2.02	13.20	0.08
EAS 63-11	EAS 63-1 AUS	15.50	0.20	571.00	7.37	3.42	0.02
EAS 63-11	EAS 63-2 AUS	16.10	0.20	589.89	7.33	3.52	0.02
EAS 64-11	EAS 64-1 AUS	15.80	0.08	847.42	4.42	1548.00	8.06
EAS 64-11	EAS 64-2 AUS	15.00	0.08	770.17	4.32	1542.00	8.65
FKP	FKP 1 GCS	8.60	0.05	66.07	0.38	25.09	0.13
FKP	FKP 2 GCS	12.47	0.06	96.01	0.50	33.74	0.17
FEM	FEM 1 GCS	4.08	0.03	107.77	0.83	18.87	0.13
FEM	FEM 2 GCS	6.16	0.04	98.52	0.58	27.16	0.15

ACID NEUTRALISING CAPACITY (ANC$_{BT}$)

%CaCO$_3$ = (5.0043675 * ((V_HCl *C1)- (V_B+ (25 –v blank))*C2))/G_M:

Equivalent Calcium Carbonate percentage Australian methods (McElnea et. Al., 2004b)

Determination of %CaCO3----2010

Sample name	Lab name	V_B	C2	V_HCL	C1	v blank	G_M	%CaCO3
EAS 61-10	EAS 1A	47.86	0.07	25.00	0.12	45.27	2.00	2.67
EAS 61-10	EAS 1B	47.71	0.07	25.00	0.12	45.27	2.00	2.70
EAS 62-10	EAS 2A	46.58	0.07	25.00	0.12	45.27	2.00	2.90
EAS 62-10	EAS 2B	47.16	0.07	25.00	0.12	45.27	2.00	2.80
EAS 63-10	EAS 3A	36.29	0.07	25.00	0.12	45.27	2.00	4.70
EAS 63-10	EAS 3B	35.39	0.07	25.00	0.12	45.27	2.00	4.86
EAS 64-10	EAS 4A	45.42	0.07	25.00	0.12	45.27	2.00	3.10
EAS 64-10	EAS 4B	45.06	0.07	25.00	0.12	45.27	2.00	3.16
T5	SA:T5A	33.11	0.07	25.00	0.12	45.27	2.00	5.26
T5	SA:T5B	32.78	0.07	25.00	0.12	45.27	2.00	5.32

T28	SA:T28A	20.38	0.07	25.00	0.12	45.27	2.00	7.49
T28	SA:T28B	17.75	0.07	25.00	0.12	45.27	2.00	7.95
SB10B	SA:SB10B SAMPLE 1	37.00	0.07	25.00	0.12	45.27	2.00	4.58
SB10B	SA:SB10B SAMPLE 2	40.66	0.07	25.00	0.12	45.27	2.00	3.94
SB11A	SA:SB11A SAMPLE 1	40.06	0.07	25.00	0.12	45.27	2.00	4.04
SB11A	SA:SB11A SAMPLE 2	41.25	0.07	25.00	0.12	45.27	2.00	3.83
Ref sample	Ref sample 1	12.63	0.07	25.00	0.12	45.27	2.00	8.84
Ref sample	Ref sample 2	12.75	0.07	25.00	0.12	45.27	2.00	8.82
Ref sample	Ref sample 3	12.79	0.07	25.00	0.12	45.27	2.00	8.82

Determination of %CaCO3----2011

Sample name	Lab name	V_HCL	C1	V_B	v blank	C2	G_M	%CaCO3
EAS 61-11	EAS 61-1 AUS	25	0.112	49.15	44.51	0.066	1.09	3.95
EAS 61-11	EAS 61-2 AUS	25	0.112	48.81	44.51	0.066	1.04	4.25
EAS 62-11	EAS 62-1 AUS	25	0.112	44.95	44.51	0.066	1.03	5.52
EAS 62-11	EAS 62-2 AUS	25	0.112	44.86	44.51	0.066	0.99	5.77
EAS 63-11	EAS 63-1 AUS	25	0.112	46	44.51	0.066	1.01	5.28
EAS 63-11	EAS 63-2 AUS	25	0.112	45.95	44.51	0.066	1.01	5.30
EAS 64-11	EAS 64-1 AUS	25	0.112	39.58	44.51	0.066	1.04	7.16
EAS 64-11	EAS 64-2 AUS	25	0.112	45.58	44.51	0.066	1.02	5.37
FKP	FKP 1 GCS	25	0.112	40.75	44.51	0.066	1.01	6.99
FKP	FKP 2 GCS	25	0.112	39.95	44.51	0.066	1	7.32
FEM	FEM 1 GCS	25	0.112	41.31	44.51	0.066	1.01	6.81
FEM	FEM 2 GCS	25	0.112	41.49	44.51	0.066	1.01	6.75
REF 1	REF 1	25	0.112	13.33	44.51	0.066	0.096	167.84
REF 2	REF 2	25	0.112	12.16	44.51	0.066	0.1	164.80
REF 3	REF 3	25	0.112	15.74	44.51	0.066	0.101	151.80

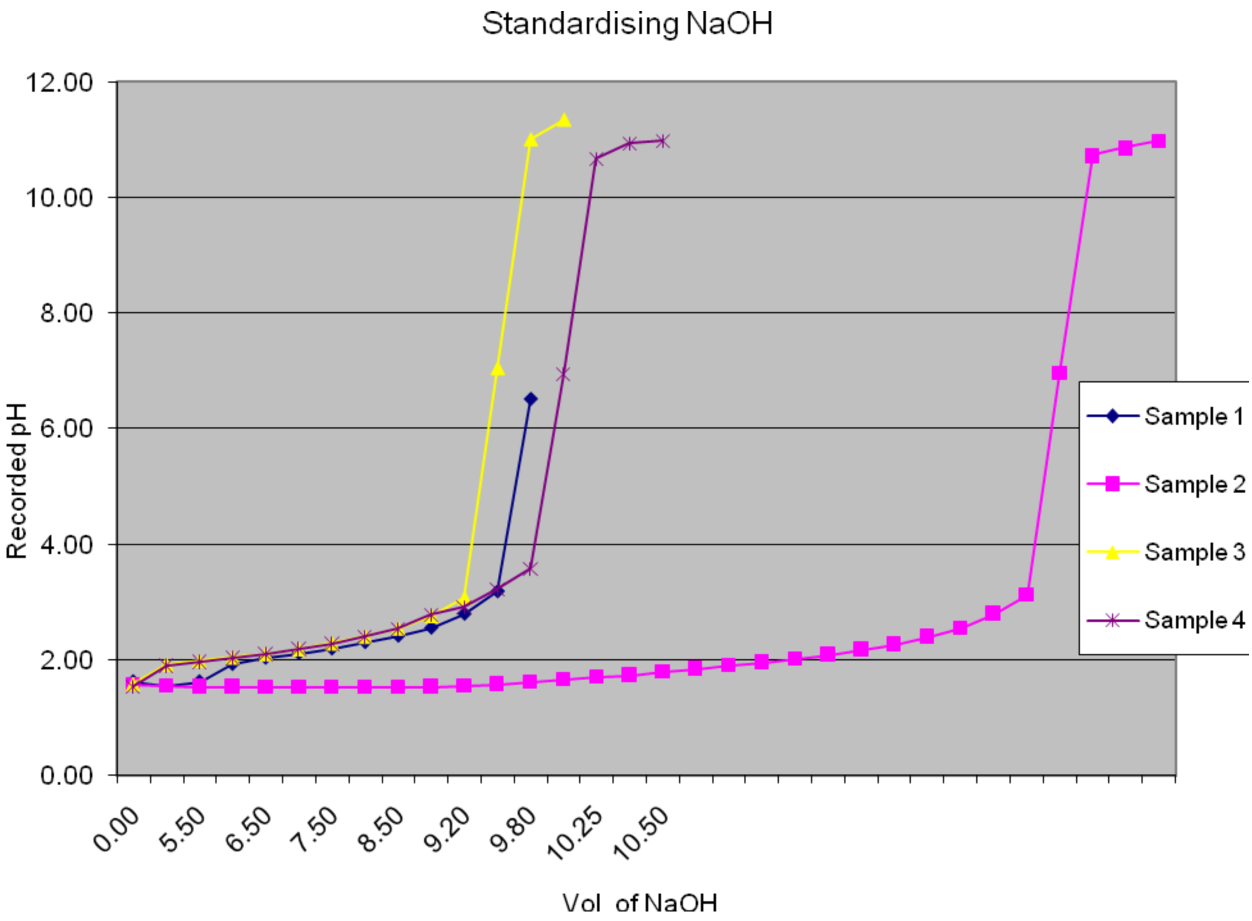
Appendix 4

SOUTH AFRICAN METHOD DATA

SOUTH AFRICAN STANDARDISATION

Calculations done for ABA need standardised reagents.

Summary of standardising NaOH for SA methods



4 Samples were used to standardise NaOH for the South African methods. The summary of the results is shown in the figure above. 10 ml of 0.06N H_2SO_4 was used to standardise NaOH. The average inflection point was 9.50 ml of NaOH

Balanced reaction for standardising NaOH: $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

$H_2SO_4 = B$

$NaOH = A$

$C_A V_A b = C_B V_B a$

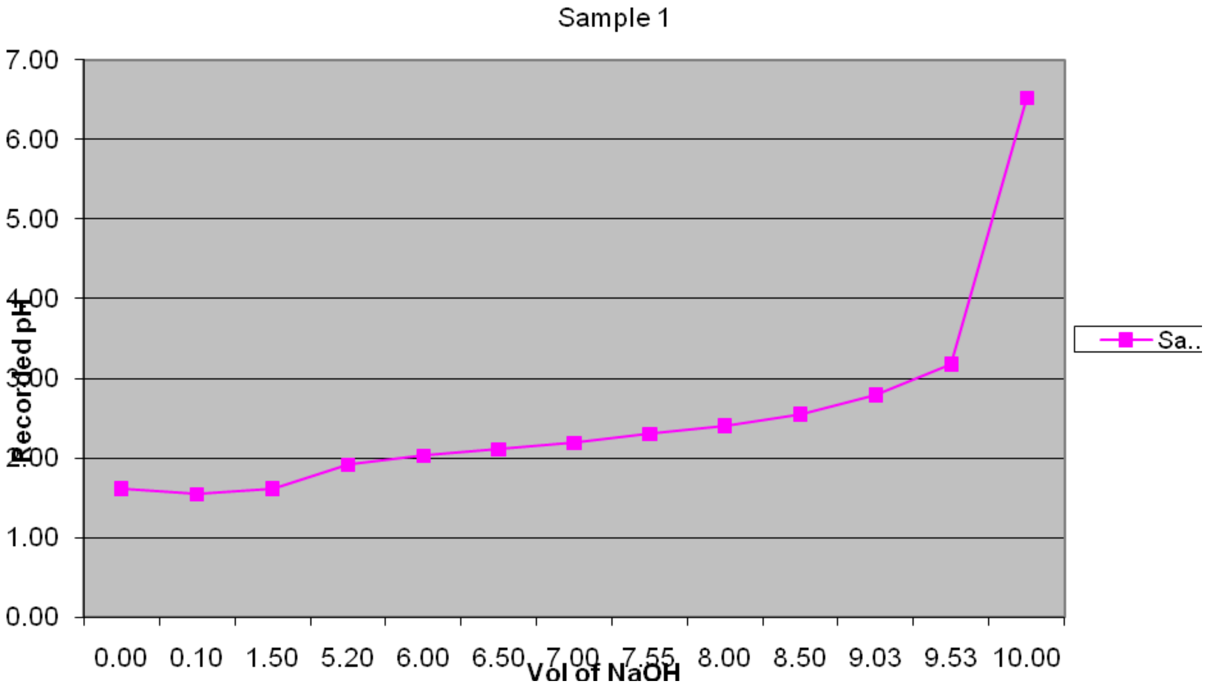
$C_A (9.50) * 1 = 0.03*10*2$

$C_A = 0.6/9.50$

$C_A = 0.06$ M

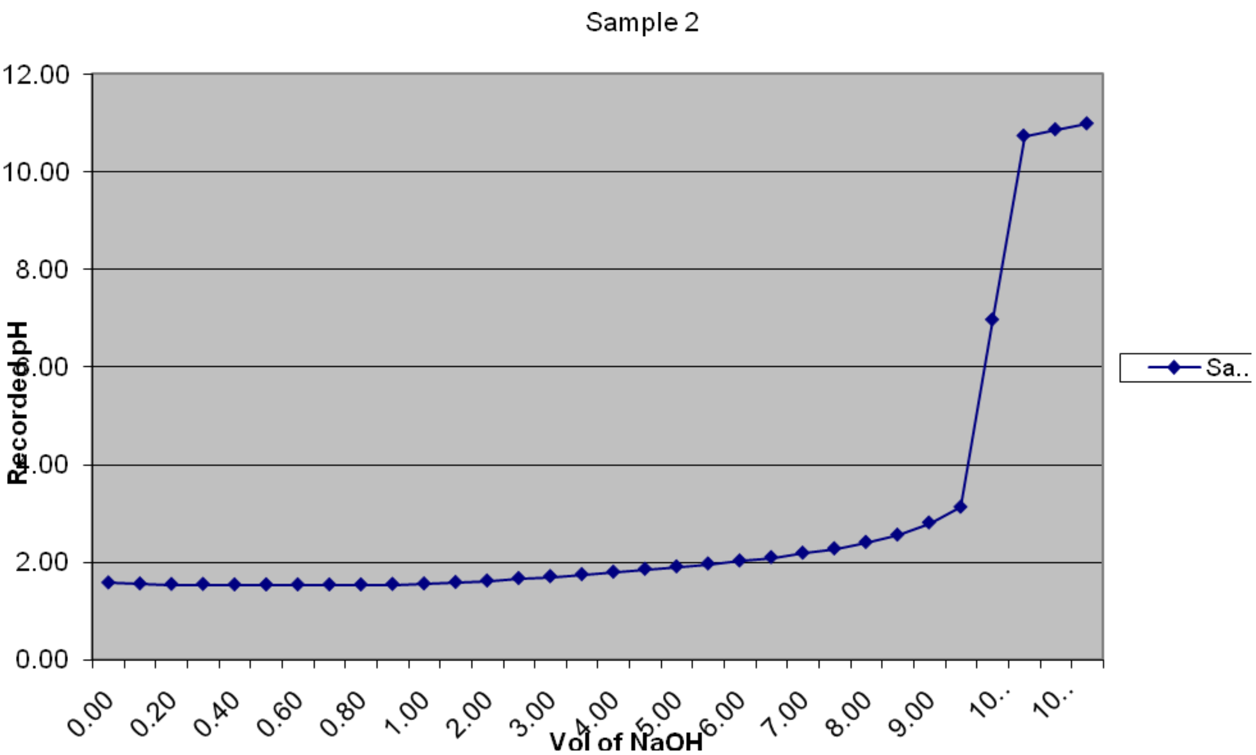
2010 STANDARDISING NaOH WITH 0.06N OF H_2SO_4

Sample 1	
Volume of NaOH	Ph
0.00	1.62
0.10	1.55
1.50	1.62
5.20	1.92
6.00	2.03
6.50	2.11
7.00	2.19
7.55	2.30
8.00	2.41
8.50	2.55
9.03	2.79
9.53	3.18
10.00	6.51

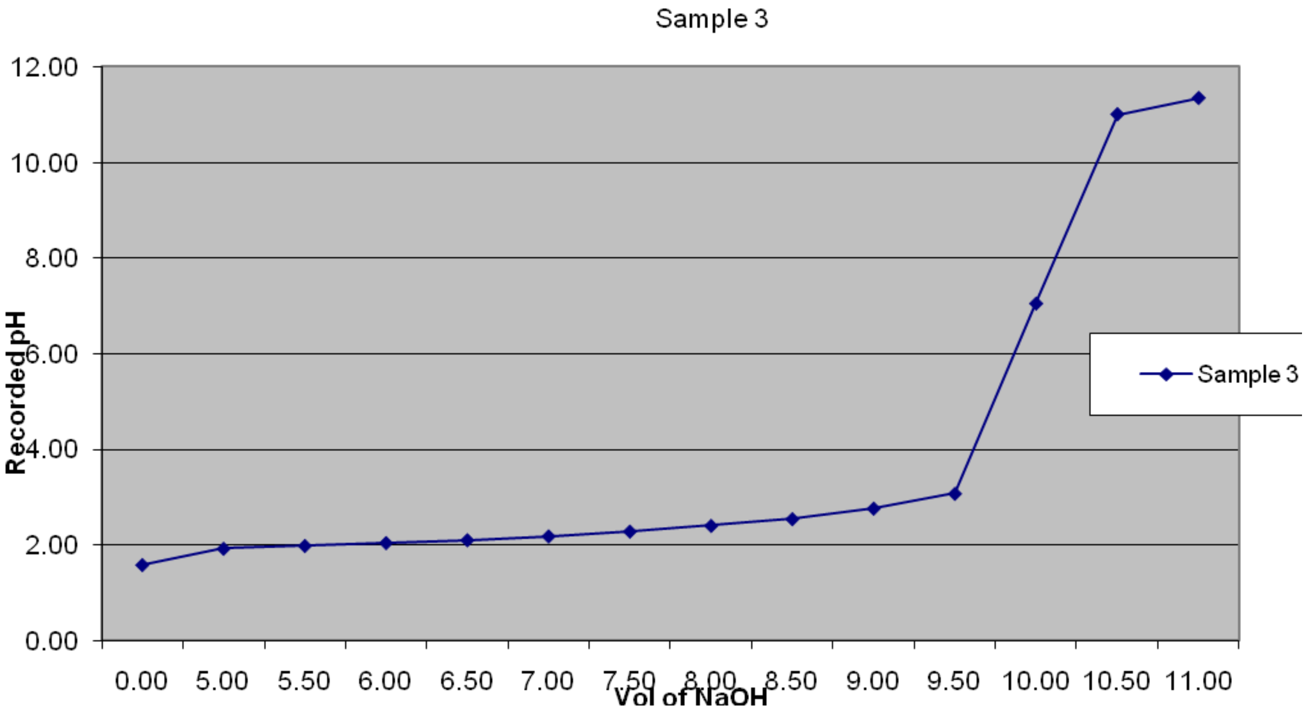


Sample 2	pH
Volume of NaOH	pH
0.00	1.57

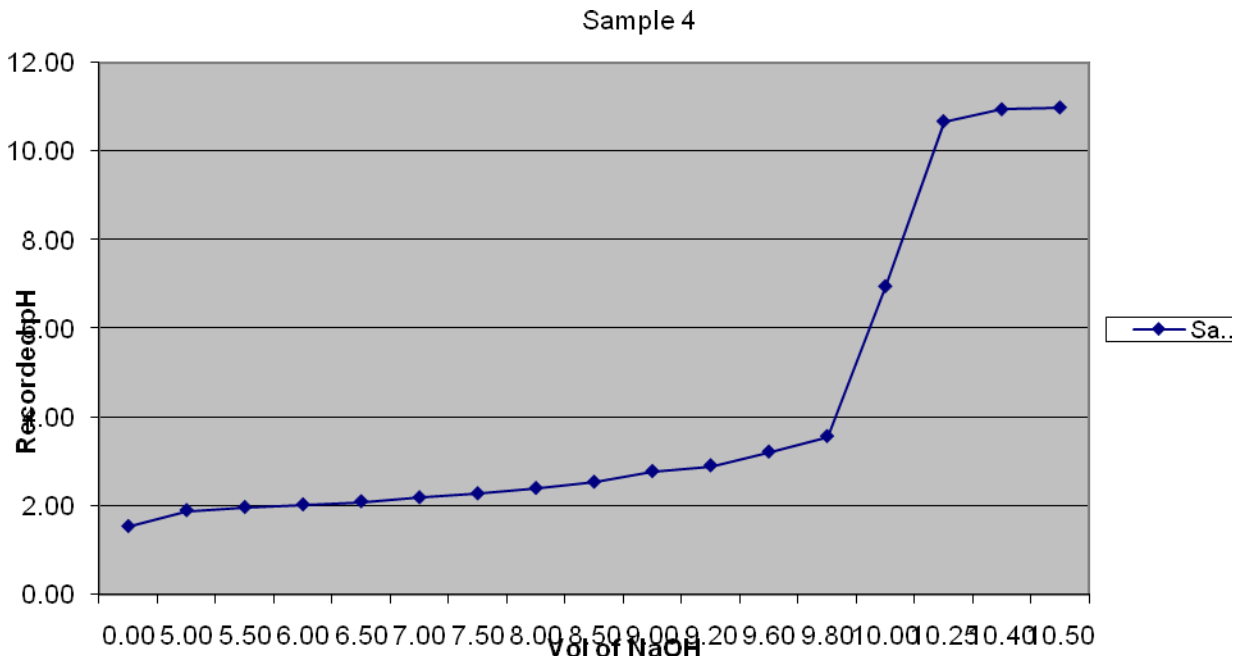
0.10	1.55
0.20	1.54
0.30	1.54
0.40	1.53
0.50	1.53
0.60	1.53
0.70	1.53
0.80	1.53
0.90	1.54
1.00	1.55
1.50	1.58
2.00	1.61
2.50	1.66
3.00	1.70
3.50	1.74
4.00	1.79
4.50	1.85
5.00	1.90
5.50	1.96
6.00	2.02
6.50	2.09
7.00	2.18
7.50	2.27
8.00	2.40
8.50	2.55
9.00	2.80
9.50	3.12
10.00	6.96
10.30	10.73
10.40	10.86
10.50	10.98



Sample 3	pH
Volume of NaOH	pH
0.00	1.58
5.00	1.92
5.50	1.98
6.00	2.04
6.50	2.10
7.00	2.18
7.50	2.28
8.00	2.40
8.50	2.54
9.00	2.76
9.50	3.07
10.00	7.05
10.50	11.01
11.00	11.35



Sample 4	pH
Volume of NaOH	pH
0.00	1.54
5.00	1.90
5.50	1.97
6.00	2.03
6.50	2.10
7.00	2.19
7.50	2.28
8.00	2.40
8.50	2.54
9.00	2.78
9.20	2.91
9.60	3.22
9.80	3.57
10.00	6.95
10.25	10.67
10.40	10.94
10.50	10.98



SOUTH AFRICAN CALCULATIONS, RESULTS AND OBSERVATIONS

INITIAL PH

Initial pH recordings__2010 results

Sample	lab name:	pH recorded
Blank 1	Blank 1	5.22
Blank 2	Blank 2	5.00
EAS 61-10	EAS 1A	3.59
EAS 61-10	EAS 1B	3.59
EAS 62-10	EAS 2A	3.48
EAS 62-10	EAS 2B	3.50
EAS 63-10	EAS 3A	8.15
EAS 63-10	EAS 3B	8.17
EAS 64-10	EAS 4A	4.67
EAS 64-10	EAS 4B	4.67
T5	SA:T5A	7.78
T5	SA:T5B	7.63
T28	SA:T28A	9.94

T28	SA:T28B	9.97
SB10B	SA:SB10B SAMPLE 1	9.16
SB10B	SA:SB10B SAMPLE 2	9.01
SB11A	SA:SB11A SAMPLE 1	8.95
SB11A	SA:SB11A SAMPLE 2	9.04

Initial pH recordings__2011 results

Sample name	Lab name	pH
Blank	BLANK	5.18
EAS 61-11	EAS 61-1 AUS	3.48
EAS 61-11	EAS 61-2 AUS	3.50
EAS 62-11	EAS 62-1 AUS	3.41
EAS 62-11	EAS 62-2 AUS	3.41
EAS 63-11	EAS 63-1 AUS	3.52
EAS 63-11	EAS 63-2 AUS	3.49
EAS 64-11	EAS 64-1 AUS	8.43
EAS 64-11	EAS 64-2 AUS	8.42
FKP	FKP 1 GCS	8.71
FKP	FKP 2 GCS	8.71
FEM	FEM 1 GCS	7.93
FEM	FEM 2 GCS	7.93

INITIAL SULPHUR (S_{H2O}), CALCIUM (CA_{H2O}) AND MAGNESIUM (MG_{H2O})

Main cations (H_2O)—2010

Sample name	Lab name	Mg (mg/l)	%Mg	SO_4 (mg/l)	%SO4	Ca (mg/l)	%Ca

EAS 61-10	EAS 1A	37.36	0.04	546.62	0.54	45.73	0.04
EAS 61-10	EAS 1B	35.01	0.03	533.75	0.53	38.68	0.04
EAS 62-10	EAS 2A	10.45	0.01	172.29	0.17	25.42	0.02
EAS 62-10	EAS 2B	8.96	0.01	145.88	0.14	20.92	0.02
EAS 63-10	EAS 3A	75.44	0.08	352.98	0.35	90.48	0.09
EAS 63-10	EAS 3B	74.66	0.07	353.41	0.35	89.65	0.09
EAS 64-10	EAS 4A	281.57	0.28	1369.94	1.37	113.50	0.11
EAS 64-10	EAS 4B	289.24	0.29	1370.69	1.37	123.81	0.12
T5	SA:T5A	35.22	0.03	934.33	0.93	310.88	0.31
T5	SA:T5B	36.41	0.04	934.63	0.93	310.09	0.31
T28	SA:T28A	20.78	0.02	154.62	0.15	22.76	0.02
T28	SA:T28B	18.13	0.02	126.68	0.12	21.48	0.02
SB10B	SA:SB10B SAMPLE 1	3.84	0.00	8.64	0.01	12.86	0.01
SB10B	SA:SB10B SAMPLE 2	3.78	0.00	5.23	0.00	12.15	0.01
SB11A	SA:SB11A SAMPLE 1	3.69	0.00	2.43	0.00	13.86	0.01
SB11A	SA:SB11A SAMPLE 2	3.40	0.00	1.76	0.00	13.03	0.01

Main cations (H_2O)—2011

Sample name	Lab name	Mg(mg/l)	%Mg	SO4(mg/l)	%SO4	Ca(mg/l)	%Ca
EAS 61-11	EAS 61-1 AUS	42.11	0.04	766.04	0.77	41.74	0.04
EAS 61-11	EAS 61-2 AUS	41.06	0.04	758.25	0.76	39.87	0.04
EAS 62-11	EAS 62-1 AUS	114.97	0.11	638.26	0.64	48.41	0.05
EAS 62-11	EAS 62-2 AUS	117.16	0.12	644.93	0.64	48.23	0.05
EAS 63-11	EAS 63-1 AUS	33.91	0.03	538.59	0.54	32.31	0.03
EAS 63-11	EAS 63-2 AUS	32.77	0.03	531.42	0.53	31.02	0.03
EAS 64-11	EAS 64-1 AUS	77.07	0.08	510.25	0.51	105.59	0.11
EAS 64-11	EAS 64-2 AUS	79.61	0.08	523.97	0.52	113.31	0.11
	FKP 1 GCS	0.16	0.00	5.14	0.01	1.72	0.00

FKP							
FKP	FKP 2 GCS	0.16	0.00	5.14	0.01	1.72	0.00
FEM	FEM 1 GCS	3.68	0.00	42.23	0.04	1.46	0.00
FEM	FEM 2 GCS	3.68	0.00	42.23	0.04	1.46	0.00

ACID POTENTIAL USING HYDROGEN PEROXIDE (H_2O_2)

This method is used to predict potential acid generation.

Table 0-1 Rough guidelines for categorising samples (Usher et.al, 2003).

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

Acid potential pH recordings__2010 results

Sample name	lab name:	Mass of sample (g)	Recorded pH(final pH)	Acid Generating potential
EAS 61-10	EAS 1A	4.00	1.89	High risk acid generating
EAS 61-10	EAS 1B	4.00	1.89	High risk acid generating
EAS 62-10	EAS 2A	4.00	1.86	High risk acid generating
EAS 62-10	EAS 2B	4.00	1.87	High risk acid generating
EAS 63-10	EAS 3A	4.00	5.27	Low risk acid generating
EAS 63-10	EAS 3B	4.00	5.25	Low risk acid generating
EAS 64-10	EAS 4A	2.00	1.07	High risk acid generating
EAS 64-10	EAS 4B	2.00	1.07	High risk acid generating
T5	SA:T5A	2.00	4.71	Low risk acid generating
T5	SA:T5B	2.00	4.66	Low risk acid generating
T28	SA:T28A	2.00	5.43	Low risk acid generating
T28	SA:T28B	2.00	5.37	Low risk acid generating

SB10B	SA:SB10B SAMPLE 1	4.00	4.51	Low risk acid generating
SB10B	SA:SB10B SAMPLE 2	4.00	4.50	Low risk acid generating
SB11A	SA:SB11A SAMPLE 1	4.00	4.97	Low risk acid generating
SB11A	SA:SB11A SAMPLE 2	4.00	5.04	Low risk acid generating

Acid potential pH recordings__2011 results

Sample name	Lab name	m	pH	Acid Generating potential
EAS 61-11	EAS 61-1 AUS	2.00	1.60	High risk acid generating
EAS 61-11	EAS 61-2 AUS	2.00	1.61	High risk acid generating
EAS 62-11	EAS 62-1 AUS	2.00	1.25	High risk acid generating
EAS 62-11	EAS 62-2 AUS	2.00	1.26	High risk acid generating
EAS 63-11	EAS 63-1 AUS	2.00	1.91	High risk acid generating
EAS 63-11	EAS 63-2 AUS	2.00	1.91	High risk acid generating
EAS 64-11	EAS 64-1 AUS	2.00	5.67	Non-acid generating
EAS 64-11	EAS 64-2 AUS	2.00	5.68	Non-acid generating
FKP	FKP 1 GCS	2.00	3.27	High risk acid generating
FKP	FKP 2 GCS	2.00	3.27	High risk acid generating
FEM	FEM 1 GCS	2.00	3.92	Low risk acid generating
FEM	FEM 2 GCS	2.00	3.92	Low risk acid generating

Acid Potential Sulphur (S_{H2O2}), Calcium (Ca_{H2O2}) and Magnesium (Mg_{H2O2})

AP = ((SO$_4$ (mg/l)/Weight (g))/ 1000) * ml H_2O_2= kg SO4/t of sample

Acid potential_South African method (Usher et. al., 2003)

Main cations (H2O2) and Acid Potential (AP)—2010

Sample name	Lab name	Mg	Mg%	SO4	SO4%	Ca	Ca%	AP
EAS 61-10	EAS 1A	29.25	0.06	6423.59	12.84	39.09	0.07	128.47

EAS 61-10	EAS 1B	32.93	0.06	7313.28	14.62	41.85	0.07	146.27
EAS 62-10	EAS 2A	4.91	0.01	133.95	0.26	13.14	0.01	2.68
EAS 62-10	EAS 2B	5.76	0.01	126.31	0.24	15.28	0.02	2.53
EAS 63-10	EAS 3A	72.42	0.14	413.85	0.82	147.35	0.28	8.28
EAS 63-10	EAS 3B	77.71	0.15	441.55	0.88	163.31	0.31	8.83
EAS 64-10	EAS 4A	138.43	0.55	2992.40	11.95	106.67	0.40	119.70
EAS 64-10	EAS 4B	116.49	0.46	2430.17	9.70	96.26	0.36	97.21
T5	SA:T5A	9.80	0.03	240.98	0.95	120.41	0.46	9.64
T5	SA:T5B	9.47	0.03	232.08	0.91	115.73	0.44	9.28
T28	SA:T28A	92.34	0.36	727.72	2.90	167.08	0.64	29.11
T28	SA:T28B	89.59	0.35	700.37	2.79	159.99	0.62	28.01
SB10B	SA:SB10B SAMPLE 1	13.07	0.02	13.46	0.02	32.71	0.05	0.27
SB10B	SA:SB10B SAMPLE 2	12.97	0.02	13.81	0.02	33.82	0.06	0.28
SB11A	SA:SB11A SAMPLE 1	9.21	0.02	6.80	0.01	51.24	0.09	0.14
SB11A	SA:SB11A SAMPLE 2	8.31	0.01	5.73	0.00	45.90	0.08	0.11

✓ EAS 61-10 duplicates have the highest SO4 percentage and as expected of this, a resultant in a h
(Peroxide Australian methods) does not depict that as true because it shows that the highest SO4,
duplicates. Nevertheless T28 duplicates in **Error! Reference source not found.** have the highest C

Main cations (H2O2) and Acid Potential (AP)—2011

Sample name	Lab name	Mg	Mg%	SO4	SO4%	Ca	Ca%	AP
EAS 61-11	EAS 61-1 AUS	11.54	0.05	361.39	1.45	12.78	0.05	14.46
EAS 61-11	EAS 61-2 AUS	11.49	0.05	356.52	1.43	12.92	0.05	14.26
EAS 62-11	EAS 62-1 AUS	33.35	0.13	623.86	2.50	18.10	0.07	24.95
EAS 62-11	EAS 62-2 AUS	31.65	0.13	587.90	2.35	17.16	0.07	23.52
EAS 63-11	EAS 63-1 AUS	11.70	0.20	2846.02	11.38	14.95	0.06	113.84
EAS 63-11	EAS 63-2 AUS	12.06	0.23	2857.84	11.43	15.95	0.06	114.31

EAS 64-11	EAS 64-1 AUS	51.03	0.05	776.11	3.10	235.77	0.94	31.04
EAS 64-11	EAS 64-2 AUS	57.81	0.05	821.49	3.29	306.70	1.22	32.86
FKP	FKP 1 GCS	5.28	0.02	129.06	0.52	0.00	0.00	5.16
FKP	FKP 2 GCS	5.28	0.02	129.06	0.52	0.00	0.00	5.16
FEM	FEM 1 GCS	37.35	0.15	398.53	1.59	0.00	0.00	15.94
FEM	FEM 2 GCS	37.35	0.15	398.53	1.59	0.00	0.00	15.94

EAS 63-11 duplicates have the highest SO4 percentage and as expected of this, a high AP as well. Peroxide Australian methods the highest SO4 and EAS 64-11 with high Ca percentage. Nevertheless FEM duplicates in Table 0-6 have the highest Mg content

2010 ICP-AES Results: Water soluble constituents in mg/

Sample	**Lab name**	**Ca**	**Mg**	**Fe**	SO4
Blank 1	Blank 1	0.82	0.29	0.21	4.17
Blank 2	Blank 2	0.96	0.29	0.11	2.55
EAS 61-10	EAS 1A	45.73	37.36	85.49	546.62
EAS 61-10	EAS 1B	38.68	35.01	80.52	533.75
EAS 62-10	EAS 2A	25.42	10.45	5.67	172.29
EAS 62-10	EAS 2B	20.92	8.96	4.81	145.88
EAS 63-10	EAS 3A	90.48	75.44	1.28	352.98
EAS 63-10	EAS 3B	89.65	74.66	0.13	353.41
EAS 64-10	EAS 4A	113.50	281.57	6.67	1369.94
EAS 64-10	EAS 4B	123.81	289.24	6.85	1370.69
T5	SA:T5A	310.88	35.22	0.21	934.33
T5	SA:T5B	310.09	36.41	0.14	934.63
T28	SA:T28A	22.76	20.78	0.14	154.62
T28	SA:T28B	21.48	18.13	0.17	126.68
SB10B	SA:SB10B SAMPLE 1	12.86	3.84	0.20	8.64
SB10B	SA:SB10B SAMPLE 2	12.15	3.78	0.20	5.23
SB11A	SA:SB11A SAMPLE 1	13.86	3.69	0.16	2.43
SB11A	SA:SB11A	13.03	3.40	0.17	1.76

	SAMPLE 2				

2010 CP Results: H2O2 reactive constituents in mg/L

Samples	Lab number	**Ca**	Mg	**Fe**	**SO4**
Blank 1	Blank 1	6.65	1.696381	0.30	3.84
Blank 2	Blank 2	5.12	1.325851	0.18	4.05
EAS 61-10	EAS 1A	39.09	29.25238	1655.95	6423.59
EAS 61-10	EAS 1B	41.85	32.92588	1898.50	7313.28
EAS 62-10	EAS 2A	13.14	4.910537	4.40	133.95
EAS 62-10	EAS 2B	15.28	5.762364	0.95	126.31
EAS 63-10	EAS 3A	147.35	72.42032	0.60	413.85
EAS 63-10	EAS 3B	163.31	77.71062	0.34	441.55
EAS 64-10	EAS 4A	106.67	138.4304	570.96	2992.40
EAS 64-10	EAS 4B	96.26	116.4927	481.61	2430.17
T5	SA:T5A	120.41	9.80406	0.55	240.98
T5	SA:T5B	115.73	9.469995	0.23	232.08
T28	SA:T28A	167.08	92.33856	0.36	727.72
T28	SA:T28B	159.99	89.5864	0.33	700.37
SB10B	SA:SB10B SAMPLE 1	32.71	13.06706	0.51	13.46
SB10B	SA:SB10B SAMPLE 2	33.82	12.9708	0.53	13.81
SB11A	SA:SB11A SAMPLE 1	51.24	9.208726	0.23	6.80
SB11A	SA:SB11A SAMPLE 2	45.90	8.314528	0.22	5.73

2010

ICP RESULTS: ACID (ACID LEACHATE) SOLUBLE CONSTITUENTS IN MG/L

Samples	Lab number	**Ca**	**Mg**	**Fe**	**SO4**
Blank 1	Blank 1	15.86	3.67	0.27	202.55
Blank 2	Blank 2	13.78	3.20	0.20	200.82
EAS 61-10	EAS 1A	71.15	58.05	321.61	880.85
EAS 61-10	EAS 1B	76.30	59.19	309.24	877.35
EAS 62-10	EAS 2A	41.19	15.88	56.96	365.30

EAS 62-10	EAS 2B	56.60	21.76	66.74	418.66
EAS 63-10	EAS 3A	912.30	394.58	333.83	5782.26
EAS 63-10	EAS 3B	925.08	346.29	200.27	4443.17
EAS 64-10	EAS 4A	337.39	491.28	288.77	3763.41
EAS 64-10	EAS 4B	363.51	528.39	375.57	4839.51
T5	SA:T5A	804.71	271.97	102.59	4141.34
T5	SA:T5B	791.04	235.46	88.70	3774.42
T28	SA:T28A	464.92	364.44	2281.67	8469.38
T28	SA:T28B	471.62	420.95	2171.88	6975.45
SB10B	SA:SB10B SAMPLE 1	600.84	123.68	211.53	6211.46
SB10B	SA:SB10B SAMPLE 2	498.95	115.09	159.90	5077.89
SB11A	SA:SB11A SAMPLE 1	769.39	76.51	77.49	5470.94
SB11A	SA:SB11A SAMPLE 2	584.11	62.27	48.71	3863.91

2010 ACID LEACHATE

Sample	lab name:	Date	Recorded pH	Date	Recorded pH
Blank 1	Blank 1	20-09-2010	1.63	21/09/2010	/
Blank 2	Blank 2	20-09-2010	1.56	21/09/2010	/
EAS 61-10	EAS 1A	20-09-2010	2.22	21/09/2010	/
EAS 61-10	EAS 1B	20-09-2010	2.17	21/09/2010	/
EAS 62-10	EAS 2A	20-09-2010	1.96	21/09/2010	/
EAS 62-10	EAS 2B	20-09-2010	2.03	21/09/2010	/
EAS 63-10	EAS 3A	20-09-2010	7.5	21/09/2010	7.15
EAS 63-10	EAS 3B	20-09-2010	7.44	21/09/2010	7.13
EAS 64-10	EAS 4A	20-09-2010	2.81	21/09/2010	2.01
EAS 64-10	EAS 4B	20-09-2010	3.3	21/09/2010	2.68
	SA:T5A	20-09-2010	7.41	21/09/2010	7.23
T5	SA:T5B	20-09-2010	7.44	21/09/2010	7.12
T28	SA:T28A	20-09-2010	8.42	21/09/2010	8.4
T28	SA:T28B	20-09-2010	8.39	21/09/2010	7.68
SB10B	SA:SB10B SAMPLE 1	20-09-2010	3.75	21/09/2010	3.59
SB10B	SA:SB10B SAMPLE 2	20-09-2010	3.71	21/09/2010	3.56
SB11A	SA:SB11A SAMPLE 1		4	21/09/2010	3.52
SB11A	SA:SB11A SAMPLE 2	20-09-2010	4	21/09/2010	3.75

2010 ACID LEACHATE cont.

Sample	Date	Recorded pH	Date	Recorded pH	Date	Recorded pH
Blank 1	27-09-2010	/	28-09-2010	/	30/09/2010	/
Blank 2	27-09-2010	/	28-09-2010	/	30/09/2010	/
EAS 61-10	27-09-2010	/	28-09-2010	/	30/09/2010	/
EAS 61-10	27-09-2010	/	28-09-2010	/	30/09/2010	/
EAS 62-10	27-09-2010	/	28-09-2010	/	30/09/2010	/
EAS 62-10	27-09-2010	/	28-09-2010	/	30/09/2010	/
EAS 63-10	27-09-2010	6.28	28-09-2010	3.7	30/09/2010	2.13
EAS 63-10	27-09-2010	6.7	28-09-2010	5.7	30/09/2010	2.57
EAS 64-10	27-09-2010	/	28-09-2010	/	30/09/2010	/
EAS 64-10	27-09-2010	2.46	28-09-2010	1.81	30/09/2010	/
	27-09-2010	7.13	28-09-2010	5.45	30/09/2010	2.02
T5	27-09-2010	7.07	28-09-2010	4.31	30/09/2010	2.03
T28	27-09-2010	7.12	28-09-2010	6.91	30/09/2010	5.89
T28	27-09-2010	7.19	28-09-2010	6.92	30/09/2010	5.89
SB10B	27-09-2010	3.36	28-09-2010	2.69	30/09/2010	2.46
SB10B	27-09-2010	3.39	28-09-2010	3.05	30/09/2010	2.57
SB11A	27-09-2010	3.4	28-09-2010	2.96	30/09/2010	2.5
SB11A	27-09-2010	3.17	28-09-2010	2.52	30/09/2010	/

2010 ACID LEACHATE cont.

Sample	Date	Recorded pH	Date	Recorded pH	Date	Recorded pH
Blank 1	15/10/2010	/	19/10/2010	/	20/10/2010	/
Blank 2	15/10/2010	/	19/10/2010	/	20/10/2010	/
EAS 61-10	15/10/2010	/	19/10/2010	/	20/10/2010	/
EAS 61-10	15/10/2010	/	19/10/2010	/	20/10/2010	/
EAS 62-10	15/10/2010	/	19/10/2010	/	20/10/2010	/
EAS 62-10	15/10/2010	/	19/10/2010	/	20/10/2010	/
EAS 63-10	15/10/2010	/	19/10/2010	/	20/10/2010	/
EAS 63-10	15/10/2010	/	19/10/2010	/	20/10/2010	/
EAS 64-10	15/10/2010	/	19/10/2010	/	20/10/2010	/
EAS 64-10	15/10/2010	/	19/10/2010	/	20/10/2010	/
	15/10/2010	/	19/10/2010	/	20/10/2010	/
T5	15/10/2010	/	19/10/2010	/	20/10/2010	/
T28	15/10/2010	5.43	19/10/2010	3.93	20/10/2010	1.8
T28	15/10/2010	5.54	19/10/2010	5.52	20/10/2010	2.55
SB10B	15/10/2010	/	19/10/2010	/	20/10/2010	/
SB10B	15/10/2010	/	19/10/2010	/	20/10/2010	/
SB11A	15/10/2010	/	19/10/2010	/	20/10/2010	/
SB11A	15/10/2010	/	19/10/2010	/	20/10/2010	/

Acid Leachate method

% of main cations (Acid Leachate method)----2010

Samples	Lab number	**%Ca**	**%Mg**	**% Fe**	**% SO4**
Blank 1	Blank 1	0	0	0	0
Blank 2	Blank 2	-0.00	-0.00	-0.01	-0.00
EAS 61-10	EAS 1A	0.14	0.14	0.03	1.69
EAS 61-10	EAS 1B	0.15	0.13	0.03	1.68
EAS 62-10	EAS 2A	0.06	0.03	0.01	0.41
EAS 62-10	EAS 2B	0.10	0.04	0.01	0.54
EAS 63-10	EAS 3A	2.24	0.98	1.15	13.95
EAS 63-10	EAS 3B	2.27	0.86	1.47	10.60
EAS 64-10	EAS 4A	0.80	1.22	2.07	8.90
EAS 64-10	EAS 4B	0.87	1.31	1.84	11.59
T5	SA:T5A	1.97	0.67	1.77	9.85
T5	SA:T5B	1.94	0.58	1.53	8.93
T28	SA:T28A	1.12	0.90	0.14	20.68
T28	SA:T28B	1.13	1.04	0.20	16.93
SB10B	SA:SB10B SAMPLE 1	1.46	0.30	0.17	15.02
SB10B	SA:SB10B SAMPLE 2	1.21	0.29	0.19	12.19
SB11A	SA:SB11A SAMPLE 1	1.88	0.18	0.17	13.17
SB11A	SA:SB11A SAMPLE 2	1.42	0.15	0.18	9.15

2010 NEUTRALISING POTENTIAL

Sample	lab name:	Date	pH recorded	Volume of NaOH	End pH
Blank 1	Blank 1	30/09/2010	1.40	22.64	10.55
Blank 2	Blank 2	30/09/2010	1.46	22.25	7.01
EAS 61-10	EAS 1A	30/09/2010	2.01	24.89	7.01
EAS 61-10	EAS 1B	30/09/2010	2.02	24.85	7.01
EAS 62-10	EAS 2A	30/09/2010	2.19	16.05	7.04
EAS 62-10	EAS 2B	30/09/2010	2.06	20.63	7.03
EAS 63-10	EAS 3A	30/09/2010	3.09	9.94	7.28
EAS 63-10	EAS 3B	30/09/2010	3.09	9.84	7.28

EAS 64-10	EAS 4A	30/09/2010	2.23	21.14	7.09
EAS 64-10	EAS 4B	30/09/2010	2.17	21.20	7.02
T5	SA:T5A	30/09/2010	2.79	6.52	7.01
T5	SA:T5B	30/09/2010	2.74	7.03	7.27
T28	SA:T28A	30/09/2010	7.14	-	7.14
T28	SA:T28B	30/09/2010	7.20	-	7.20
SB10B	SA:SB10B SAMPLE 1	30/09/2010	3.54	15.40	7.02
SB10B	SA:SB10B SAMPLE 2	30/09/2010	3.53	15.25	7.08
SB11A	SA:SB11A SAMPLE 1	30/09/2010	3.40	14.75	7.36
SB11A	SA:SB11A SAMPLE 2	30/09/2010	3.50	14.78	7.25

2010 NEUTRALISING POTENTIAL Cont.

Sample	lab name:	Date	pH recorded	Volume of NaOH	End pH
Blank 1	Blank 1	15/10/2010	8.27	0.00	8.27
Blank 2	Blank 2	15/10/2010	7.38	0.00	7.38
EAS 61-10	EAS 1A	15/10/2010	4.50	4.51	7.08
EAS 61-10	EAS 1B	15/10/2010	4.57	4.11	7.40
EAS 62-10	EAS 2A	15/10/2010	6.60	0.18	7.37
EAS 62-10	EAS 2B	15/10/2010	6.13	0.34	7.37
EAS 63-10	EAS 3A	15/10/2010	6.04	0.57	7.22
EAS 63-10	EAS 3B	15/10/2010	6.04	1.00	7.71
EAS 64-10	EAS 4A	15/10/2010	5.49	1.07	7.00
EAS 64-10	EAS 4B	15/10/2010	5.39	1.04	7.02
T5	SA:T5A	15/10/2010	6.01	0.59	7.34
T5	SA:T5B	15/10/2010	6.38	0.27	7.05
T28	SA:T28A	15/10/2010	7.39	0.00	7.39
T28	SA:T28B	15/10/2010	7.28	0.00	7.28
SB10B	SA:SB10B SAMPLE 1	15/10/2010	6.86	0.24	7.58
SB10B	SA:SB10B SAMPLE 2	15/10/2010	7.05	0.00	7.05
SB11A	SA:SB11A SAMPLE 1	15/10/2010	7.01	0.00	7.01
SB11A	SA:SB11A SAMPLE 2	15/10/2010	6.96	0.04	7.02

2010 NEUTRALISING POTENTIAL Cont.

Sample	lab name:	Date	pH recorded	Volume of NaOH	End pH
Blank 1	Blank 1	18/10/2010	8.10	0.00	8.10
Blank 2	Blank 2	18/10/2010	7.38	0.00	7.38
EAS 61-10	EAS 1A	18/10/2010	5.61	0.75	7.01
EAS 61-10	EAS 1B	18/10/2010	5.61	0.93	7.04
EAS 62-10	EAS 2A	18/10/2010	6.69	0.09	7.04
EAS 62-10	EAS 2B	18/10/2010	6.40	0.28	7.73
EAS 63-10	EAS 3A	18/10/2010	6.82	0.21	7.08
EAS 63-10	EAS 3B	18/10/2010	6.82	0.14	7.08
EAS 64-10	EAS 4A	18/10/2010	5.79	2.81	7.53
EAS 64-10	EAS 4B	18/10/2010	5.70	1.27	7.88

T5	SA:T5A	18/10/2010	6.83	0.09	7.09
T5	SA:T5B	18/10/2010	6.70	0.09	7.49
T28	SA:T28A	18/10/2010	7.46	0.00	7.49
T28	SA:T28B	18/10/2010	7.38	0.00	7.38
SB10B	SA:SB10B SAMPLE 1	18/10/2010	7.27	0.00	7.27
SB10B	SA:SB10B SAMPLE 2	18/10/2010	6.95	0.08	7.03
SB11A	SA:SB11A SAMPLE 1	18/10/2010	6.90	0.06	7.07
SB11A	SA:SB11A SAMPLE 2	18/10/2010	6.89	0.07	7.07

2010 NEUTRALISING POTENTIAL Cont.

Sample	lab name:	Date	pH recorded	Volume of NaOH	End pH
Blank 1	Blank 1	19/10/2010	7.83	0.00	7.83
Blank 2	Blank 2	19/10/2010	7.22	0.00	7.22
EAS 61-10	EAS 1A	19/10/2010	6.42	0.32	7.04
EAS 61-10	EAS 1B	19/10/2010	6.21	0.46	7.04
EAS 62-10	EAS 2A	19/10/2010	6.57	0.22	7.17
EAS 62-10	EAS 2B	19/10/2010	6.82	0.14	7.13
EAS 63-10	EAS 3A	19/10/2010	7.13	0.00	7.13
EAS 63-10	EAS 3B	19/10/2010	6.85	0.34	7.96
EAS 64-10	EAS 4A	19/10/2010	6.67	0.28	7.12
EAS 64-10	EAS 4B	19/10/2010	6.50	0.48	7.23
T5	SA:T5A	19/10/2010	6.76	0.12	7.17
T5	SA:T5B	19/10/2010	6.93	0.11	7.23
T28	SA:T28A	19/10/2010	7.19	0.00	7.19
T28	SA:T28B	19/10/2010	7.40	0.00	7.40
SB10B	SA:SB10B SAMPLE 1	19/10/2010	7.07	0.00	7.07
SB10B	SA:SB10B SAMPLE 2	19/10/2010	6.85	0.13	7.29
SB11A	SA:SB11A SAMPLE 1	19/10/2010	7.05	0.00	7.05
SB11A	SA:SB11A SAMPLE 2	19/10/2010	6.93	0.09	7.31

2010 NEUTRALISING POTENTIAL cont.

Sample	lab name:	Date	pH recorded	Volume of NaOH	End pH
Blank 1	Blank 1	20/10/2010	8.25	0.00	8.25
Blank 2	Blank 2	20/10/2010	7.24	0.00	7.24
EAS 61-10	EAS 1A	20/10/2010	6.41	0.30	7.19
EAS 61-10	EAS 1B	20/10/2010	6.53	0.25	7.15
EAS 62-10	EAS 2A	20/10/2010	6.91	0.13	7.33
EAS 62-10	EAS 2B	20/10/2010	7.00	0.00	7.00
EAS 63-10	EAS 3A	20/10/2010	6.80	0.11	7.20
EAS 63-10	EAS 3B	20/10/2010	7.19	0.00	7.19
EAS 64-10	EAS 4A	20/10/2010	6.85	0.12	7.04
EAS 64-10	EAS 4B	20/10/2010	6.63	0.16	7.07

T5	SA:T5A	20/10/2010	6.92	0.16	7.42
T5	SA:T5B	20/10/2010	7.09	0.00	7.09
T28	SA:T28A	20/10/2010	7.38	0.00	7.38
T28	SA:T28B	20/10/2010	7.49	0.00	7.49
SB10B	SA:SB10B SAMPLE 1	20/10/2010	7.33	0.00	7.33
SB10B	SA:SB10B SAMPLE 2	20/10/2010	7.16	0.00	7.16
SB11A	SA:SB11A SAMPLE 1	20/10/2010	7.01	0.00	7.01
SB11A	SA:SB11A SAMPLE 2	20/10/2010	7.04	0.00	7.04

2010 NEUTRALISING POTENTIAL cont.

Sample	lab name:	pH recorded	Volume of NaOH	End pH	End pH
Blank 1	Blank 1	0.00	0.00	0.00	7.83
Blank 2	Blank 2	0.00	0.00	0.00	7.22
EAS 61-10	EAS 1A	5.18	1.18	7.18	7.04
EAS 61-10	EAS 1B	5.32	0.87	1.04	7.04
EAS 62-10	EAS 2A	6.91	0.07	7.12	7.17
EAS 62-10	EAS 2B	6.98	0.01	7.00	7.13
EAS 63-10	EAS 3A	6.84	0.17	7.44	7.13
EAS 63-10	EAS 3B	7.05	0.00	7.05	7.96
EAS 64-10	EAS 4A	6.70	0.24	7.06	7.12
EAS 64-10	EAS 4B	6.53	0.31	7.03	7.23
T5	SA:T5A	7.02	0.00	7.02	7.17
T5	SA:T5B	7.00	0.00	7.00	7.23
T28	SA:T28A	0.00	0.00	0.00	7.19
T28	SA:T28B	0.00	0.00	0.00	7.40
SB10B	SA:SB10B SAMPLE 1	0.00	0.00	0.00	7.07
SB10B	SA:SB10B SAMPLE 2	0.00	0.00	0.00	7.29
SB11A	SA:SB11A SAMPLE 1	0.00	0.00	0.00	7.05
SB11A	SA:SB11A SAMPLE 2	0.00	0.00	0.00	7.31

Neutralising potential

Acid/base calculations emphasis on Neutralising potential

Samples	Lab number	Initial pH	Final pH	NP	NNP (Open)	NNP (Closed)
EAS 61-10	EAS 1A	5.22	1.89	-53.85	-187.67	-321.50
EAS 61-10	EAS 1B	5.00	1.89	-34.92	-187.28	-339.64
EAS 62-10	EAS 2A	3.59	1.86	-11.37	-14.16	-16.95
EAS 62-10	EAS 2B	3.59	1.87	-25.17	-27.80	-30.43

EAS 63-10	EAS 3A	3.48	5.27	5.19	-3.43	-12.05
EAS 63-10	EAS 3B	3.50	5.25	4.89	-4.31	-13.51
EAS 64-10	EAS 4A	8.15	1.07	-37.44	-162.12	-286.81
EAS 64-10	EAS 4B	8.17	1.07	-33.54	-134.80	-236.05
T5	SA:T5A	4.67	4.71	16.50	6.46	-3.58
T5	SA:T5B	4.67	4.66	16.50	6.83	-2.84
T28	SA:T28A	7.78	5.43	60.00	29.68	-0.64
T28	SA:T28B	7.63	5.37	60.00	30.82	1.64
SB10B	SA:SB10B SAMPLE 1	9.94	4.51	13.08	12.80	12.52
SB10B	SA:SB10B SAMPLE 2	9.97	4.50	13.62	13.33	13.04
SB11A	SA:SB11A SAMPLE 1	9.16	4.97	15.57	15.43	15.29
SB11A	SA:SB11A SAMPLE 2	9.01	5.04	15.06	14.94	14.82

Acid/base calculations emphasis on Neutralising potential

Samples	Lab number	Initial pH	Final pH	Base	NNP (Open)	NNP (Closed)
EAS 61-11	EAS 61-1 AUS	3.48	1.600	-26.900	-34.429	-41.958
EAS 61-11	EAS 61-2 AUS	3.50	1.610	-29.327	-36.755	-44.182
EAS 62-11	EAS 62-1 AUS	3.41	1.250	-14.149	-27.146	-40.143
EAS 62-11	EAS 62-2 AUS	3.41	1.260	-11.312	-23.560	-35.808
EAS 63-11	EAS 63-1 AUS	3.52	1.910	-26.661	-85.953	-145.245
EAS 63-11	EAS 63-2 AUS	3.49	1.910	-26.866	-86.404	-145.943
EAS 64-11	EAS 64-1 AUS	8.43	5.670	187.029	154.691	122.353
EAS 64-11	EAS 64-2 AUS	8.42	5.680	128.925	94.696	60.468
FKP	FKP 1 GCS	8.71	3.270	19.147	13.769	8.392
FKP	FKP 2 GCS	8.71	3.270	18.053	12.676	7.298
FEM	FEM 1 GCS	7.93	3.920	16.959	0.354	-16.252
FEM	FEM 2 GCS	7.93	3.920	15.865	-0.740	-17.346

2010: Acid/base calculations

Samples	Lab number	Initial pH	Final pH	Acid (Open)	Acid (Closed)	NP	NNP (Open)	NNP (Closed)
EAS 61-10	EAS 1A	5.22	1.89	133.82	267.65	-53.85	-187.67	-321.50
EAS 61-10	EAS 1B	5.00	1.89	152.36	304.72	-34.92	-187.28	-339.64
EAS 62-10	EAS 2A	3.59	1.86	2.79	5.58	-11.37	-14.16	-16.95
EAS 62-10	EAS 2B	3.59	1.87	2.63	5.26	-25.17	-27.80	-30.43
EAS 63-10	EAS 3A	3.48	5.27	8.62	17.24	5.19	-3.43	-12.05
EAS 63-10	EAS 3B	3.50	5.25	9.20	18.40	4.89	-4.31	-13.51
EAS 64-10	EAS 4A	8.15	1.07	124.68	249.37	-37.44	-162.12	-286.81
EAS 64-10	EAS 4B	8.17	1.07	101.26	202.51	-33.54	-134.80	-236.05
T5	SA:T5A	4.67	4.71	10.04	20.08	16.50	6.46	-3.58
T5	SA:T5B	4.67	4.66	9.67	19.34	16.50	6.83	-2.84
T28	SA:T28A	7.78	5.43	30.32	60.64	60.00	29.68	-0.64
T28	SA:T28B	7.63	5.37	29.18	58.36	60.00	30.82	1.64
SB10B	SA:SB10B SAMPLE 1	9.94	4.51	0.28	0.56	13.08	12.80	12.52
SB10B	SA:SB10B SAMPLE 2	9.97	4.50	0.29	0.58	13.62	13.33	13.04
SB11A	SA:SB11A SAMPLE 1	9.16	4.97	0.14	0.28	15.57	15.43	15.29
SB11A	SA:SB11A SAMPLE 2	9.01	5.04	0.12	0.24	15.06	14.94	14.82

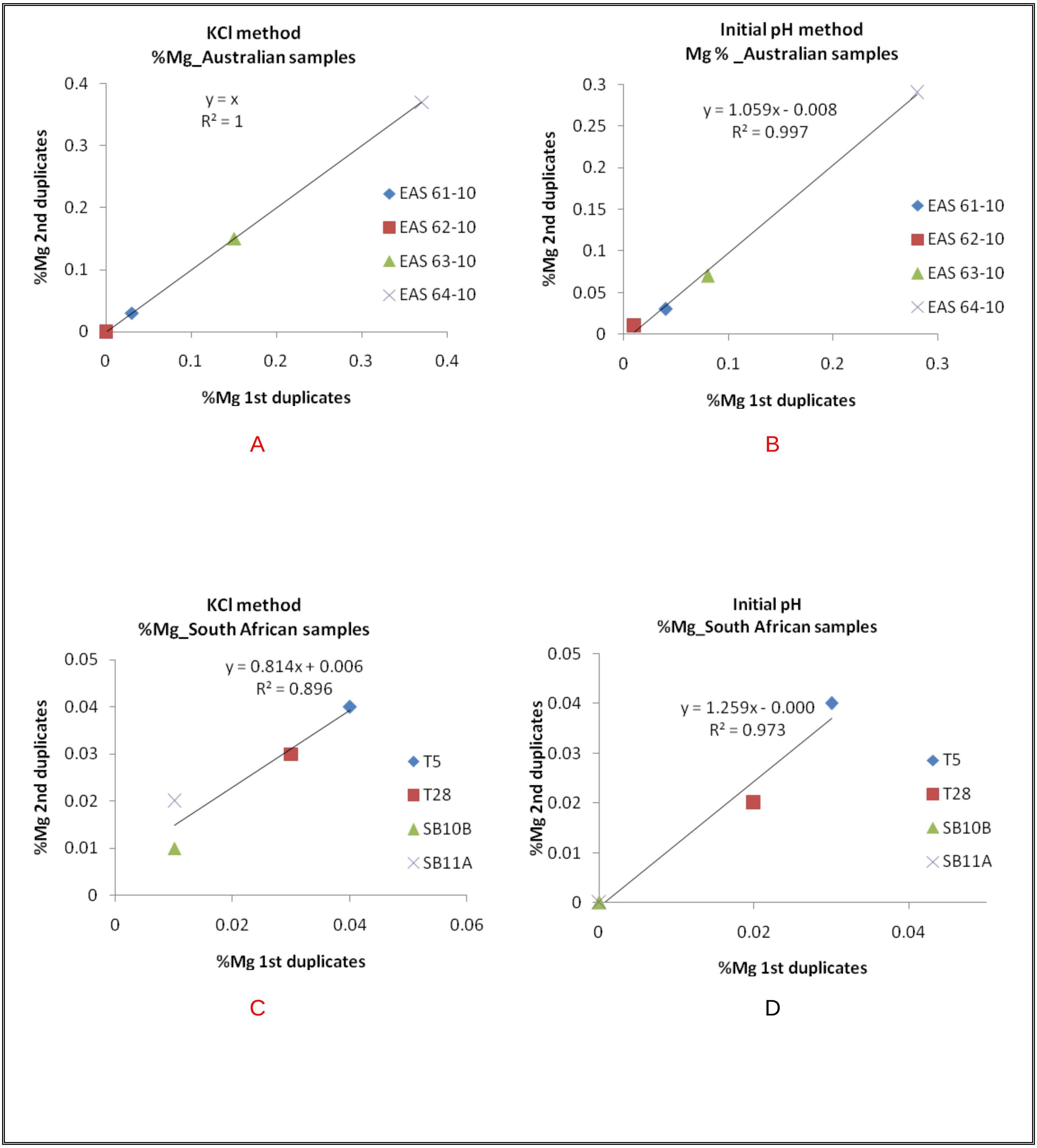
2011: Acid/base calculations

Samples	Lab number	Initial pH	Final pH	Acid (Open)	Acid (Closed)	Base	NNP (Open)	NNP (Closed)
EAS 61-11	EAS 61-1 AUS	3.48	1.600	7.529	15.058	-26.900	-34.429	-41.958
EAS 61-11	EAS 61-2 AUS	3.50	1.610	7.428	14.855	-29.327	-36.755	-44.182
EAS 62-11	EAS 62-1 AUS	3.41	1.250	12.997	25.994	-14.149	-27.146	-40.143
EAS 62-11	EAS 62-2 AUS	3.41	1.260	12.248	24.496	-11.312	-23.560	-35.808
EAS 63-11	EAS 63-1 AUS	3.52	1.910	59.292	118.584	-26.661	-85.953	-145.245
EAS 63-11	EAS 63-2 AUS	3.49	1.910	59.538	119.077	-26.866	-86.404	-145.943
EAS 64-11	EAS 64-1 AUS	8.43	5.670	32.338	64.676	187.029	154.691	122.353
EAS 64-11	EAS 64-2 AUS	8.42	5.680	34.229	68.458	128.925	94.696	60.468
FKP	FKP 1 GCS	8.71	3.270	5.378	10.755	19.147	13.769	8.392
FKP	FKP 2 GCS	8.71	3.270	5.378	10.755	18.053	12.676	7.298
FEM	FEM 1 GCS	7.93	3.920	16.605	33.211	16.959	0.354	-16.252
FEM	FEM 2 GCS	7.93	3.920	16.605	33.211	15.865	-0.740	-17.346

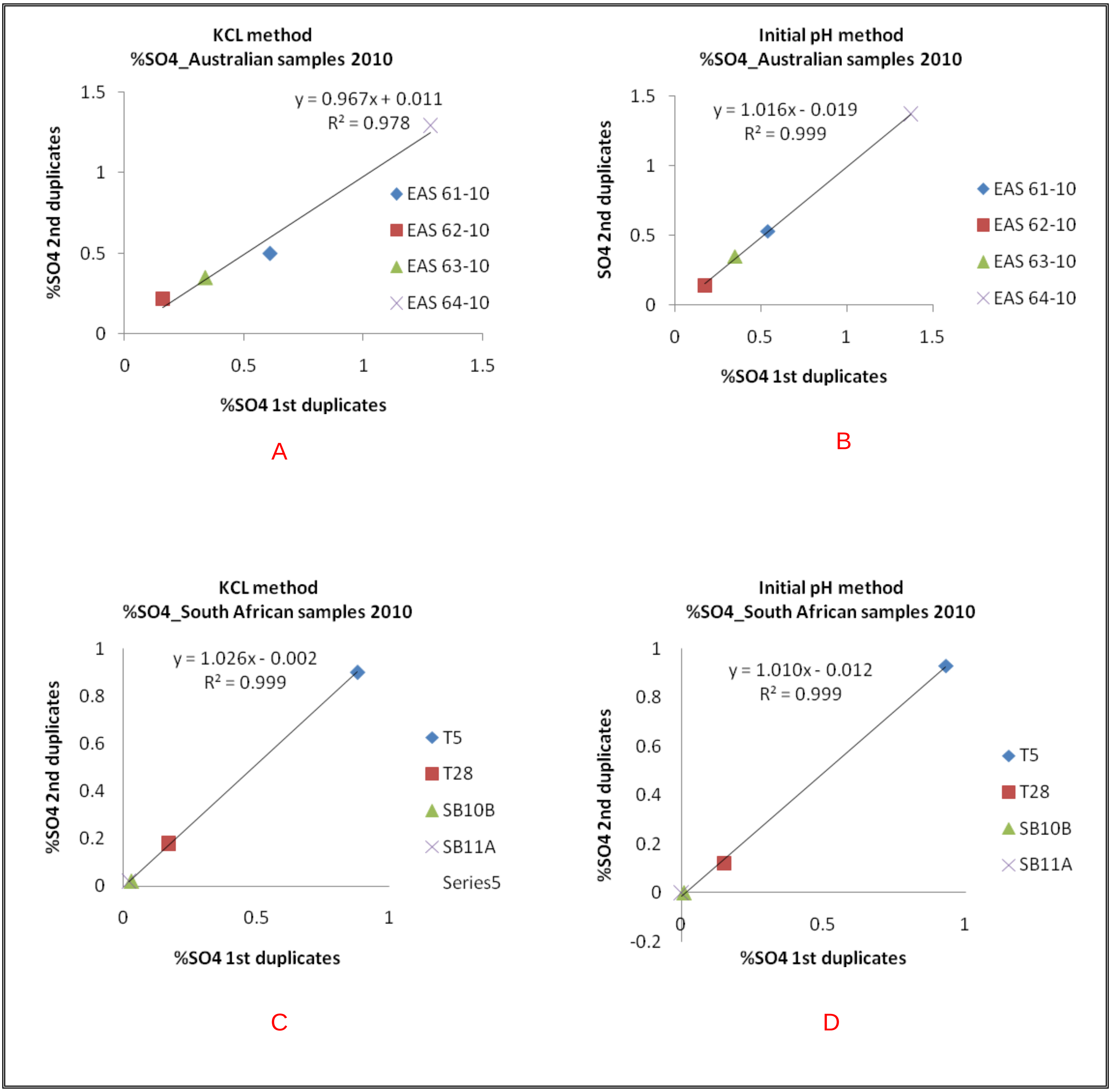
Appendix 5

COMPARISON DATA

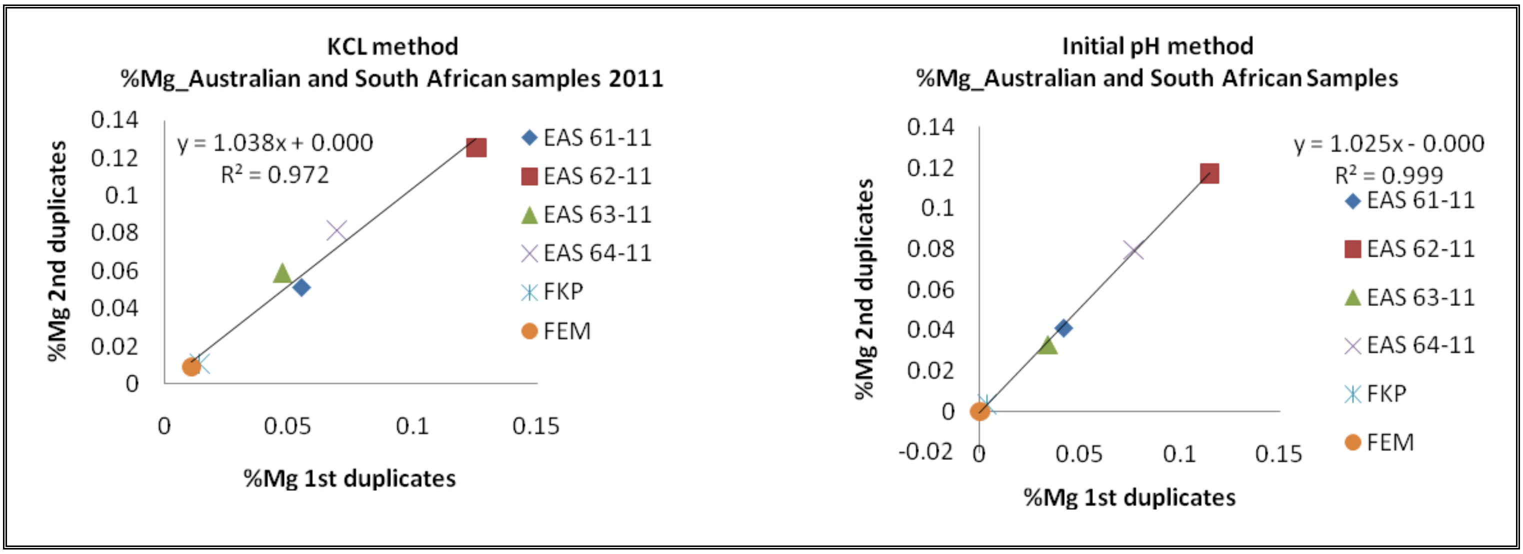
%Mg cation correlation for existing acidity method _2010



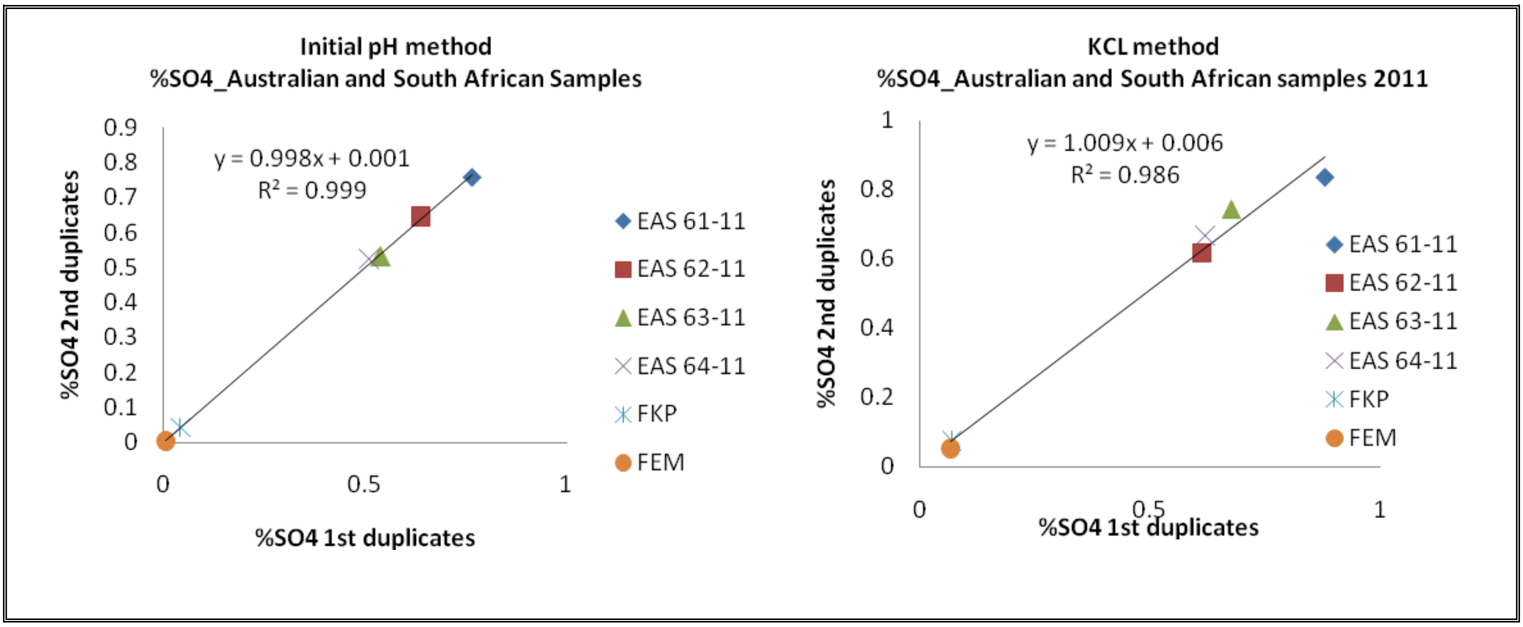
%SO4 cation correlation for existing acidity method _2010



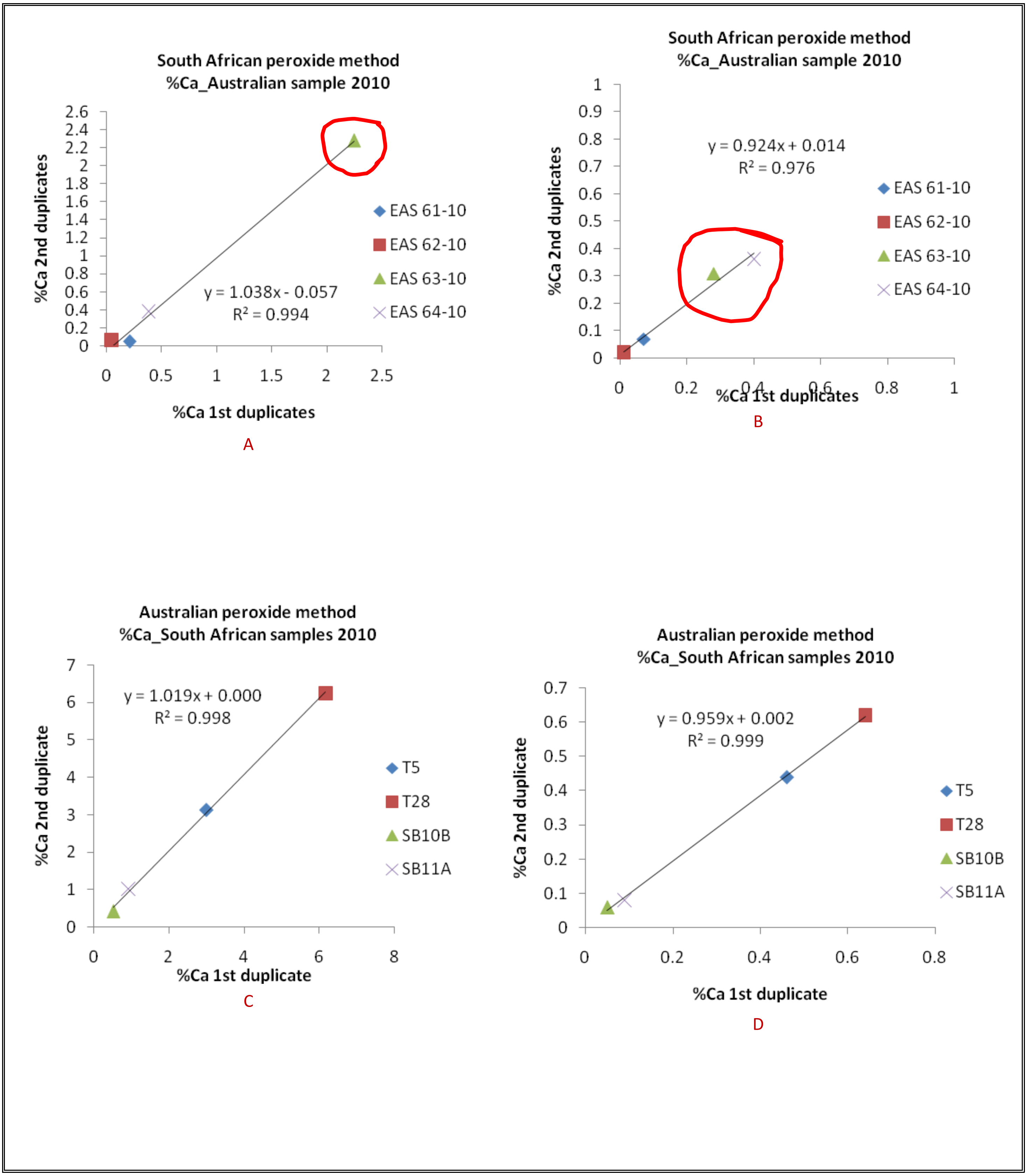
%Mg cation correlation for existing acidity method _2011



%SO4 cation correlation for existing acidity method _2011



%Ca cation correlation for peroxide method _2010



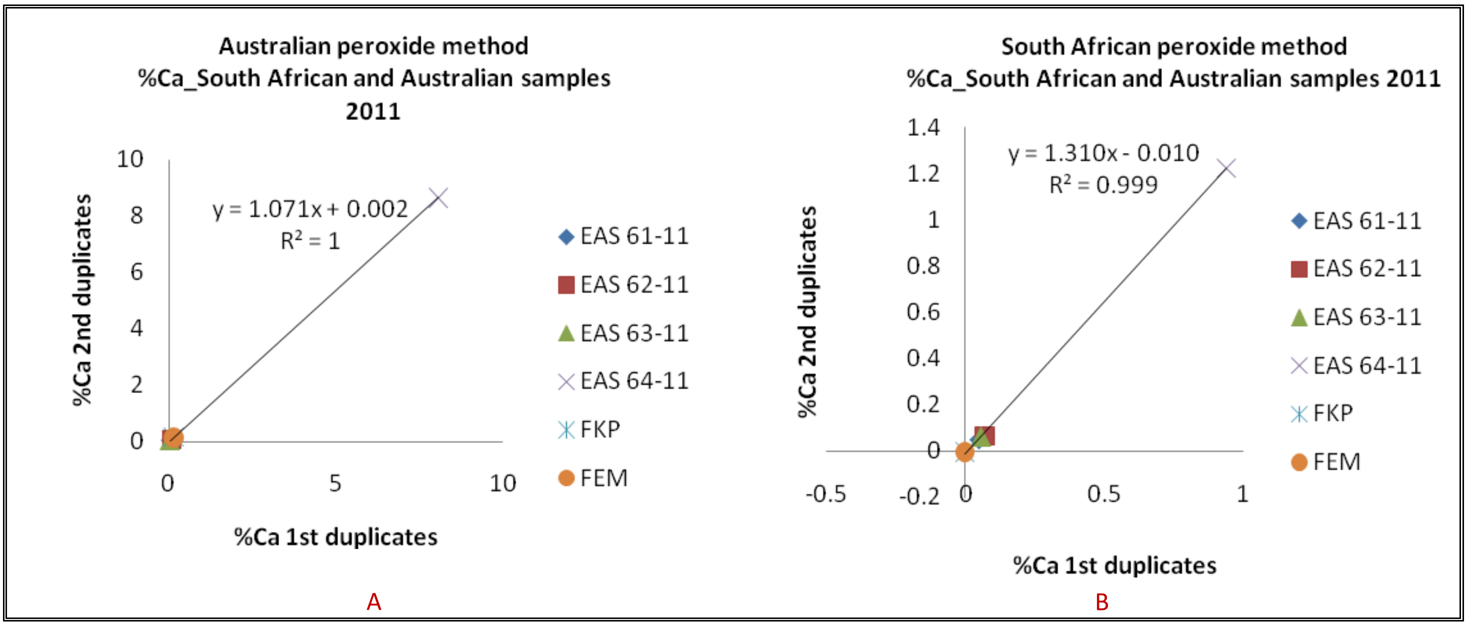
A

B

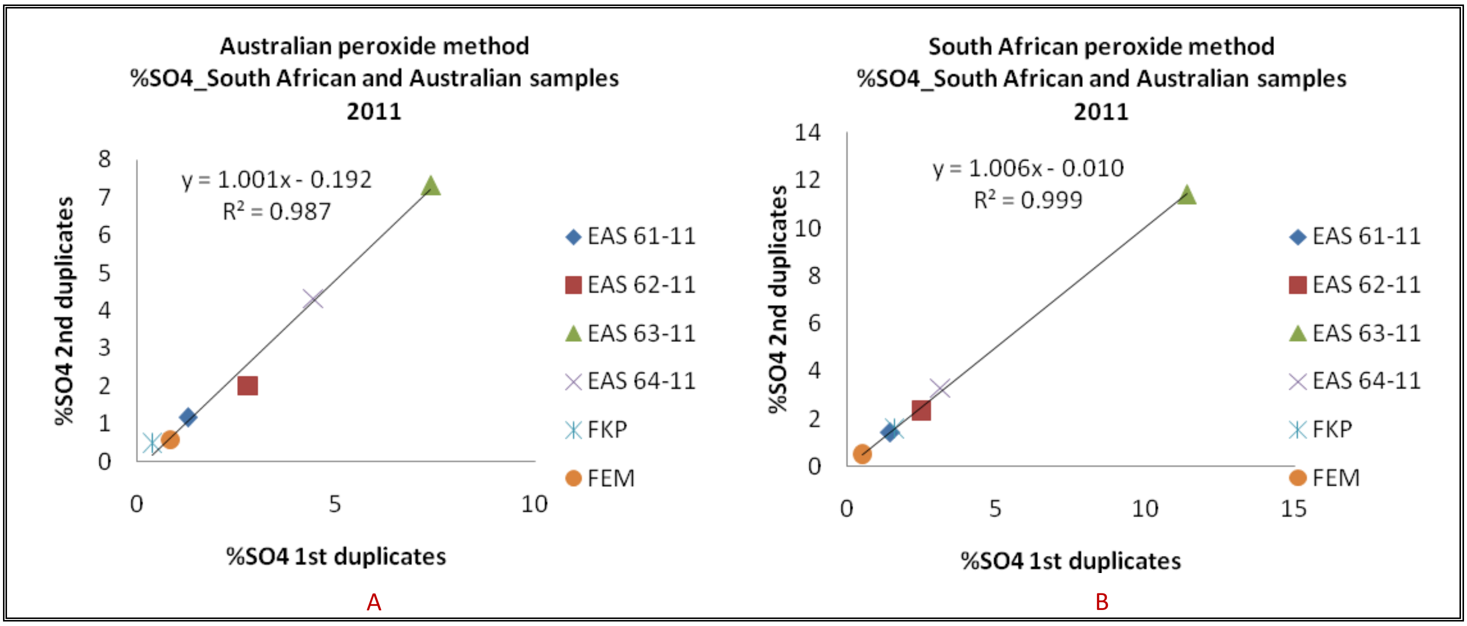
C

D

%Ca cation correlation for peroxide method _2011



%Ca cation correlation for peroxide method _2011



Appendix 5

MIDDELBURG DATA

WATER QUALITY OF THE VOIDS SAMPLED.

Site No	pH	EC	Ca	Mg	Na	K	PAlk	MAlk	F
		mS/m	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
G1 Pit	6.82	324	453	255	21	28.1	0	88	0.61
G7 Pit	3.03	174	120	77	6	7.6	0	0	4.18
G8 Pit	7.54	258	353	225	12	16.4	0	103	1.88
G10 Pit	6.62	299	416	251	14	16.3	0	39	0.44
KSI Pit	3.40	246	390	142	9	17.7	0	0	1.07
KS2 Pit	7.12	253	432	172	13	17.4	0	47	0.17
H3 Pit	6.46	100	90	57	23	12.2	0	15.3	0.30
Site No	**Cl**	**NO2(N)**	**Br**	**NO3(N)**	**PO4**	**SO4**	**Al**	**Fe**	**Mn**
	mg/L	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
G1 Pit	8	0.08	<0.4	5.37	<1	2301	<0.004	0.163	0.85
G7 Pit	6	<0.1	<0.4	0.09	<1	1007	38.663	24.2	12.94
G8 Pit	7	<0.1	0.61	0.05	<1	1808	0.006	0.164	0.27
G10 Pit	7	<0.1	0.31	0.23	<1	2179	0.001	0.049	0.17
KSI Pit	6	<0.1	0.12	1.69	<1	1713	7.497	2.710	4.54
KS2 Pit	7	0.08	<0.4	2.96	<1	1830	0.007	0.074	3.99
H3 Pit	19	<0.01	<0.04	0.12	<0.1	482	0.042	0.005	2.91
Site No	**Ba**	**Co**	**Cr**	**Cu**	**Ni**	**V**	**Zn**	Pb	
	mg/L	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	
G1 Pit	0.019	0.033	<0.006	0.004	0.084	0.000	0.015	0.007	
G7 Pit	0.037	0.349	0.010	0.049	0.552	0.003	1.341	0.025	
G8 Pit	0.016	0.002	<0.006	0.003	0.011	0.000	0.009	0.009	
G10 Pit	0.015	0.001	<0.006	0.004	0.017	0.000	0.010	0.009	
KSI Pit	0.033	0.158	<0.006	0.070	0.273	0.000	0.752	0.014	
KS2 Pit	0.025	0.084	<0.006	0.004	0.169	<0.0002	0.352	0.010	
H3 Pit	0.060	0.019	<0.006	0.014	0.082	<0.0001	0.116	0.013	

WATER QUALITY OF THE BOREHOLES SAMPLED.

Site No	pH	EC	Ca	Mg	Na	K	PAlk	MAlk	F
		mS/m	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
G1	5.8	30	19	11	6	3.5	0	29	0.16
G2	6.2	14	7	5	11	3.1	0	38	0.05
G3	7.0	20	3	2	40	2.1	0	97	0.32
G4	6.1	7	3	2	10	1.8	0	32	0.02
G5	6.8	39	34	18	7	10.7	0	132	0.16
G6	5.9	189	183	152	15	7.6	0	44	1.31
G7	6.1	23	23	9	6	3.7	0	118	0.08
G10-D	6.7	11	6	4	10	4.3	0	51	0.01
G10-S	5.2	4	1	0	5	2.9	0	4.98	0.01
E1	6.6	53	37	36	6	5.3	0	75.7	0.30
E2	5.6	210	193	98	9	5.9	0	15.8	0.20
E6	6.8	299	234	336	86	13.0	0	113	7.97
E7	6.5	493	454	734	29	27.2	0	74.5	0.38
H1	7.4	375	164	593	49	20.1	0	226	0.25

Site No	Cl	NO2(N)	Br	NO3(N)	PO4	SO4	Al	Fe	Mn
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
G1	3	0.02	<0.04	0.30	<0.1	118	0.029	20.29	1.78
G2	3	<0.01	<0.04	0.18	<0.1	28	0.007	0.25	0.06
G3	4	0.13	<0.04	0.20	<0.1	6	0.005	0.26	0.03
G4	5	<0.01	<0.04	0.18	<0.1	2	0.004	0.06	0.03
G5	27	<0.01	1.85	0.20	<0.1	26	0.005	0.16	0.47
G6	6	<0.1	<0.4	0.14	<1	1840	0.176	514.00	36.73
G7	5	0.01	0.06	0.35	<0.1	2	0.003	6.30	0.27
G10-D	4	<0.01	<0.04	1.10	<0.1	3	0.007	0.40	0.01
G10-S	4	<0.01	<0.04	0.57	<0.1	3	0.015	0.05	0.00
E1	4	<0.01	0.07	0.07	<0.1	191	0.029	1.70	0.19
E2	4	<0.1	0.18	0.09	<1	1298	0.142	307.56	15.13
E6	6	<0.1	0.09	0.16	<1	1814	0.119	3.38	8.27
E7	5	<0.1	0.06	0.04	<1	3788	0.036	3.15	14.86
H1	17	<0.1	0.53	0.32	<1	2389	0.019	<0.08	0.99

Site No	Ba	Co	Cr	Cu	Ni	V	Zn	Pb
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
G1	0.176	0.065	<0.006	0.002	0.105	0.003	0.172	0.010
G2	0.230	0.001	<0.006	0.003	0.005	0.0004	0.012	0.007
G3	0.051	0.001	<0.006	0.005	0.002	0.0003	0.008	0.006
G4	0.045	0.001	<0.006	0.002	0.003	0.0003	0.004	0.006
G5	0.303	0.000	<0.006	0.003	0.006	0.0003	0.002	0.005
G6	0.016	0.157	<0.006	0.002	0.240	0.048	0.180	0.050
G7	0.687	0.002	<0.006	0.002	0.006	0.001	0.008	0.009
G10-D	0.031	0.001	<0.006	0.002	0.000	0.0004	0.004	0.008
G10-S	0.014	0.001	<0.006	0.003	0.001	0.0004	0.004	0.008
E1	0.304	0.001	<0.006	0.003	0.003	0.0004	0.045	0.015
E2	0.038	0.050	<0.006	0.002	0.142	0.020	0.167	0.050
E6	0.082	0.061	<0.006	0.005	0.099	<0.002	0.043	0.013
E7	0.052	0.022	<0.006	0.007	0.026	<0.003	0.033	0.011
H1	0.054	0.001	<0.006	0.022	0.004	0.000	0.024	0.009

2 Goedehoop

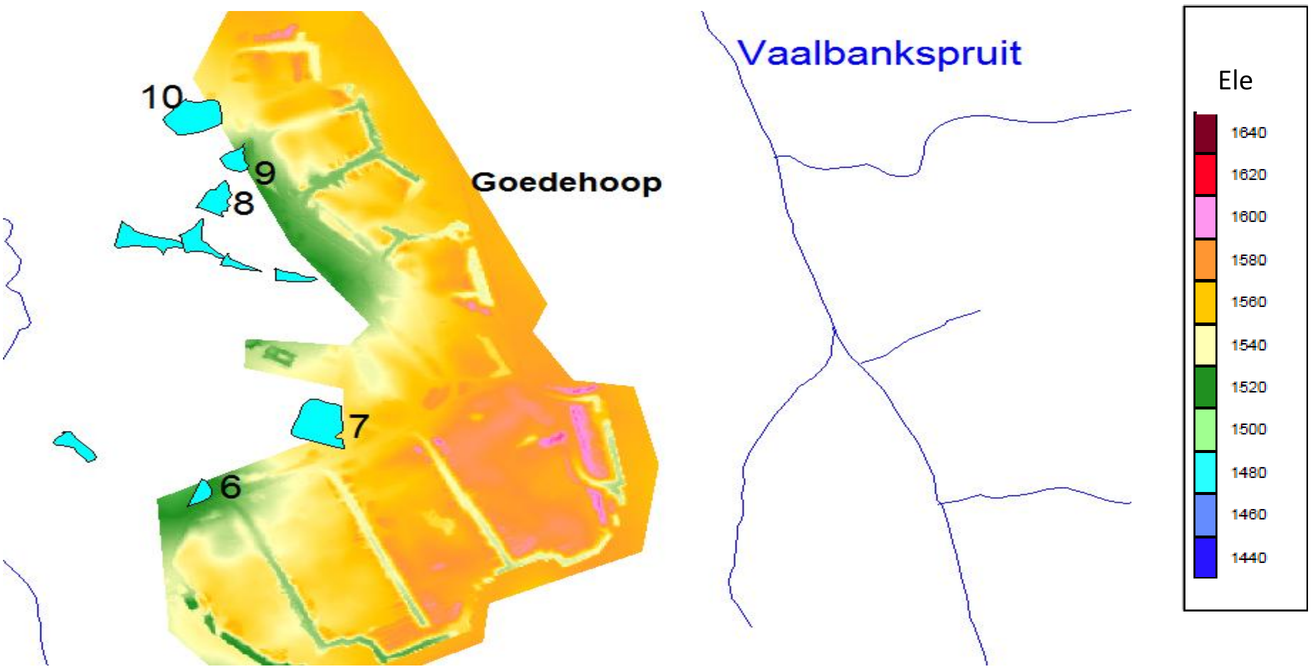

10
9
8
7
6
Goedehoop
Vaalbankspruit
Ele
1640
1620
1600
1580
1560
1540
1520
1500
1480
1460
1440

Figure 0-1Goedehoop mining site

There are 10 ramps at the Goedehoop mine and only 8 ramps were investigated (Figure 0-1)

4.5.2.1Goedehoop 1

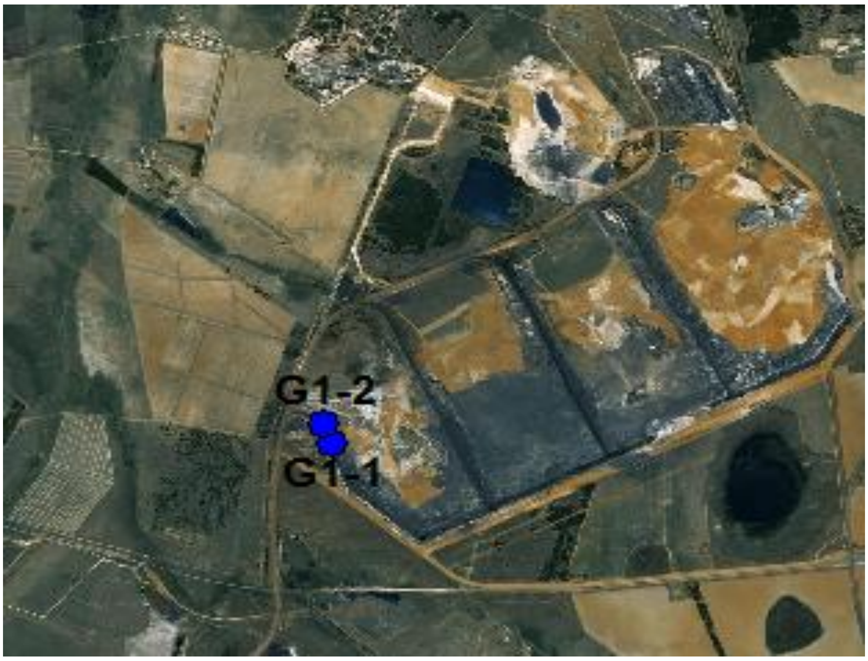


Figure 0-2Location of Goedehoop ramp 1

Only two samples were analysed for Goedehoop ramp 1 (Figure 0-2)

Mineralogical analysis

Table 0-1Mineralogical analysis of Goedehoop ramp 1(left) and classification table (right)

Sample	Q	Kaol	Illite	Gyp
G1-1	XX	X		xx
G1-2	X	XX	<x	xx

Dominant	XX	>40%
Major	X	15-40%
Minor	xx	5-15%
Accessory	x	2-5%
Rare	<x	<2%

Goedehoop ramp 1 mine consists predominantly of quartz and kaolinite and minor components of gypsum (Table 0-1).

Static results

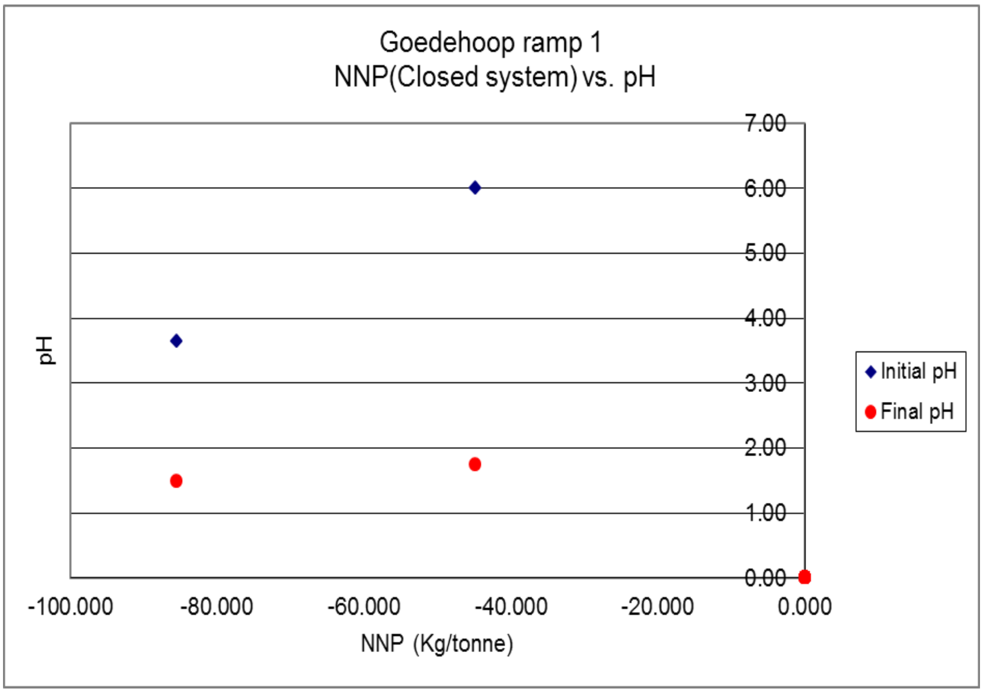


Figure 0-3NNP for Goedehoop ramp 1

All the Goedehoop ramp 1 values show (Figure 0-3) a negative net neutralising potential therefore suggesting that the samples will likely produce AMD.

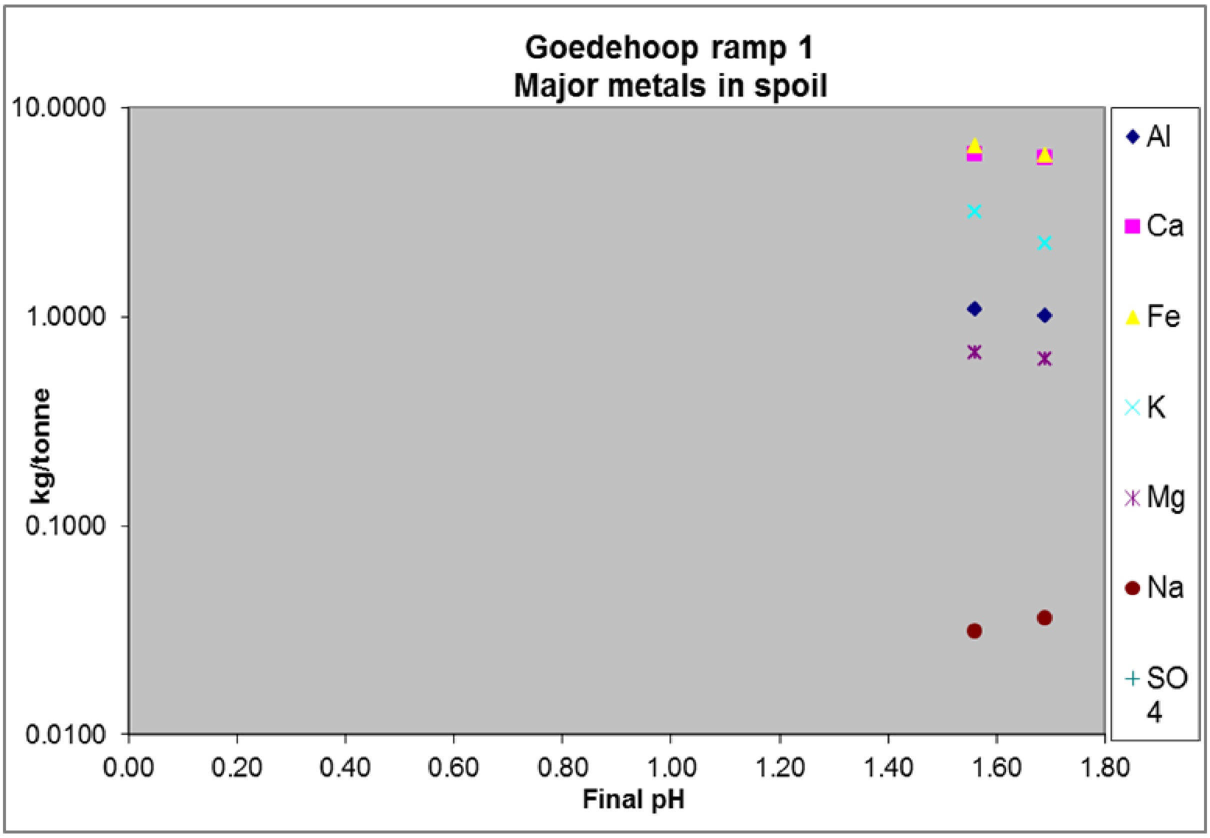


Figure 0-4Major metal from the Goedehoop ramp 1 samples

Ca , $SO_4$and Fe have the highest values with Na as the lowest (Figure 0-4).

Table 0-2Interpretation of ABA pH and NAG results for Goedehoop ramp 1 samples

Site Name	**Initial pH**	**Final pH**	**Interpretation**
G1-1	3.65	1.48	Higher Risk Acid Generation
G1-2	6.00	1.75	Higher Risk Acid Generation

G1-1 sample was already partly oxidised prior to the final pH method (Table 0-2). Both of the samples indicate that they have a higher risk of acid generation.

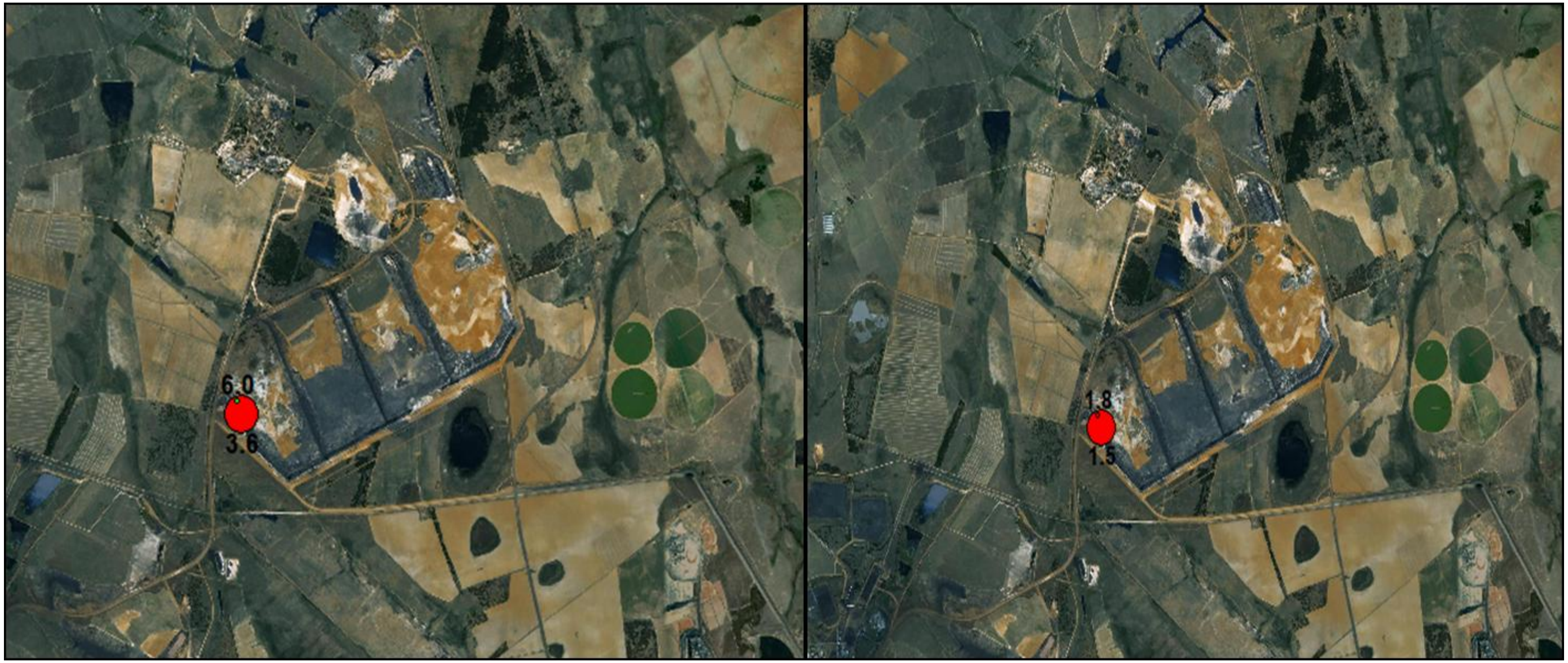


Figure 0-5 Initial pH (left) and final pH (right) showing Goedehoop ramp 1 samples.

The average initial pH is 4.8 and the average final pH is 1.6. Both samples dropped to a value less than 2, indicating a high of acid generation upon oxidization (**Error! Reference source not found.**).

Table 0-3Interpretation of ABA Net Neutralising Potential results for Goedehoop ramp 1 samples.

Site Name	Net Neutralising Potential (Open)	Net Neutralising Potential (Closed)	Interpretation
G1-1	-13.02	-26.04	Potential Acid Generator
G1-2	-6.29	-13.53	Verify with other tests

The open and closed NNP is interpreted in Table 0-3where it indicates negative values as potential Acid generator and that G1-2 needs to be verified with Kinetic tests.

Table 0-4Interpretation and NP/AP ratios for the Goedehoop ramp 1 samples.

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Interpretation Open System	Interpretation Closed System
G1-1	0.00	Likely Acid Generator	Likely Acid Generator
G1-2	0.13	Likely Acid Generator	Likely Acid Generator

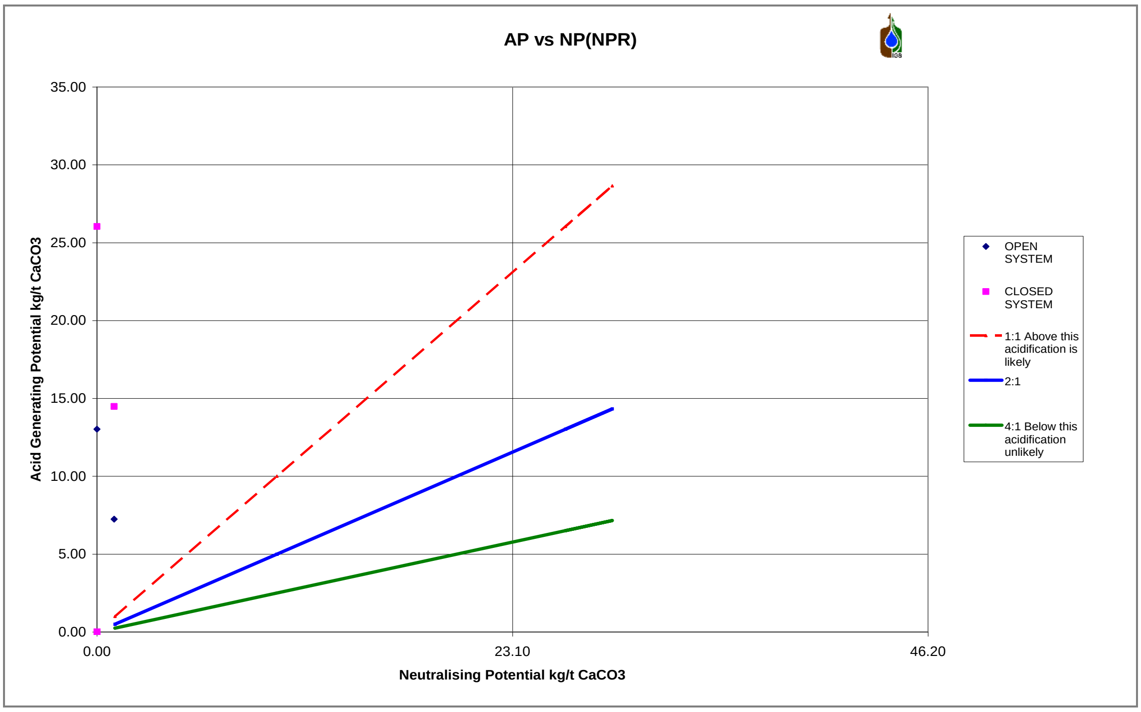


Figure 0-6Graphical presentation of NPR results for Goedehoop ramp 1

Both Goedehoop ramp 1 samples batch in both open and closed system showed acid generating potential since they plotted above the red line (Figure 0-6).

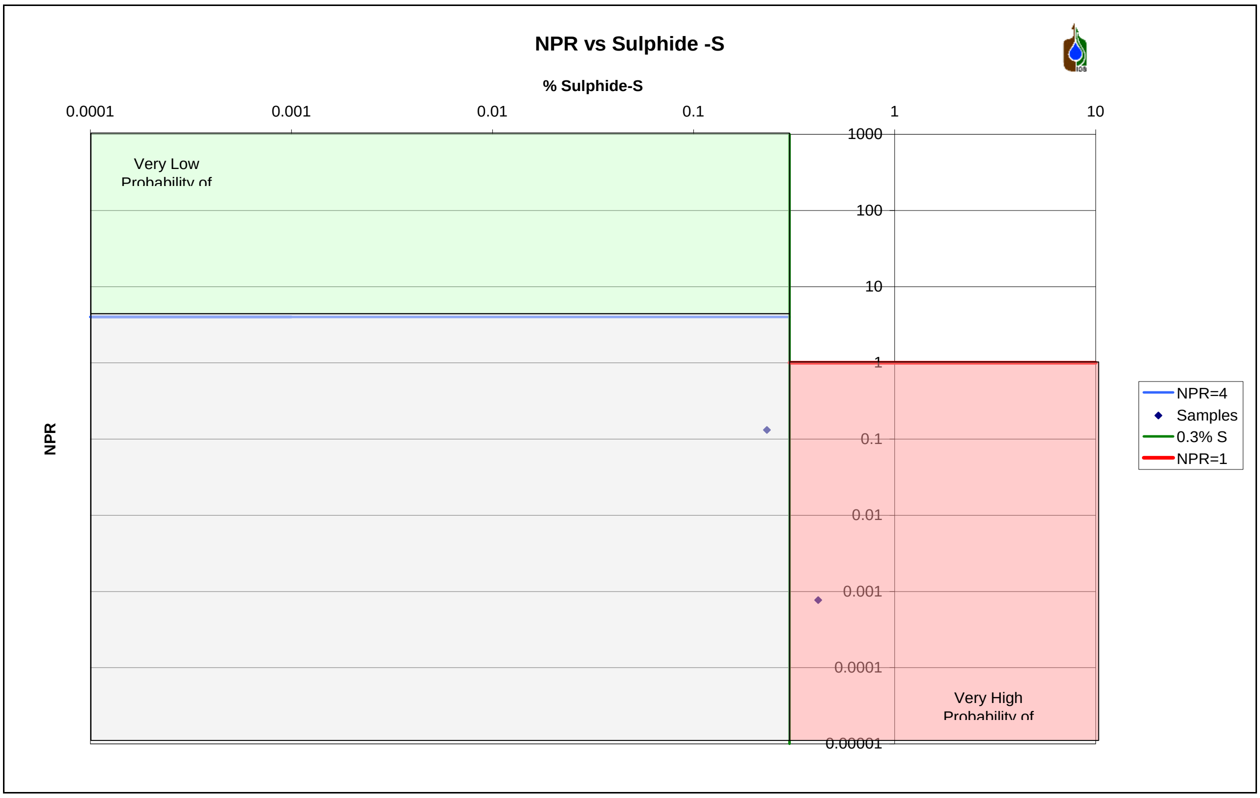
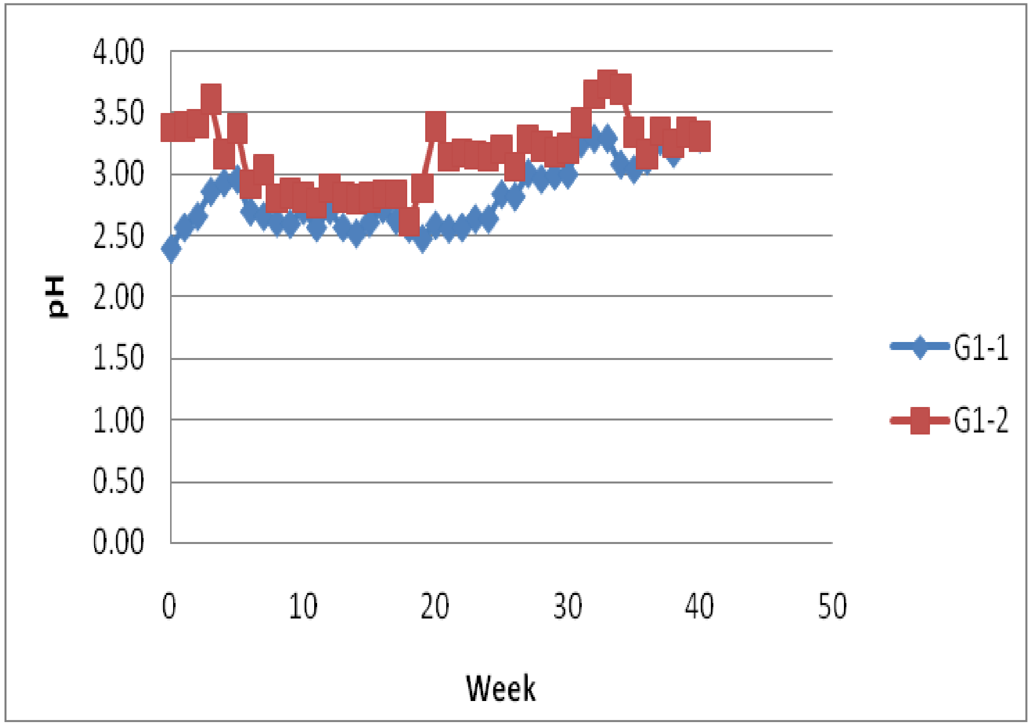


Figure 0-7 % S vs NPR for the Goedehoop ramp 1 samples.

The percentage sulphur in the samples plotted against the NPR (Figure 0-7) indicates one sample that has an uncertain risk of acid production and another one having a high probability of acid generation plotting in the red, indicating a high risk of AMD.

Kinetic results



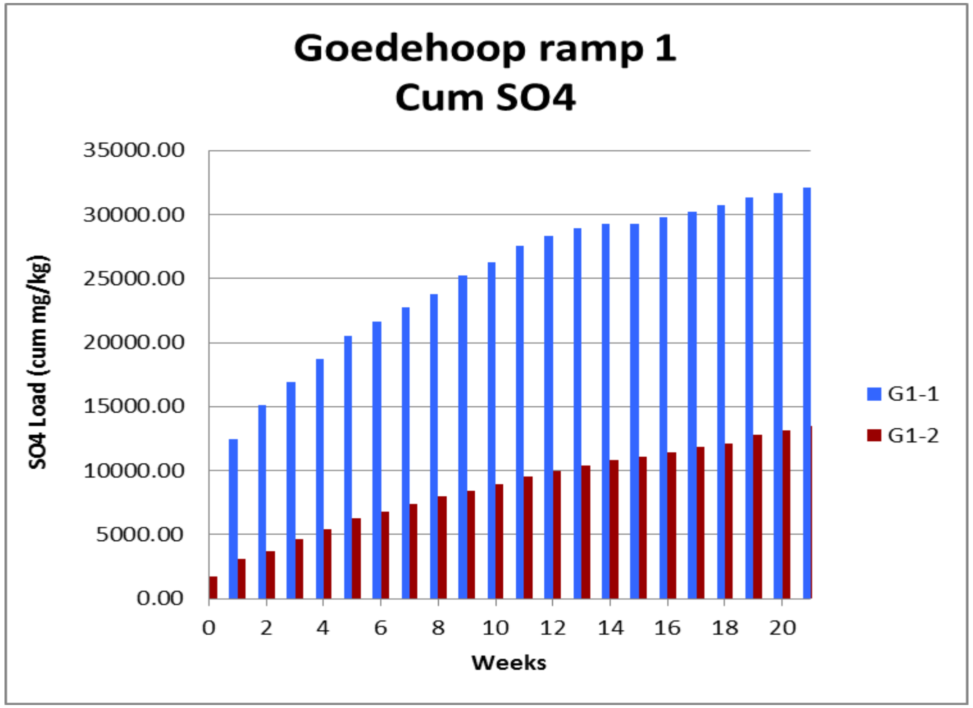


Figure 0-8 Kinetic cell pH value(left) with the Cummulative SO4 (right) of Goedehoop ramp 1 samples

From week 1 the pH for both Goedehoop G1-1 and G1-2 was already acidic and stayed constact till week 40. The cummulative SO4 of G1-1 is higher than G1-2(

Figure 0-8).

4.5.2.2Goedehoop 2

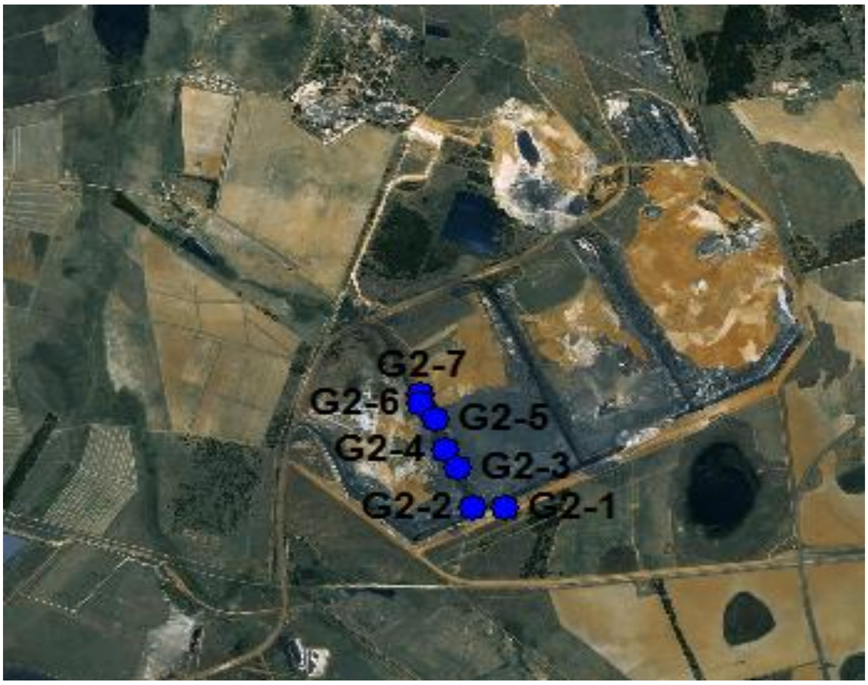


Figure 0-9 Location of samples for Goedehoop ramp 2

7 samples were collected and analysed for Goedehoop ramp 2(Figure 0-9)

Mineralogical analysis

Table 0-5 Mineralogical analysis of Goedehoop ramp 2 (left) and classification table (right)

Sample	Q	Kaol	Illite	Kvsp	Gyp
G2-1	XX	X	x	<x	
G2-2	XX	X		<x	
G2-3	XX	X		<x	
G2-4	XX	xx			x
G2-5	XX	xx	<x	<x	
G2-6	XX	xx		<x	x
G2-7	XX	X		<x	

Dominant	XX	>40%
Major	X	15-40%
Minor	xx	5-15%
Accessory	x	2-5%
Rare	<x	<2%

Goedehoop ramp 2 mine consists predominantly of quartz and kaolinite with accessory components of gypsum and k-feldspar.

Static results

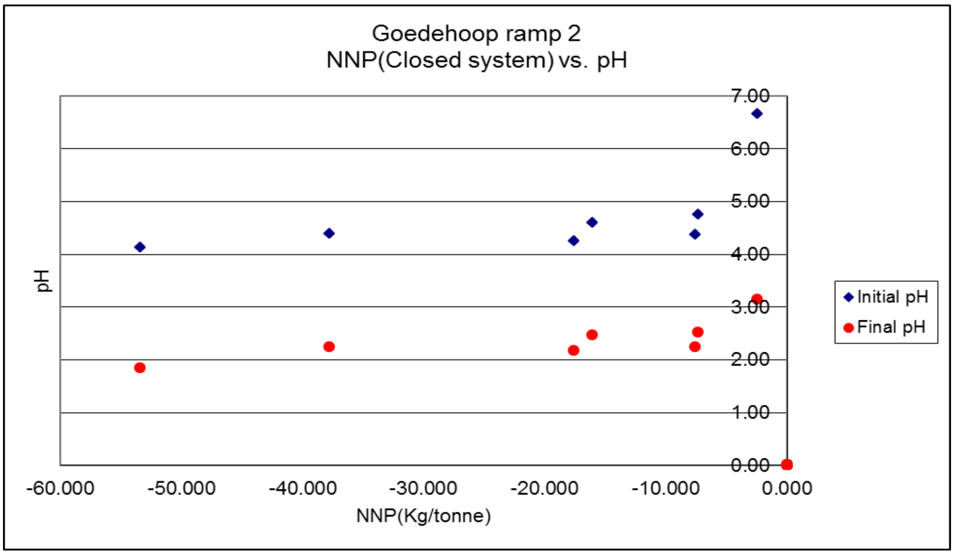


Figure 0-10NNP results for Goedehoop ramp 2

All the Goedehoop ramp 2 values show a negative net neutralising potential therefore suggesting that the samples will likely produce AMD (Figure 0-10).

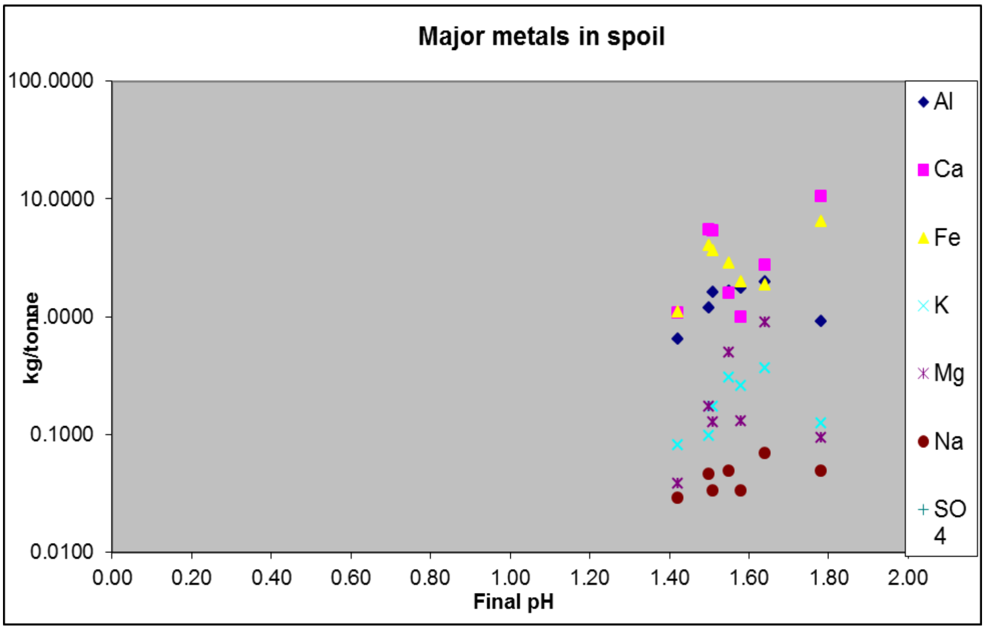


Figure 0-11Major metal from the Goedehoop ramp 2 samples

Caand Fe have the highest values with Na as the lowest (Figure 0-11).

Table 0-6 Interpretation of ABA pH and NAG results for Goedehoop ramp 2 samples

Site Name	Initial pH	Final pH	Interpretation
G2-1	4.75	2.53	Higher Risk Acid Generation
G2-2	4.61	2.47	Higher Risk Acid Generation
G2-3	6.66	3.14	Higher Risk Acid Generation
G2-4	4.14	1.84	Higher Risk Acid Generation
G2-5	4.37	2.24	Higher Risk Acid Generation
G2-6	4.40	2.25	Higher Risk Acid Generation
G2-7 Overburden	4.26	2.18	Higher Risk Acid Generation

All the samples were already partly oxidised prior to the final pH method (Table 0-6)

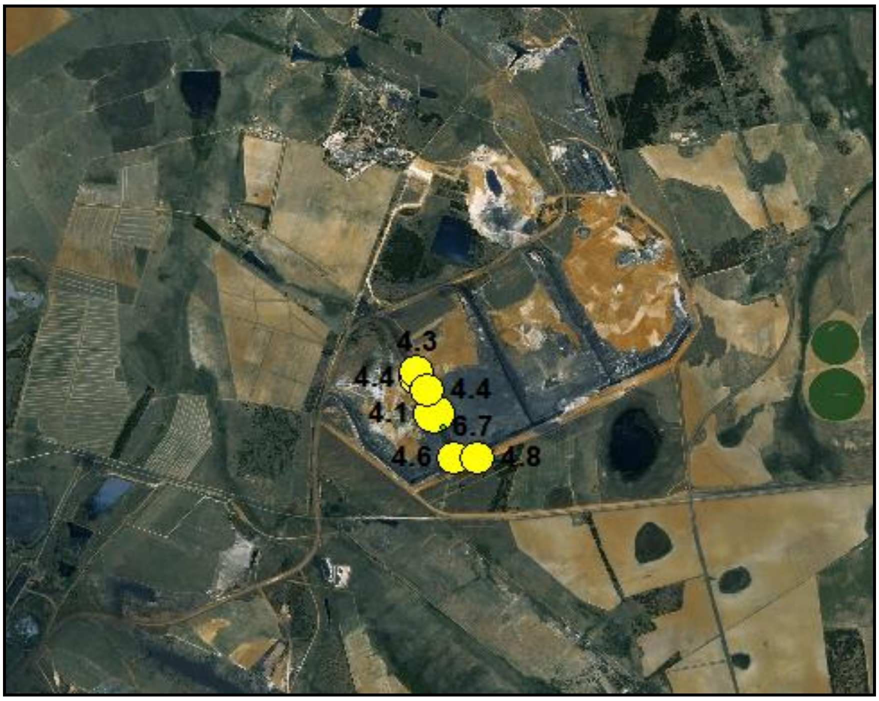


Figure 0-12 Initial pH showing Goedehoop ramp 2 samples

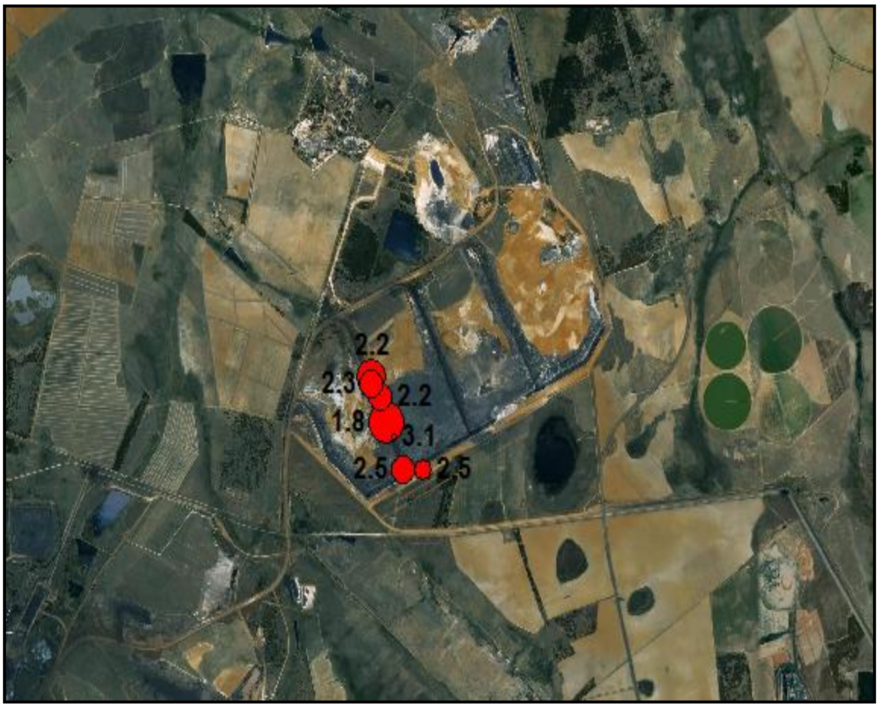


Figure 0-13 final pH showing Goedehoop ramp 2 samples.

The average initial pH is 4.7 and the average final pH is 2.4.pH of all sampled dropped to values ranging 1-3, indicating a high risk of acid generation upon oxidization (Figure 0-12 and Figure 0-13)

Table 0-7 Interpretation of ABA Net Neutralising Potential results.

Site Name	Net Neutralising Potential (Open)	Net Neutralising Potential (Closed)	Interpretation
G2-1	-0.687	-1.374	Verify with other tests
G2-2	-0.272	-0.544	Verify with other tests
G2-3	2.975	4.555	Verify with other tests
G2-4	-4.470	-8.940	Verify with other tests
G2-5	-0.952	-1.905	Verify with other tests
G2-6	2.155	4.309	Verify with other tests
G2-7 Overburden	-0.065	-0.130	Verify with other tests

The open and closed NNP is interpreted in Table 0-7where it indicates negative values as potential Acid generator and that all samples need to be verified with Kinetic tests.

Table 0-8 Interpretation and NP/AP ratios for the Goedehoop ramp 2 samples.

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Interpretation Open System	Interpretation Closed System
G2-1	0.01	Likely Acid Generator	Likely Acid Generator
G2-2	0.04	Likely Acid Generator	Likely Acid Generator
G2-3	13.94	No Acid Potential	No Acid Potential
G2-4	0.00	Likely Acid Generator	Likely Acid Generator
G2-5	0.01	Likely Acid Generator	Likely Acid Generator
G2-6	0.10	Likely Acid Generator	Likely Acid Generator
G2-7 Overburden	0.15	Likely Acid Generator	Likely Acid Generator

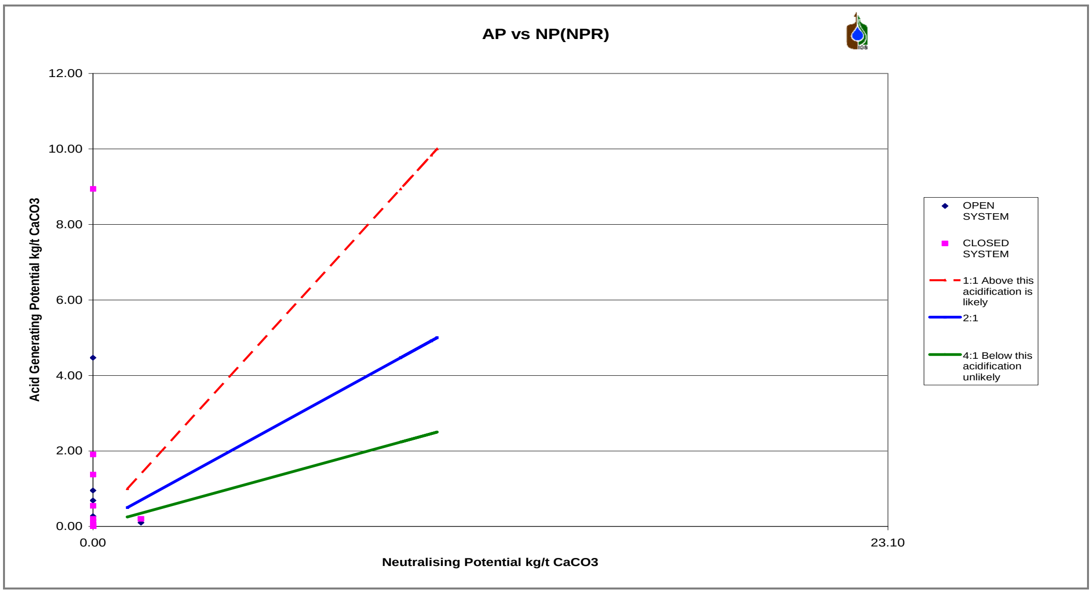


Figure 0-14 Graphical presentation of NPR results for Goedehoop ramp 2

Only one sample in both open and closed system illustrated the unlikelihood of acidification since it plotted under the green line, the rest of the sample plotted along the y-axis and is inconclusive (Figure 0-14).

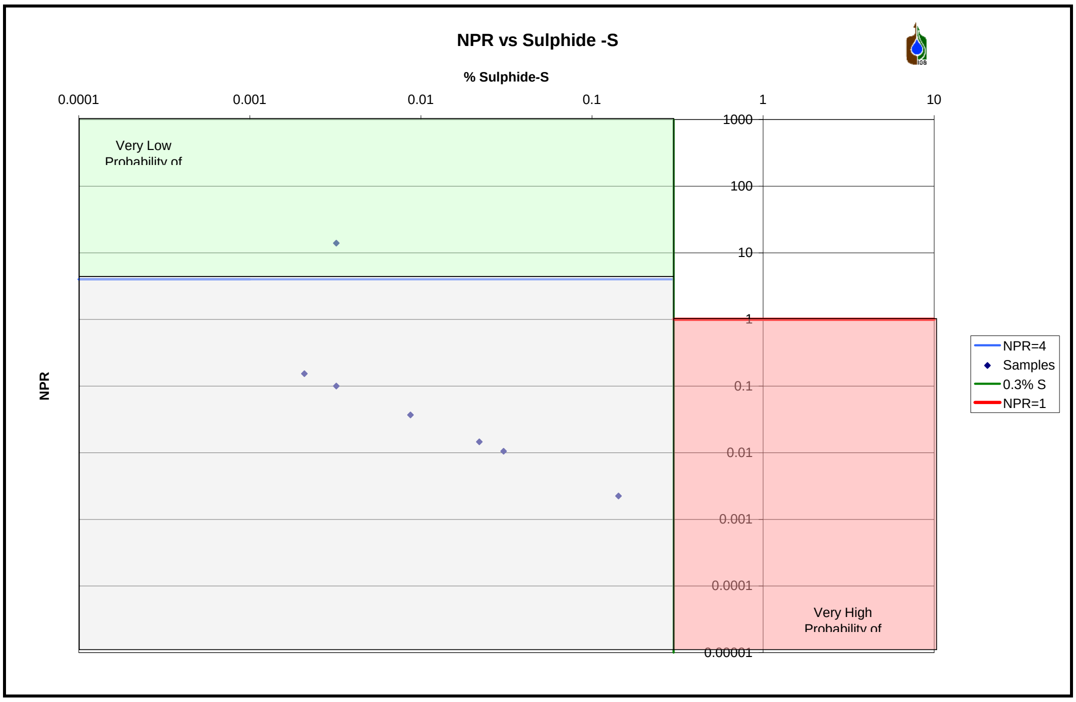


Figure 0-15 % S vs NPR for the Goedehoop ramp 2 samples.

The percentage sulphur in the samples plotted against the NPR (Figure 0-15) indicates most of the samples have an uncertain risk of acid production and one samplehas very low probability of acid generation.

Kinetic results

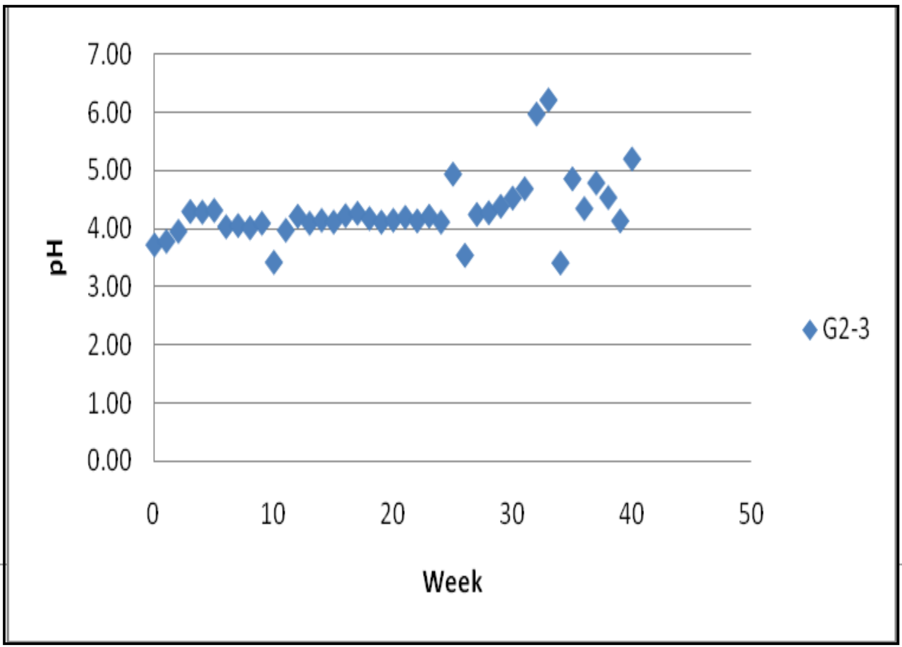


Figure 0-16 Kinetic cell pH value of Goedehoop ramp 2 samples

From week 1 the pH for G2-3 was already acidic but gave erratic reading from week 21 till week 40 (Figure 0-16).

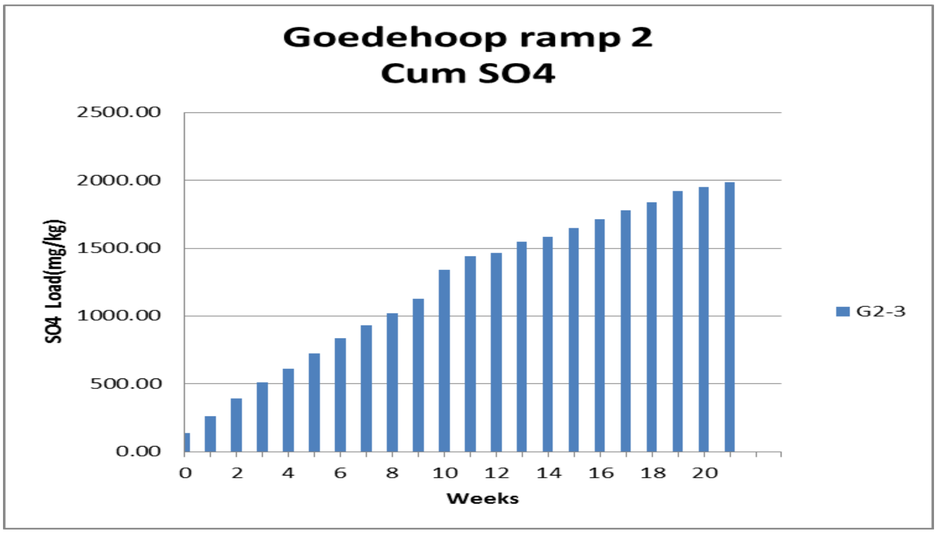


Figure 0-17 Cumulative SO4 of Goedehoop ramp 2 samples

The cummulative SO4 of G2-3at week 20 is about 2000 mg/kg/week (Figure 0-17)

4.5.2.3Goedehoop 3

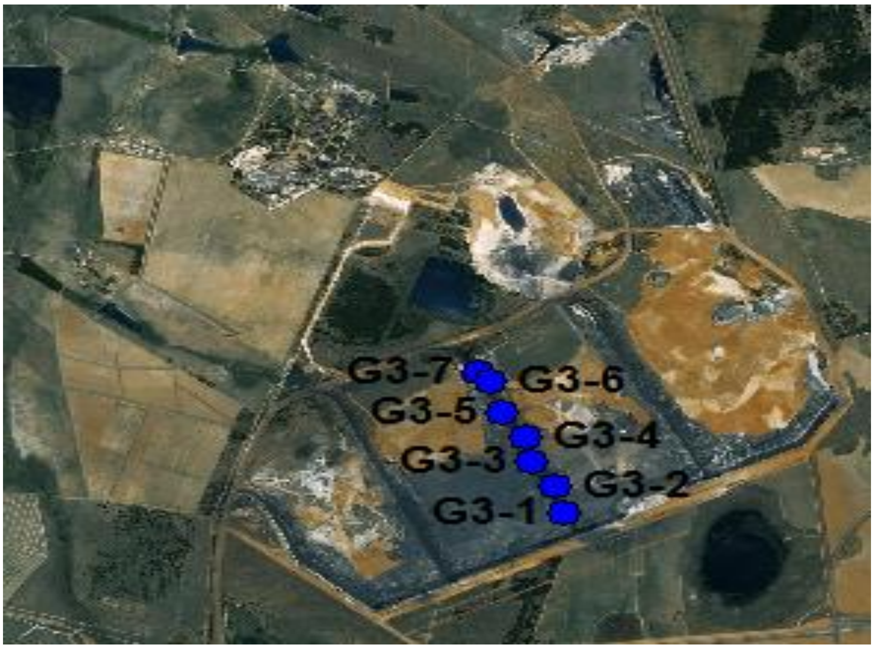


Figure 0-18 Goedehoop ramp 3 sample site

7 samples were analysed for Goedehoop ramp 3 (Figure 0-18).

Mineralogical analysis

Table 0-9Mineralogical analysis of Goedehoop ramp 3 (left) and classification table (bottom right)

Sample	Q	Kaol	Illite	Kvsp	Gyp
G3-1	XX	XX		x	
G3-2	XX	XX	<x	x	x
G3-3	XX	XX	x	x	
G3-4	XX	XX	<x	x	
G3-5	XX	XX	x	x	
G3-6	XX	X	<x		xx
G3-7	XX	X			

Dominant	XX	>40%
Major	X	15-40%
Minor		5-15%
Accessory	x	2-5%
Rare	<x	<2%

Goedehoop ramp 3 mine consists predominantly of quartz and kaolinite with accessory components of gypsum and K-Feldspar (Table 0-9).

Static results

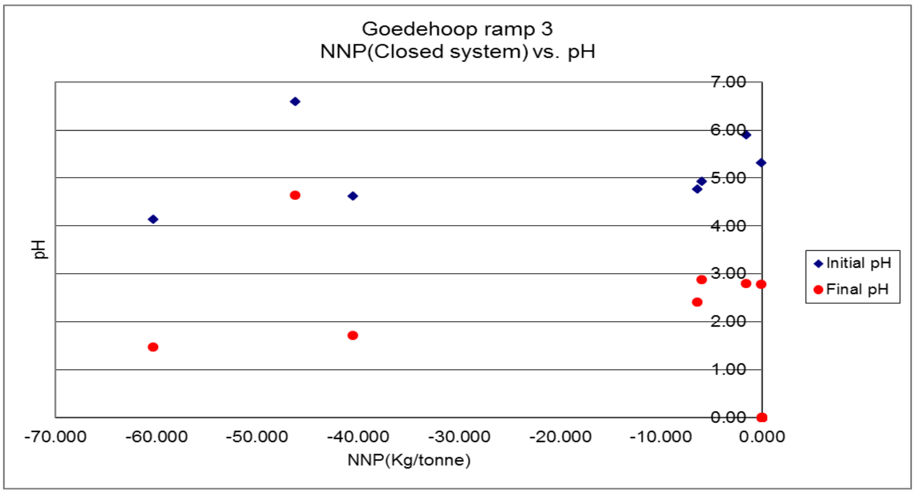


Figure 0-19 NNP Goedehoop ramp 3 results

All the Goedehoop ramp 3 values show a negative net neutralising potential therefore suggesting that the samples will likely produce AMD. Some samples rest on the zero point therefore other test should be done to verify (Figure 0-19).

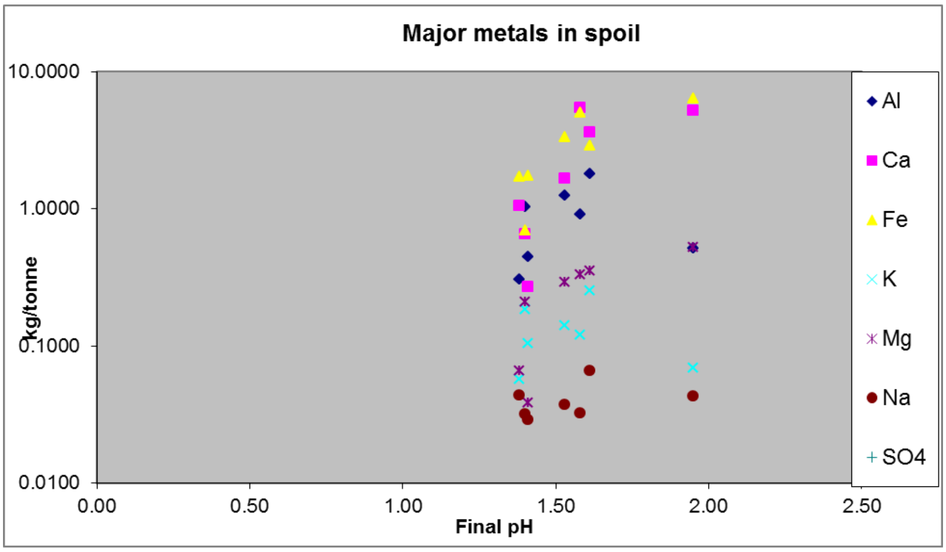


Figure 0-20Major metal from the Goedehoop ramp 3 samples

Ca , $SO_4$and Fe have the highest values with Na as the lowest.

Table 0-10Interpretation of ABA pH and NAG results for Goedehoop ramp 3 samples

Site Name	Initial pH	Final pH	Interpretation
G3-1	4.62	1.71	Higher Risk Acid Generation
G3-2	4.14	1.46	Higher Risk Acid Generation
G3-3	5.89	2.80	Higher Risk Acid Generation
G3-4	5.32	2.77	Higher Risk Acid Generation
G3-5 overburden	4.93	2.87	Higher Risk Acid Generation
G3-6	6.59	4.64	Medium Risk Acid Generation
G3-7	4.76	2.41	Higher Risk Acid Generation

All the samples were already partly oxidised prior to the final pH method (Table 0-10).

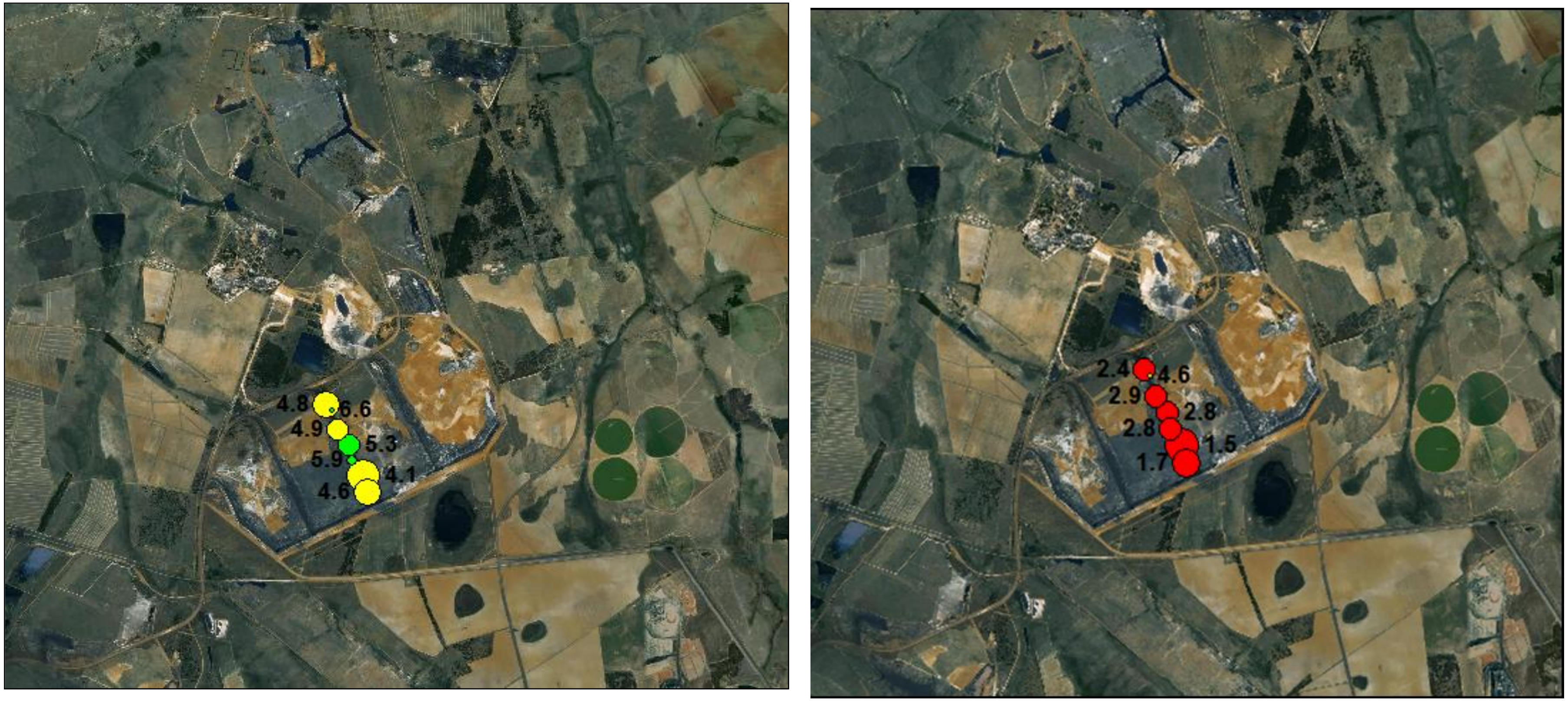


Figure 0-21Initial pH (left) and final pH (right) showing Goedehoop ramp 3 samples

The average initial pH values were between 4-6.6 meaning that they are partly oxidised and the average final pH was 2.7. This is an indication that upon oxidation the samples have a high-medium potential of acid generation (Figure 0-21).

Table 0-11Interpretation of ABA Net Neutralising Potential results.

Site Name	Net Neutralising Potential (Open)	Net Neutralising Potential (Closed)	Interpretation
G3-1	-3.946	-7.892	Verify with other tests
G3-2	-7.847	-15.694	Verify with other tests
G3-3	0.387	-0.417	Verify with other tests
G3-4	1.294	0.718	Verify with other tests
G3-5 overburden	-0.021	-0.042	Verify with other tests
G3-6	0.720	-13.317	Verify with other tests
G3-7	-0.306	-0.613	Verify with other tests

The open and closed NNP is interpreted inTable 0-11where it indicates negative values as potential Acid generator and that all samples need to be verified with Kinetic tests.

Table 0-12 Interpretation and NP/AP ratios for the Goedehoop ramp 3 samples.

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Interpretation Open System	Interpretation Closed System

G3-1	0.00	Likely Acid Generator	Likely Acid Generator
G3-2	0.00	Likely Acid Generator	Likely Acid Generator
G3-3	1.48	Acid under certain conditions	Likely Acid Generator
G3-4	3.25	Acid under certain conditions	Acid under certain conditions
G3-5 overburden	0.47	Likely Acid Generator	Likely Acid Generator
G3-6	1.05	Acid under certain conditions	Likely Acid Generator
G3-7	0.03	Likely Acid Generator	Likely Acid Generator

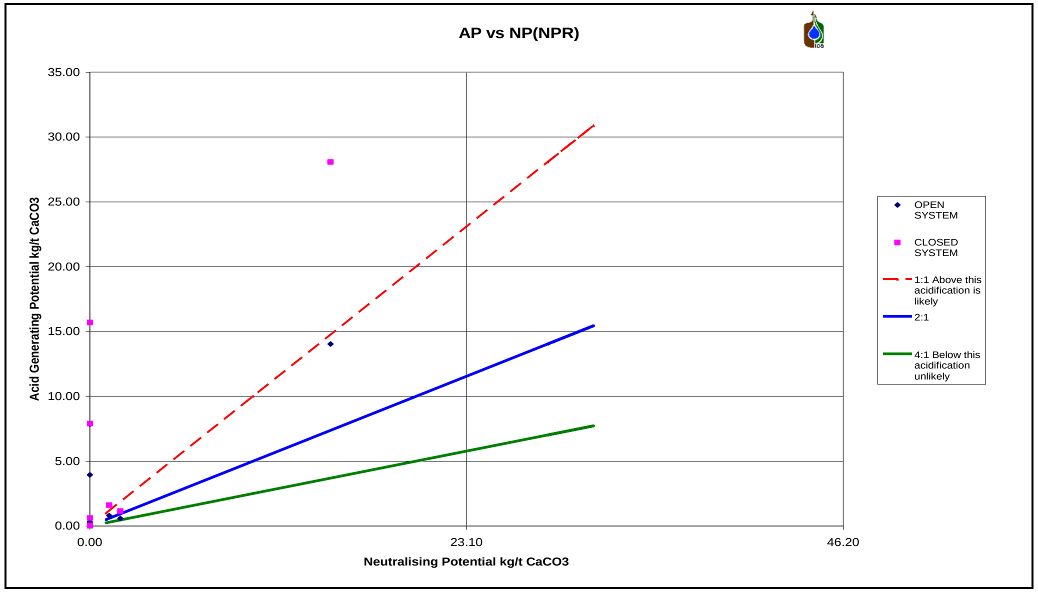


Figure 0-22 Graphical presentation of NPR results for Goedehoop ramp 3

The Goedehoop ramp 3samples batch in the closed system shows that some samples are likely to acidify while the rest are inconclusive (Figure 0-22).

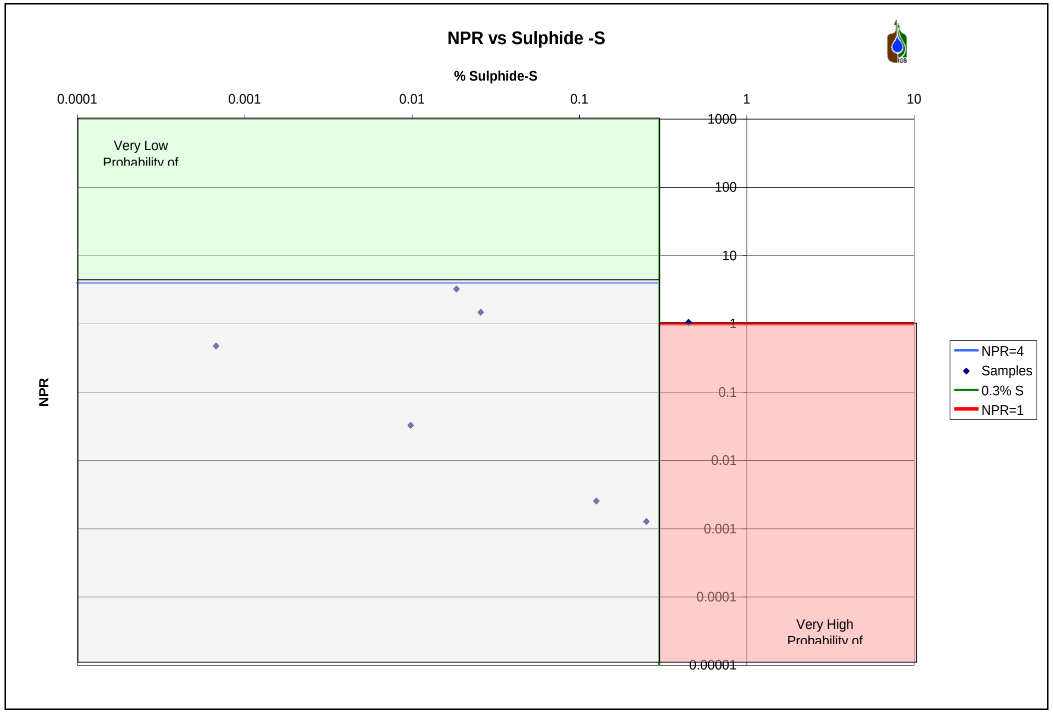


Figure 0-23 % S vs NPR for the Goedehoop ramp 3 samples

The percentage sulphur in the samples plotted against the NPR (Figure 0-23) indicates all samples have an uncertain risk of acid production.

Kinetic results

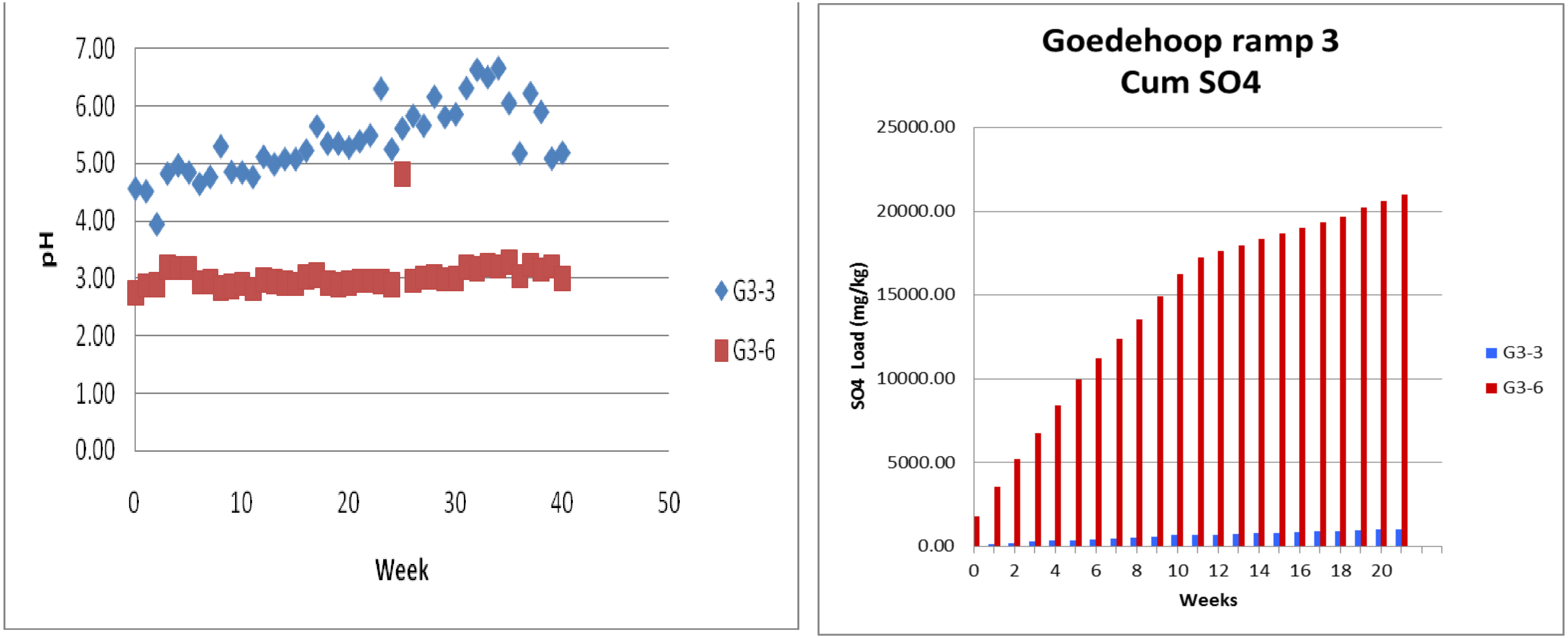


Figure 0-24 Kinetic cell pH value (left) and Cumulative SO4 (right) of Goedehoop ramp 3 samples

From week 1 the pH for both Goedehoop G1-1 and G1-2 were already acidic However G3-3 had was not as constant as G3-6. G3-6 stayed constact till week 40 and had the highest SO4 load (Figure 0-24).

4.5.2.5Goedehoop 5

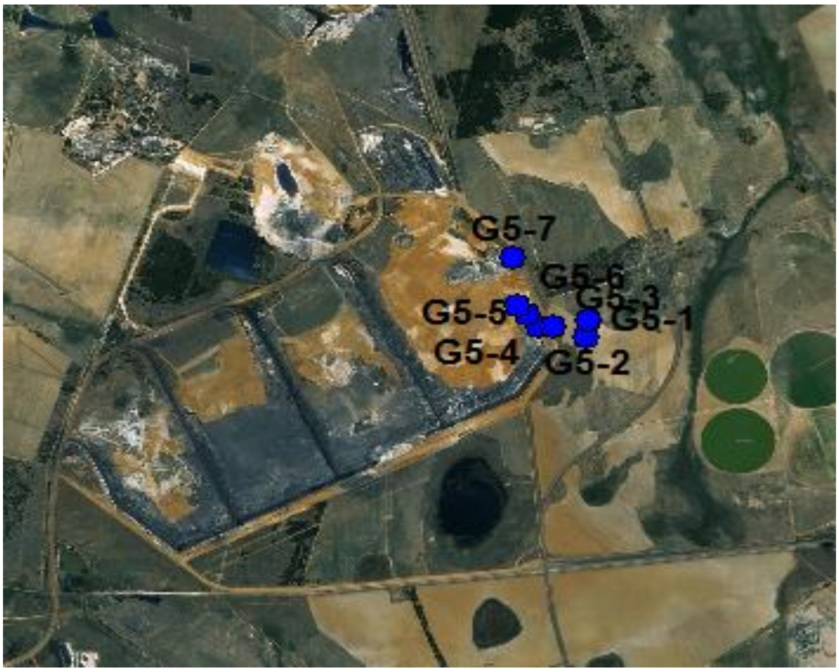


Figure 0-25 Sampling point of Goedehoop ramp 5

7 samples were analysed for Goedehoop ramp 5 (Figure 0-25)

Mineralogical analysis

Table 0-13 Mineralogical analysis of Goedehoop ramp 5 (left) and classification table (right)

Sample	Q	Kaol	Illite	Kvsp	Pyrite	Gyp
G5-1	XX	X	<x			
G5-2	XX	X	<x	x		
G5-3	XX	XX		<x	x	
G5-4	XX	XX	<x	<x		x
G5-5	XX	XX	x	x		
G5-6	XX	XX	xx	X		

Dominant	XX	>40%
Major	X	15-40%
Minor	xx	5-15%
Accessory	x	2-5%
Rare	<x	<2%

G5-7	XX	XX		<x		

Goedehoop ramp 5 mine consists predominantly of quartz and kaolinite with accessory components of gypsum and K-Feldspar. G5-3 has a pyrite as an accessory mineral (Table 0-13).

Static results

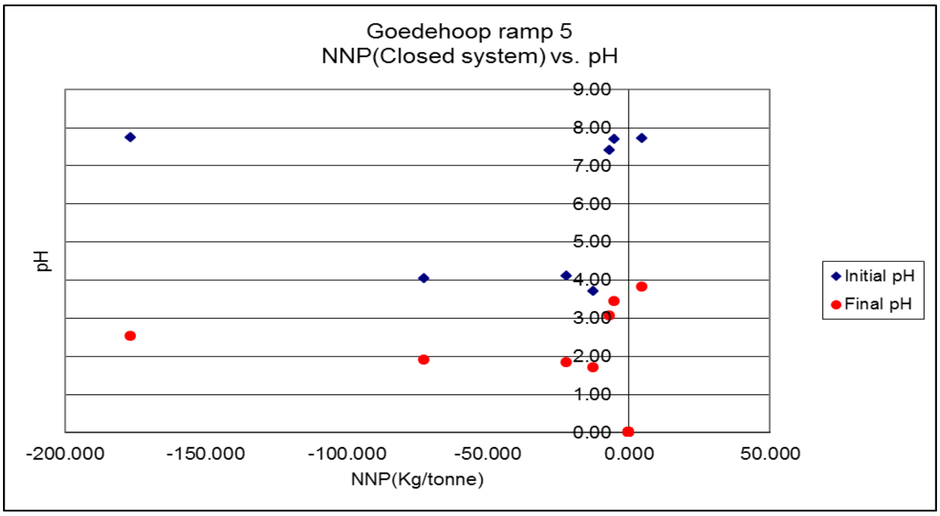


Figure 0-26 NNP Goedehoop ramp 5 results

Goedehoop ramp 5 values (Figure 0-26) of sample shows a negative net neutralising potential therefore suggesting that the sample will likely produce AMD. One sample show a positive Net Neutralisng potential suggests that the samples would unlikely generate acidic conditions.

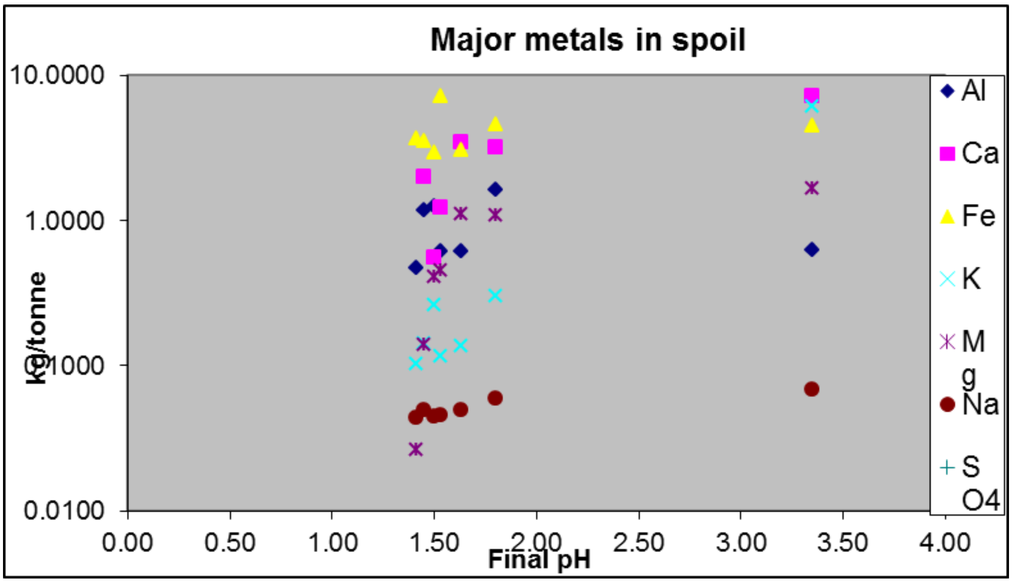


Figure 0-27 Major metal from the Goedehoop ramp 5 samples

Ca , $SO_4$and Fe have the highest values with Na as the lowest(Figure 0-27).

Table 0-14: Interpretation of ABA pH and NAG results of Goedehoop ramp 5

Site Name	Initial pH	Final pH	Interpretation
G5-1	4.05	1.90	Higher Risk Acid Generation
G5-2	3.71	1.71	Higher Risk Acid Generation
G5-3	7.75	2.52	Higher Risk Acid Generation
G5-4	4.12	1.83	Higher Risk Acid Generation
G5-5	7.72	3.82	Medium Risk Acid Generation
G5-6	7.42	3.07	Higher Risk Acid Generation
G5-7	7.69	3.45	Higher Risk Acid Generation

G5-1, G5-2 and G5-4 sample was already partly oxidised prior to the final pH method (Table 0-14) whereas the rest of the sample had alkaline pH values.The samples indicate a medium- high risk of acid generation.

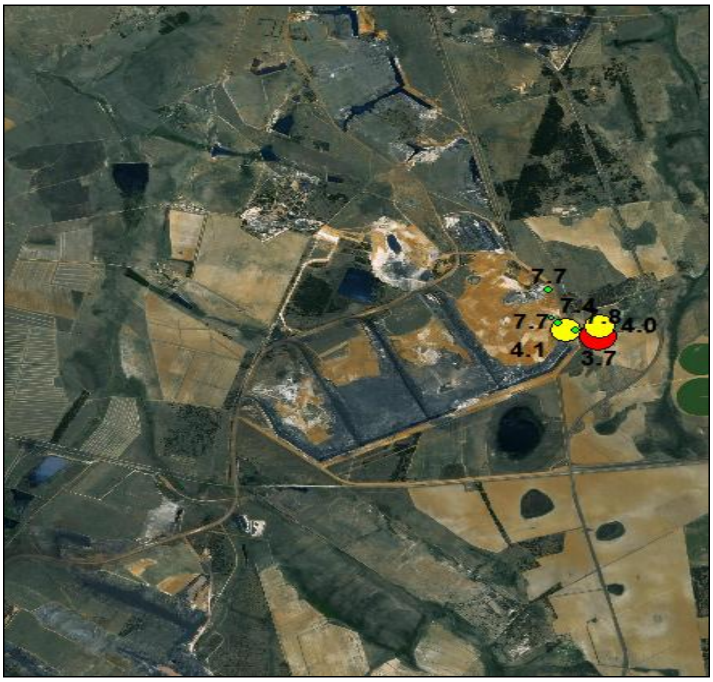


Figure 0-28 Initial pH showing Goedehoop ramp 5 samples

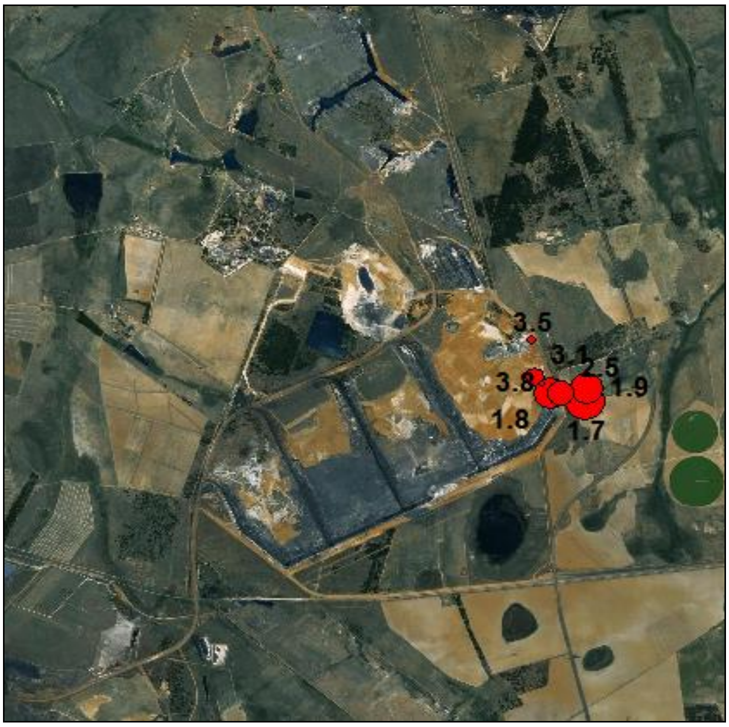


Figure 0-29 Final pH showing Goedehoop ramp 5 samples

An average initial pH value of 6.1 and an average final pH is 2.06 is calculated from the recorded values. Some of these samples are partly oxidized with initial pH (Figure 0-28) values between 3-7 and the pH of all sampled dropped to values ranging 1-3 (Figure 0-29), indicating a high risk of acid generation upon oxidation.

Table 0-15 Interpretation of ABA Net Neutralising Potential results.

Site Name	Net Neutralising Potential (Open)	Net Neutralising Potential (Closed)	Interpretation
G5-1	-25.375	-50.750	Potential Acid Generator
G5-2	-0.833	-1.667	Verify with other tests
G5-3	-79.563	-159.126	Potential Acid Generator
G5-4	-0.026	-0.052	Verify with other tests
G5-5	8.429	6.557	Verify with other tests
G5-6	-2.166	-4.331	Verify with other tests
G5-7	6.236	-0.279	Verify with other tests

The open and closed NNP is interpreted inTable 0-15where it indicates negative values as potential Acid generator and that most of the samples need to be verified with Kinetic tests.

Table 0-16 Interpretation and NP/AP ratios for Goedehoop 5.

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Interpretation Open System	Interpretation Closed System
G5-1	0.00	Likely Acid Generator	Likely Acid Generator
G5-2	0.01	Likely Acid Generator	Likely Acid Generator
G5-3	0.00	Likely Acid Generator	Likely Acid Generator
G5-4	0.38	Likely Acid Generator	Likely Acid Generator
G5-5	5.50	No Acid Potential	Acid under certain conditions
G5-6	0.00	Likely Acid Generator	Likely Acid Generator
G5-7	1.96	Acid under certain conditions	Likely Acid Generator

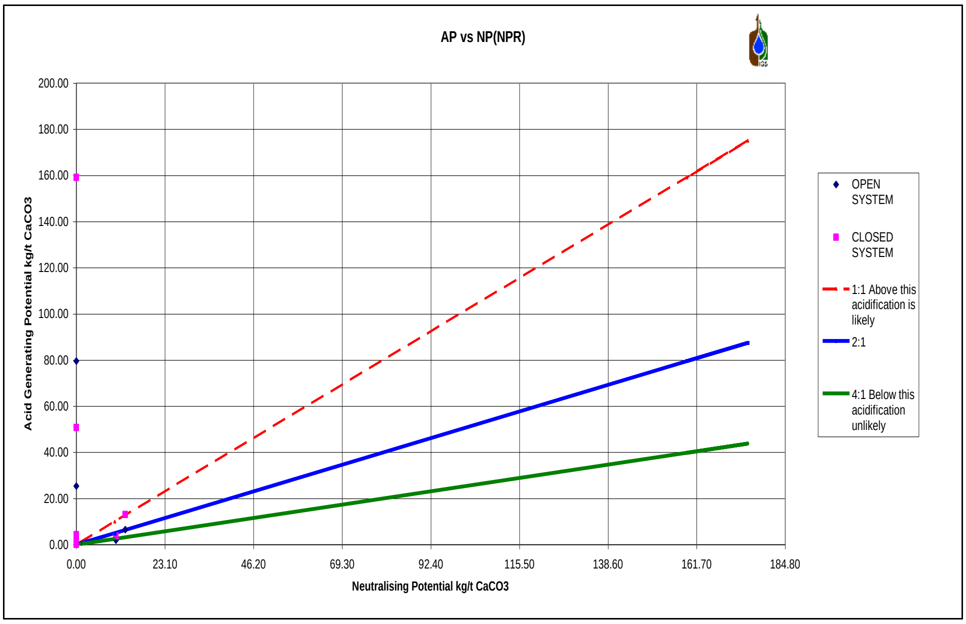


Figure 0-30 Graphical presentation of NPR results for Goedehoop ramp 5

Most of the samples in both open and closed system do not show a clear indication of where all the samples have acid generating potential or not (Figure 0-30).

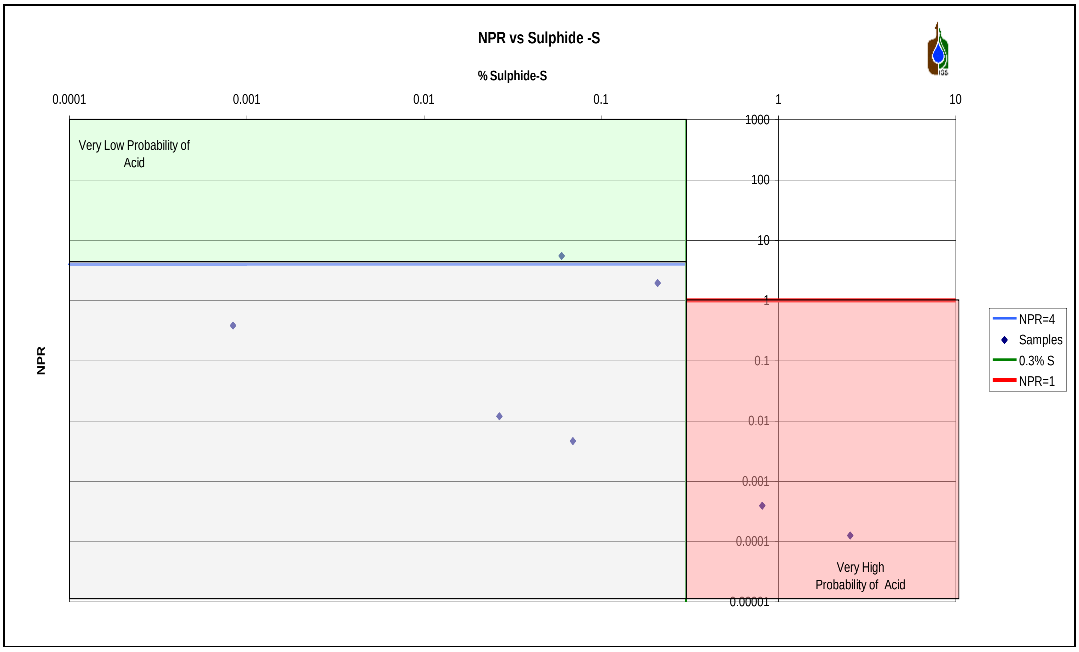
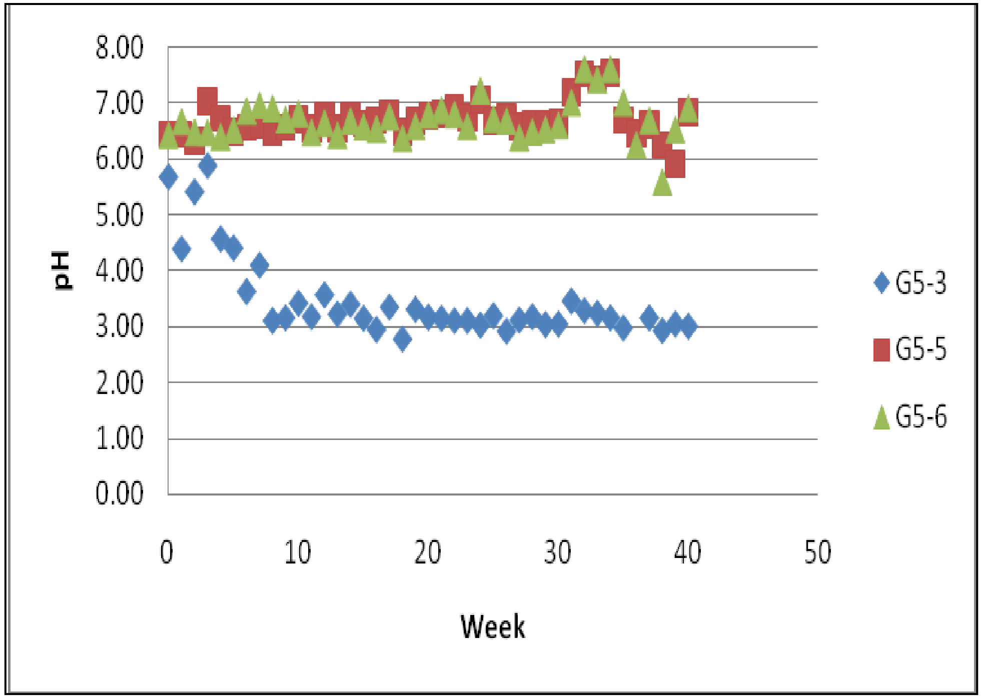


Figure 0-31 % S vs NPR for the Goedehoop ramp 5 samples

The percentage sulphur in the samples plotted against the NPR (Table 0-16) indicates four samples that have an uncertain risk of acid production and two samples with a high probability of acid generation plotting in the red, indicating a high risk of AMD. Only one sample had a very low probability to acidify.

Kinetic results



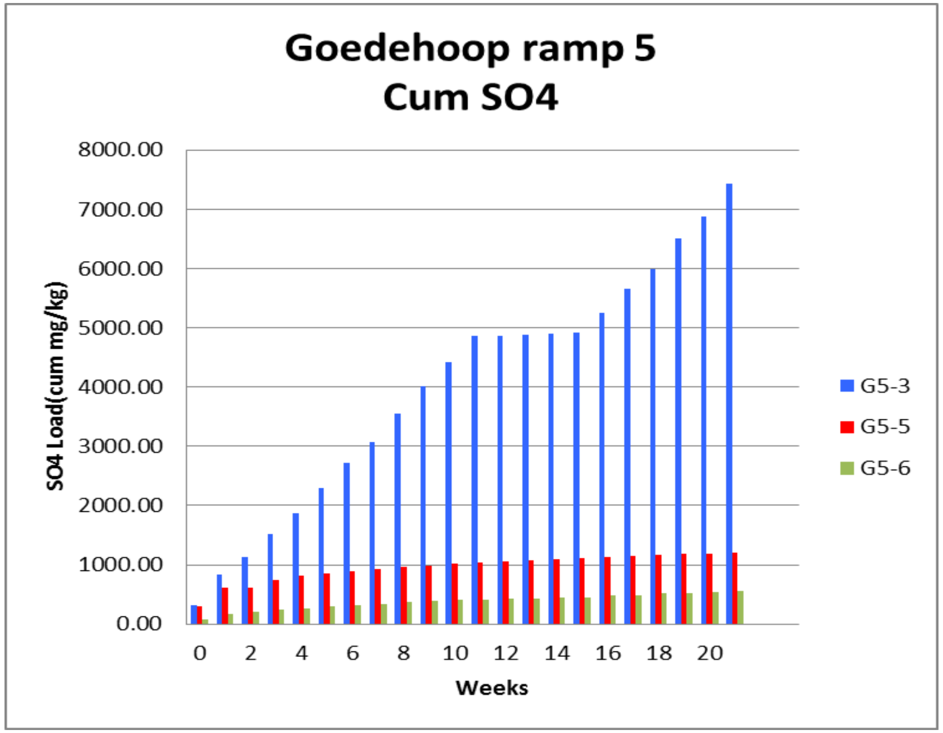


Figure 0-32 Kinetic cell pH value(left) with the Cumulative SO4 (right) of Goedehoop ramp 5 samples

G5-3 starts of as partialy oxidised, the pH decreases with time and stays constant till week 40. G5-5 and G5-6had high values of pH which stayed constant till the erratic period from week 30 to 40. The cummulative SO4 of G5-3 is therefore the highest(Figure 0-32).

4.5.2.6Goedehoop 6

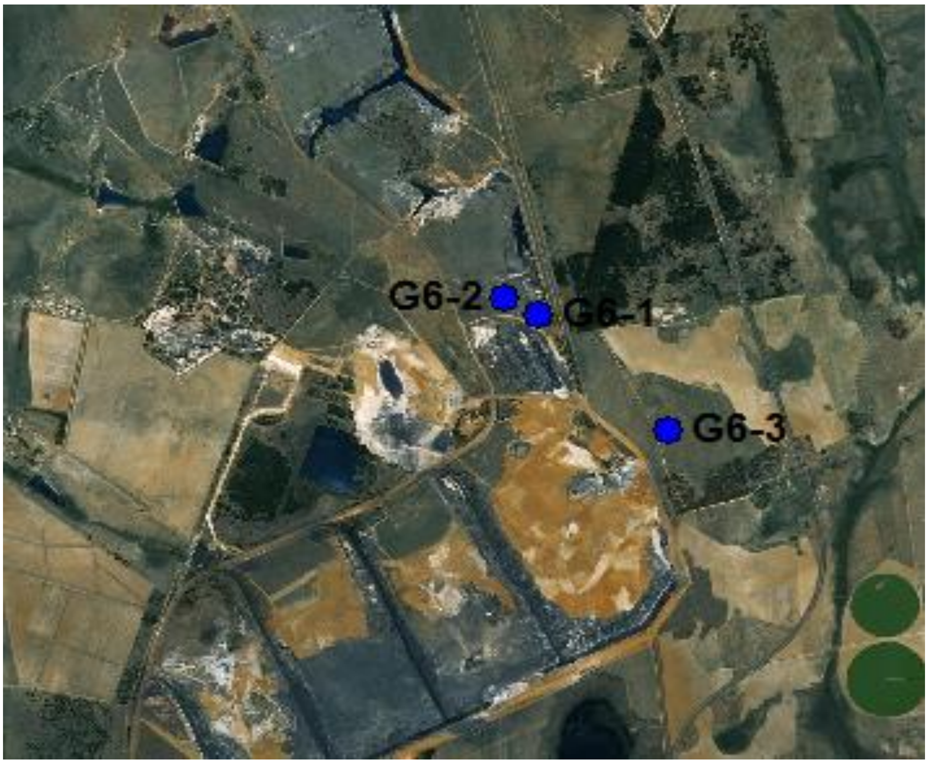


Figure 0-33 Sampling point of Goedehoop ramp 6

3 samples were analysed for Goedehoop ramp 6 (Figure 0-33)

Mineralogical analysis

Table 0-17 Mineralogical analysis of Goedehoop ramp 6 (left) and classification table (right)

Sample	Q	Kaol	Illite	Kfsp
G6-1	XX	XX	<x	<x
G6-2	XX	XX	x	xx
G6-3	XX	XX	x	xx

Dominant	XX	>40%
Major	X	15-40%
Minor	xx	5-15%
Accessory	x	2-5%
Rare	<x	<2%

Goedehoop ramp 6 mine consists predominantly of quartz and kaolinite with minor components of K-Feldspar (Table 0-17).

Static results

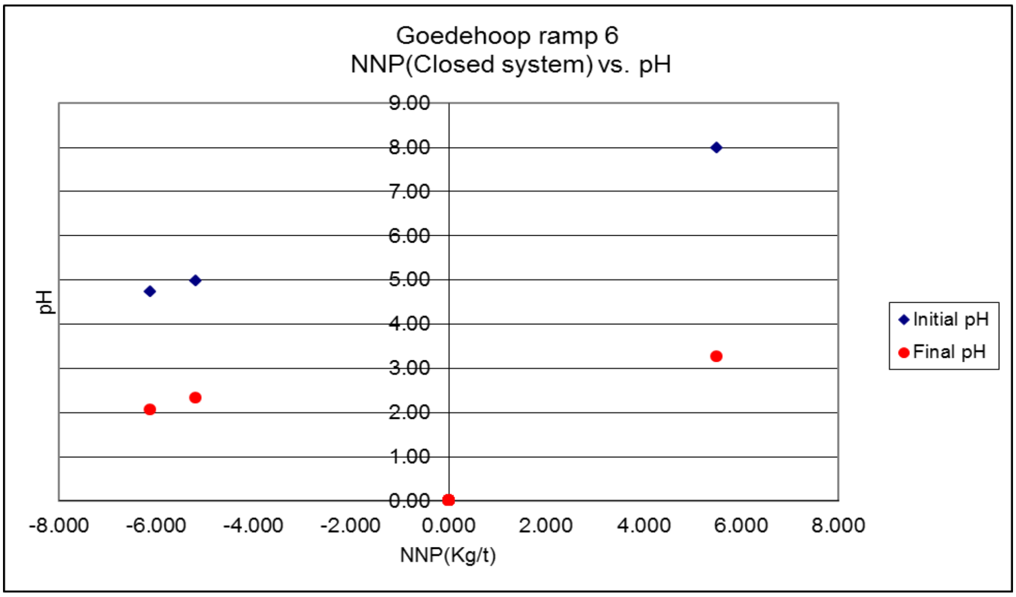


Figure 0-34NNP Goedehoop ramp 6 results

Goedehoop ramp 6 values (Figure 0-34) of two sample show a negative net neutralising potential therefore suggesting that the sample will likely produce AMD. One sample show a positive Net Neutralising potential suggests that the samples would unlikely generate acidic conditions.

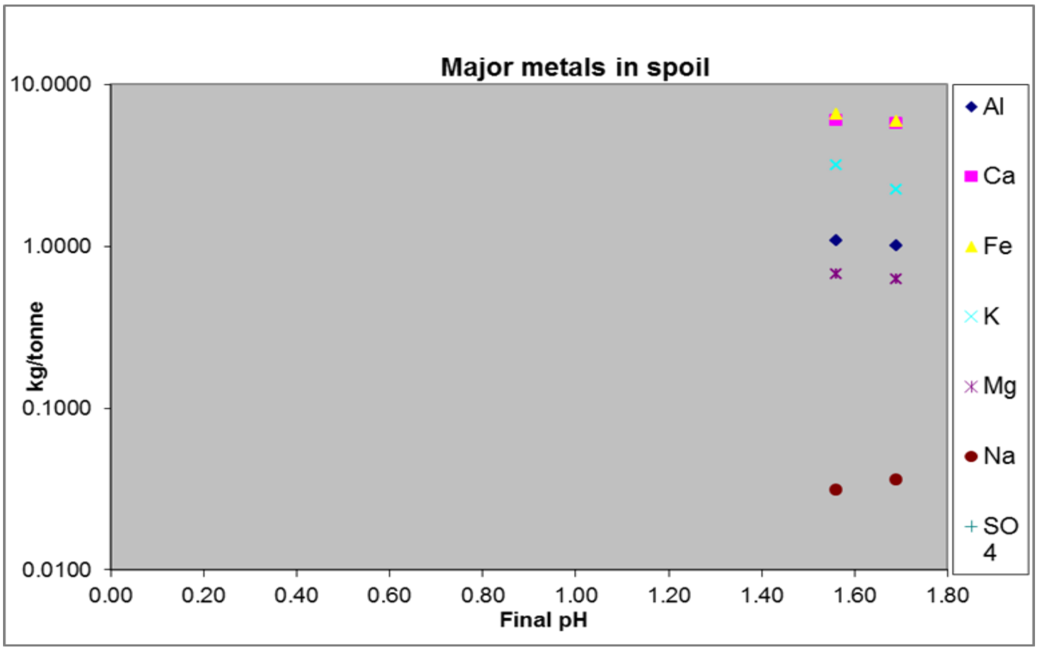


Figure 0-35Major metal from the Goedehoop ramp 6 samples

Ca , $SO_4$and Fe have the highest values with Na as the lowest (Figure 0-35).

Table 0-18: Interpretation of ABA pH and NAG results for Goedehoop ramp 6

Site Name	Initial pH	Final pH	Interpretation
G6-1	4.73	2.06	Higher Risk Acid Generation
G6-2	4.99	2.33	Higher Risk Acid Generation
G6-3	8.00	3.27	Higher Risk Acid Generation

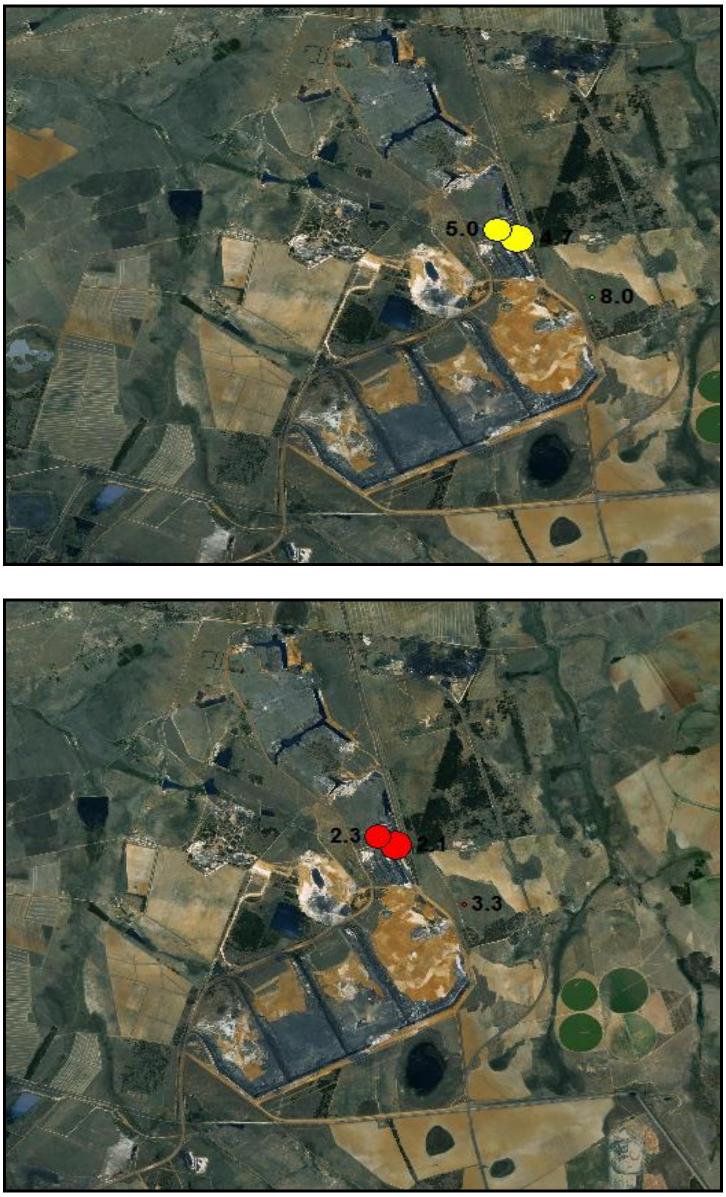


Figure 0-36 Initial pH (top) and final pH (bottom) showing Goedehoop ramp 6 samples

An average initial pH value of 5.9 (Some of these samples are partly oxidized) and an average final pH is 2.6 (Figure 0-36) is calculated from the recorded values. The pH of all sampled dropped to values ranging 2-3, indicating a high risk of acid generation upon oxidation.

Table 0-19 Interpretation of ABA Net Neutralising Potential results.

Site Name	Net Neutralising Potential (Open)	Net Neutralising Potential (Closed)	Interpretation
G6-1	-0.272	-0.544	Verify with other tests
G6-2	-0.692	-1.384	Verify with other tests
G6-3	7.311	5.713	Verify with other tests

The open and closed NNP is interpreted in Table 0-19 where it indicates negative values as potential Acid generator and that all samples need to be verified with Kinetic tests.

Table 0-20 Interpretation and NP/AP ratios for Goedehoop 6.

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Interpretation Open System	Interpretation Closed System
G6-1	0.04	Likely Acid Generator	Likely Acid Generator
G6-2	0.01	Likely Acid Generator	Likely Acid Generator
G6-3	5.58	No Acid Potential	Acid under certain conditions

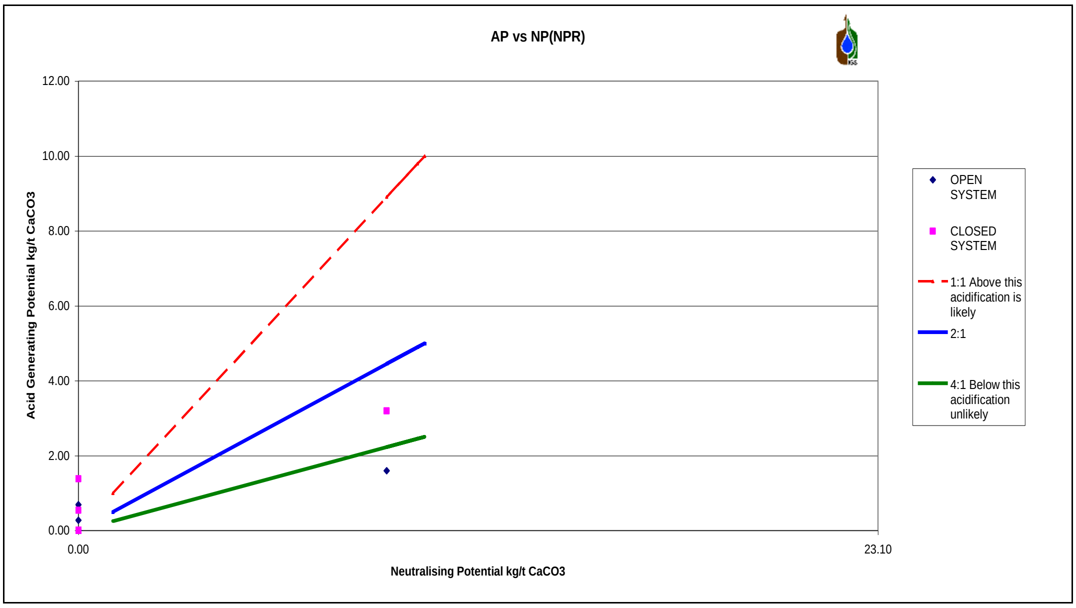


Figure 0-37 Graphical presentation of NPR results for Goedehoop ramp 6

One sample in the open system is unlikely to acidify but uncertain in the open system. The rest of the samples in both open and closed system are inconclusive (Figure 0-37).

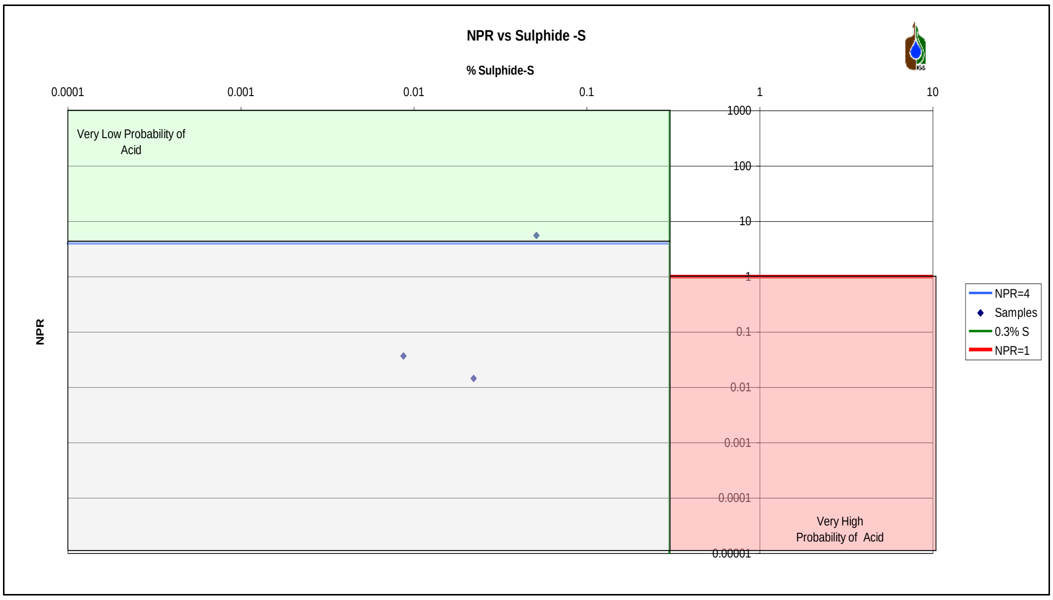


Figure 0-38 % S vs NPR for the Goedehoop ramp 6 samples

The percentage sulphur in the samples plotted against the NPR (Figure 0-38) indicates two samples illustrates an uncertain risk of acid production and the othersample as having a low probability of acid generation.

Kinetic results

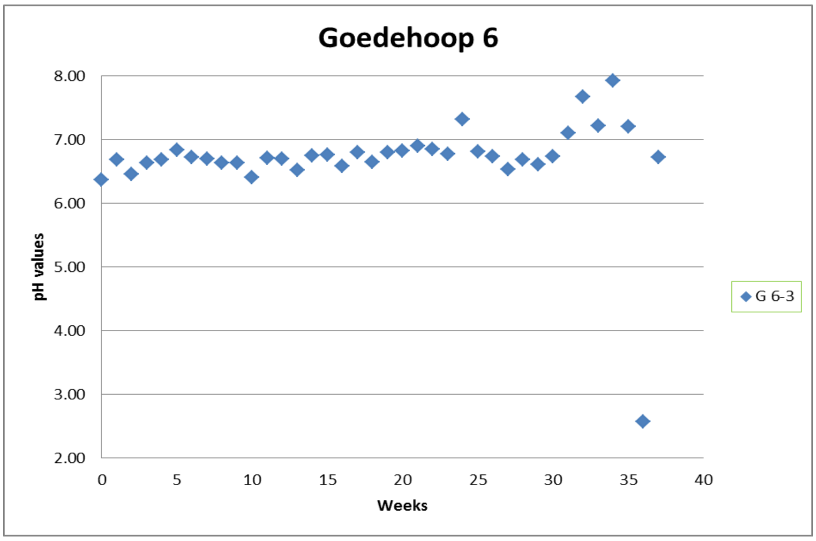


Figure 0-39 Kinetic cell pH values of Goedehoop ramp 6 samples

G6-3 starts at an approximate value of 6.5, the pH stays constant with time till week 27 where erratic measurements are recorded (Figure 0-39).

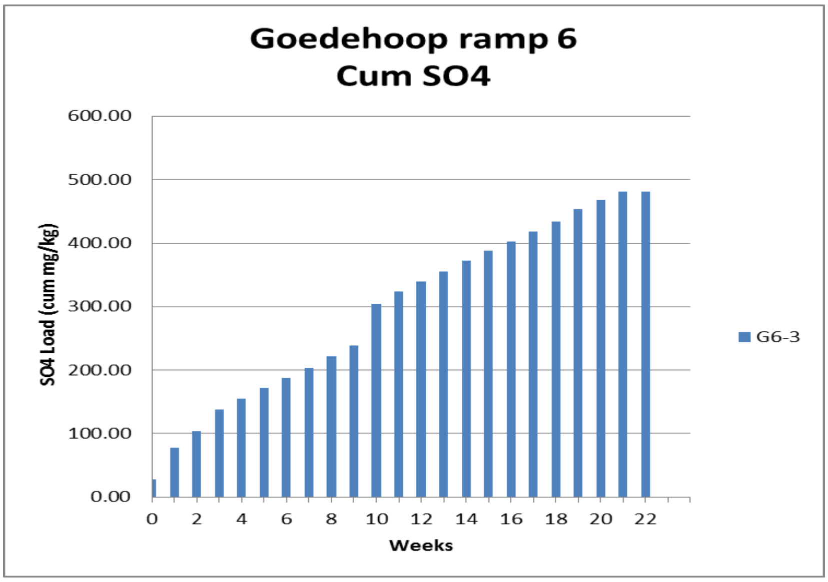


Figure 0-40C umulative SO4 of Goedehoop ramp 6 samples

The cumulative SO4 of G6-3 increases till about 500 at week 21 (Figure 0-40).

4.5.2.7Goedehoop 7

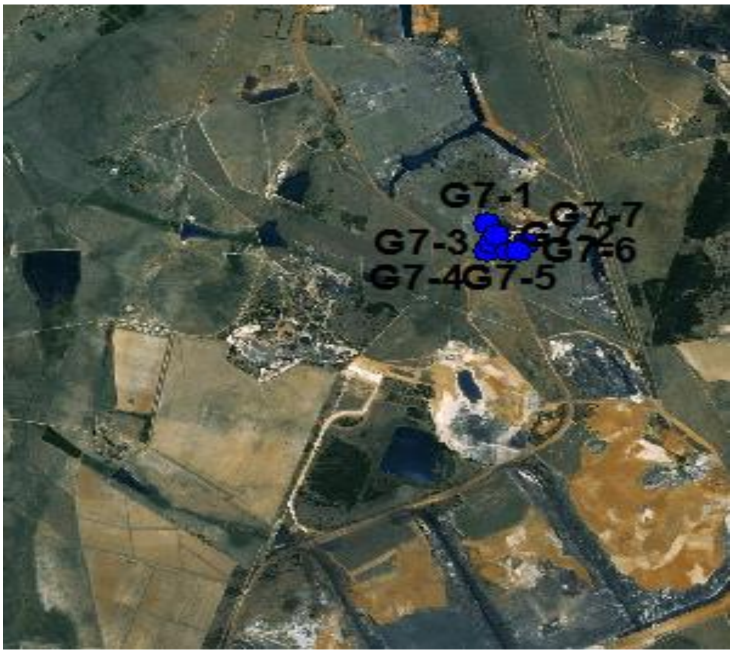


Figure 0-41 Location site for Goedehoop ramp 7 samples

7 samples were analysed for Goedehoop ramp 7 (Figure 0-41).

Mineralogical analysis

Table 0-21 Mineralogical analysis of Goedehoop ramp 7 (left) and classification table (right)

Sample	Q	Kaol	Illite	Kvsp	Pyrite
G7-1	XX	XX	x	x	
G7-2	XX	XX	x	xx	
G7-3	XX	XX	x	x	
G7-4	XX	XX	x		
G7-5	XX	X			<x
G7-6	XX	XX	x	x	
G7-7	XX	XX	x	<x	<x

Goedehoop ramp 7 mine consists predominantly of quartz and kaolinite with accessory components of illite and K-Feldspar. G7-5 has pyrite as an accessory mineral (Table 0-21).

Static results

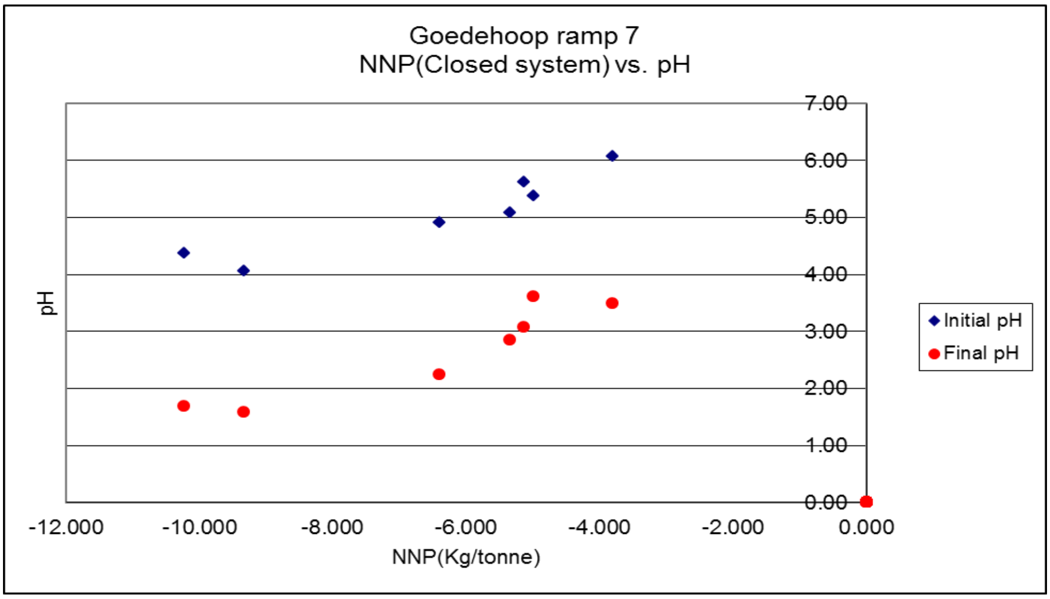


Figure 0-42 NNP Goedehoop ramp 7 results

All Goedehoop ramp 7 values (Figure 0-42) show a negative net neutralising potential therefore suggesting that the sample will likely produce AMD.

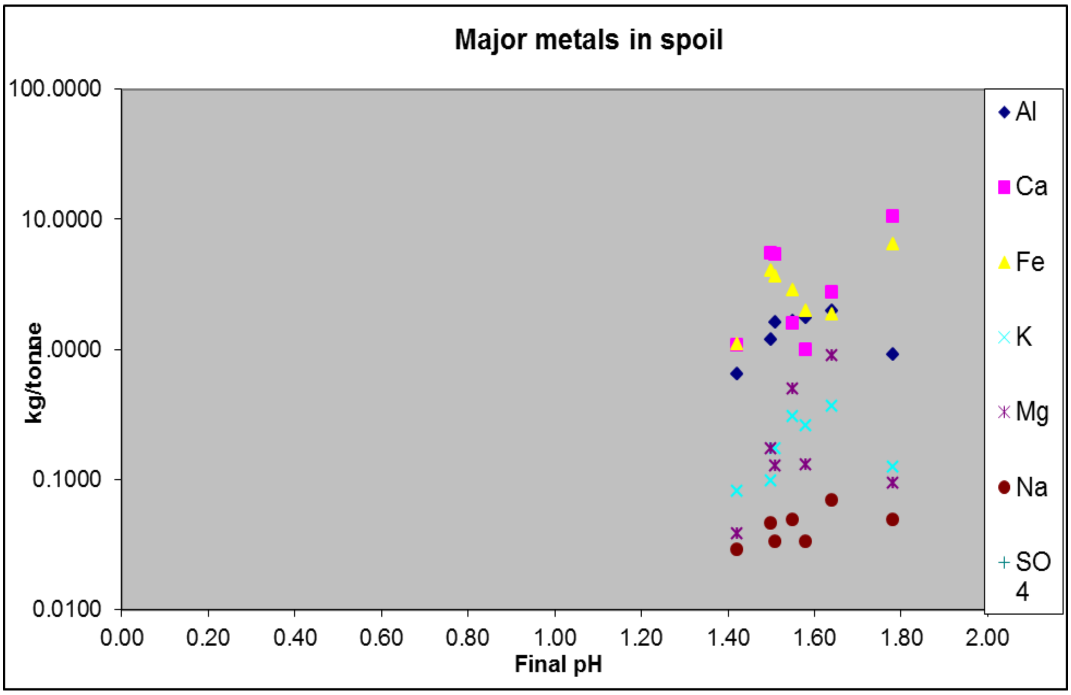


Figure 0-43 Major metal from the Goedehoop ramp 7 samples

Ca , $SO_4$and Fe have the highest values with Na as the lowest (Figure 0-43).

Table 0-22 Interpretation of ABA pH and NAG results for Goedehoop ramp 7

Site Name	Initial pH	Final pH	Interpretation
G7-1	5.08	2.86	Higher Risk Acid Generation
G7-2	6.08	3.50	Lower Acid Risk
G7-3	4.92	2.25	Higher Risk Acid Generation
G7-4	4.06	1.59	Higher Risk Acid Generation
G7-5	5.38	3.62	Medium Risk Acid Generation
G7-6	5.62	3.08	Higher Risk Acid Generation
G7-7	4.37	1.69	Higher Risk Acid Generation

The samples were partly oxidised prior to the final pH method (Table 0-22). Most of the samples indicated medium-high risk of acid generation.

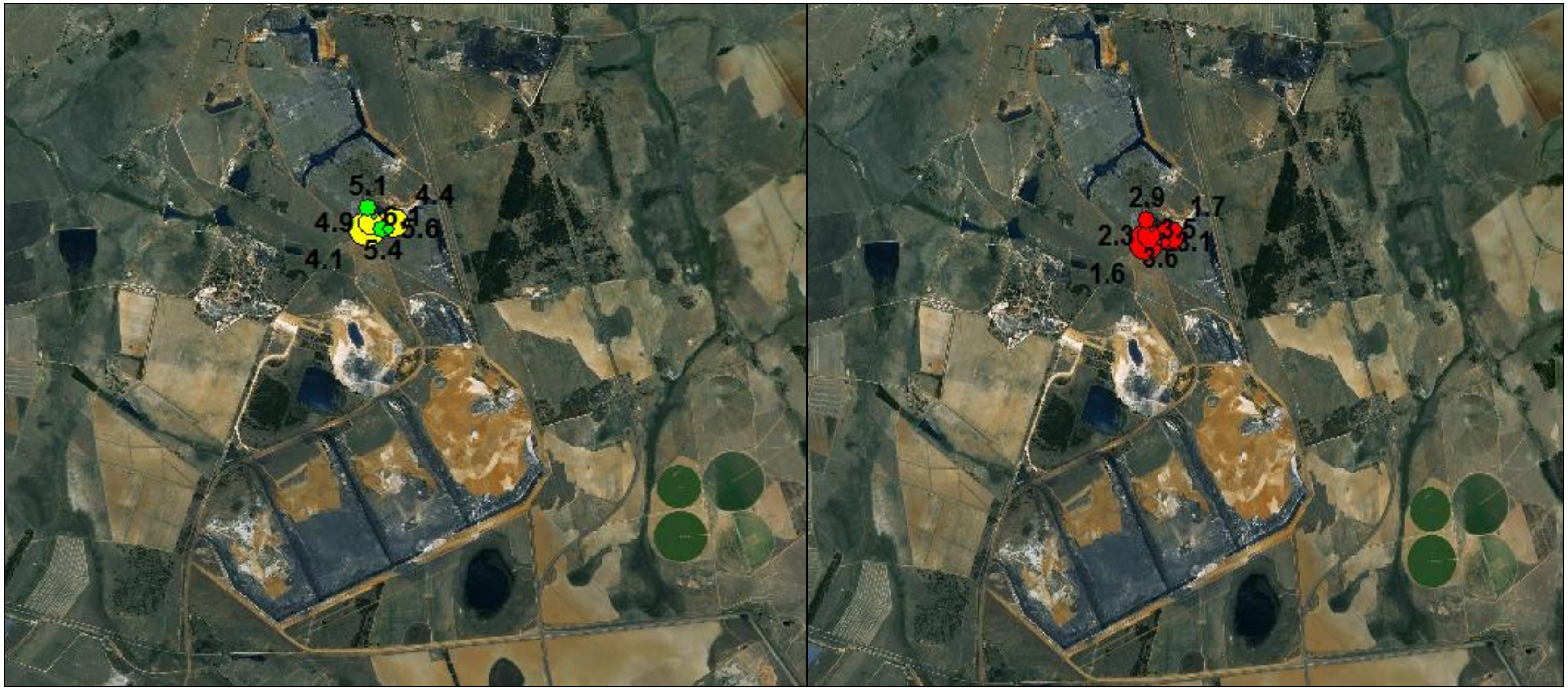


Figure 0-44 Initial pH (left) and final pH (right) showing Goedehoop ramp 7 samples

An average initial pH value of 5.1 and an average final pH is 2.07 (Figure 0-44) is calculated from the recorded values. Some of these samples are partly oxidized with initial pH values between 4 and 6. The pH of all sampled dropped to values ranging 1-3, indicating a high risk of acid generation upon oxidation.

Table 0-23 Interpretation of ABA Net Neutralising Potential results.

Site Name	**Net Neutralising Potential (Open)**	**Net Neutralising Potential (Closed)**	**Interpretation**
G7-1	0.00	0.00	Verify with other tests
G7-2	-0.14	-0.27	Verify with other tests
G7-3	-0.28	-0.57	Verify with other tests
G7-4	-0.10	-0.21	Verify with other tests
G7-5	-0.10	-0.20	Verify with other tests
G7-6	0.00	0.00	Verify with other tests
G7-7	-0.33	-0.66	Verify with other tests

The open and closed NNP is interpreted in Table 0-23where it indicates negative or zero values as potential acid generator and that all samples need to be verified with Kinetic tests.

Table 0-24 Interpretation and NP/AP ratios for Goedehoop 7.

Site Name	**Neutralising Potential Ratio(NP/AP) for Open System**	**Interpretation Open System**	**Interpretation Closed System**
G7-1	0.80	Likely Acid Generator	Likely Acid Generator
G7-2	0.07	Likely Acid Generator	Likely Acid Generator
G7-3	0.04	Likely Acid Generator	Likely Acid Generator
G7-4	0.10	Likely Acid Generator	Likely Acid Generator
G7-5	0.10	Likely Acid Generator	Likely Acid Generator
G7-6	0.80	Likely Acid Generator	Likely Acid Generator
G7-7	0.03	Likely Acid Generator	Likely Acid Generator

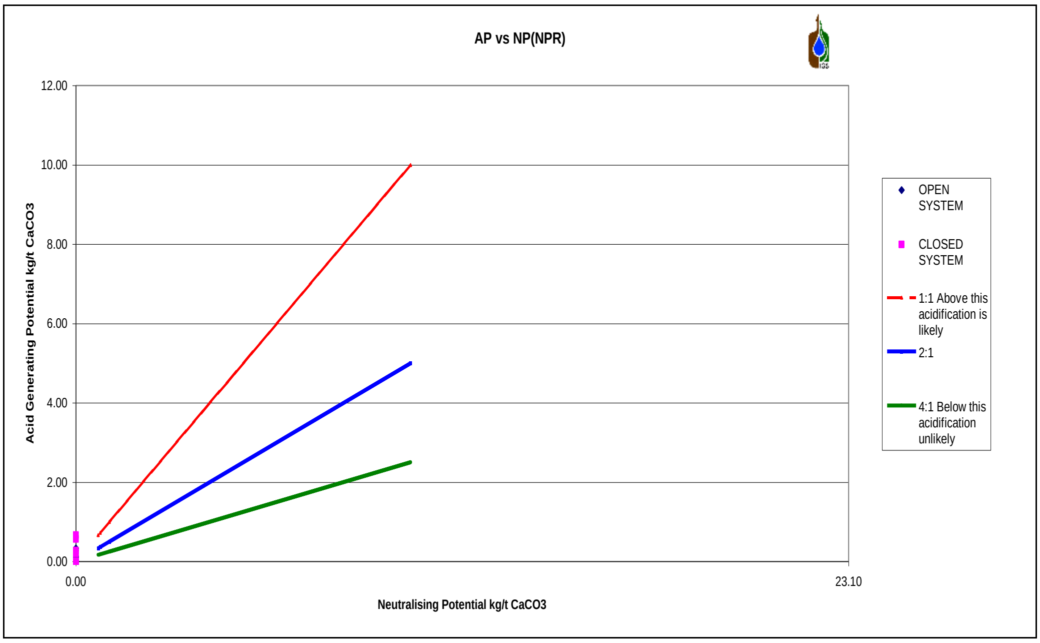


Figure 0-45 Graphical illustration of NPR results

All the samples plot along the y-axis resulting in the outcome being inconclusive (Figure 0-45).

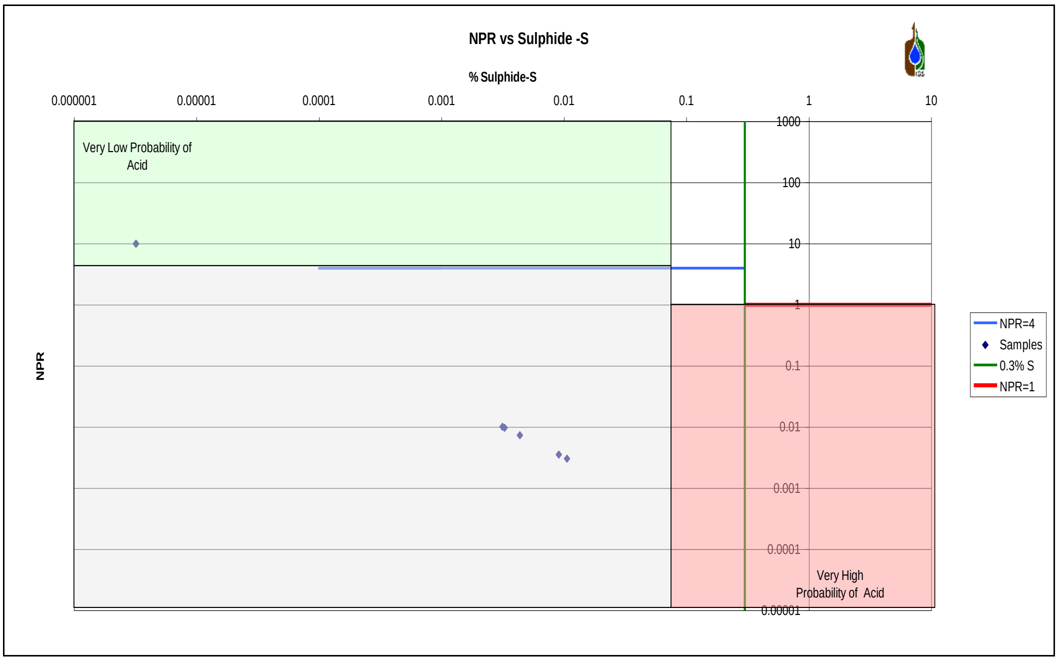


Figure 0-46 % S vs NPR for the Goedehoop ramp 7 samples

The percentage sulphur in the samples plotted against the NPR (Figure 0-46) indicates six samples that have an uncertain risk of acid production and another one has a low probability of acid generation plotting in the green.

Kinetic results

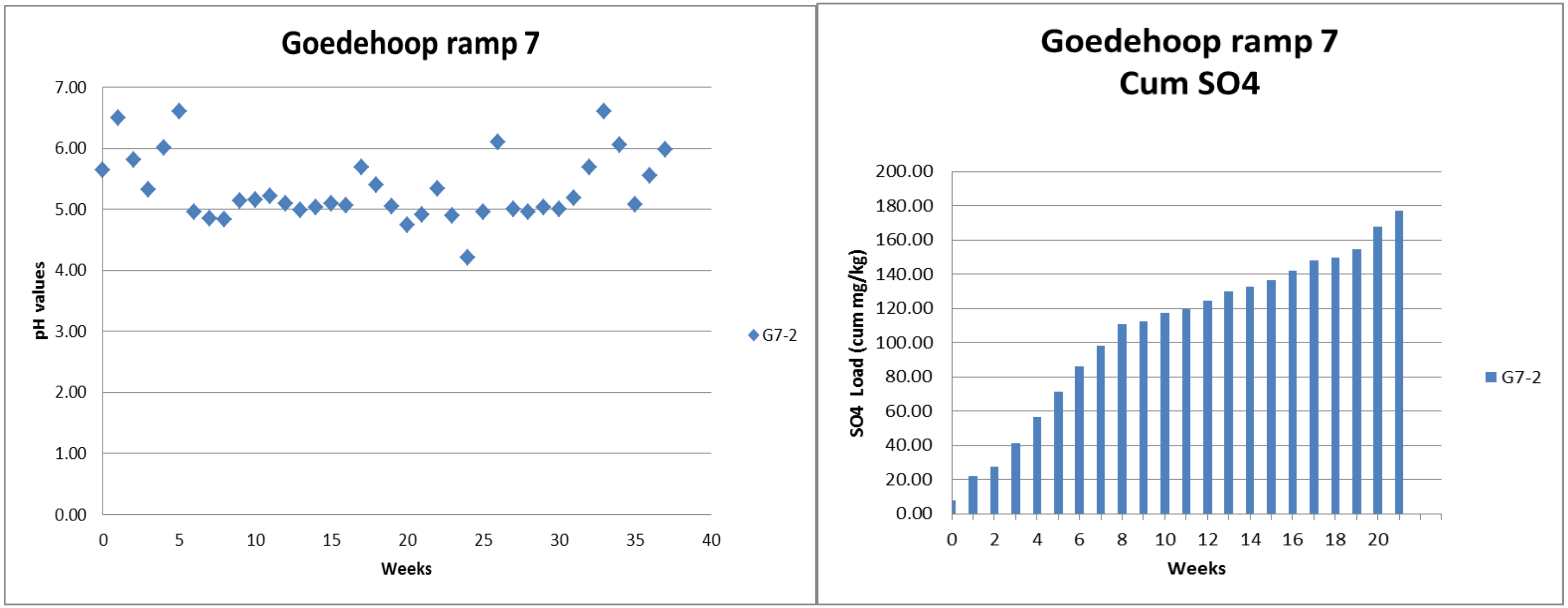


Figure 0-47 Kinetic cell pH value (left) with the Cumulative SO4 (right) of Goedehoop ramp 7 samples

G7-2show erratic measurements of the pH that is recorded and has a sulphate load of about 180 mg/kg/week (Figure 0-47).

4.5.2.8Goedehoop 10

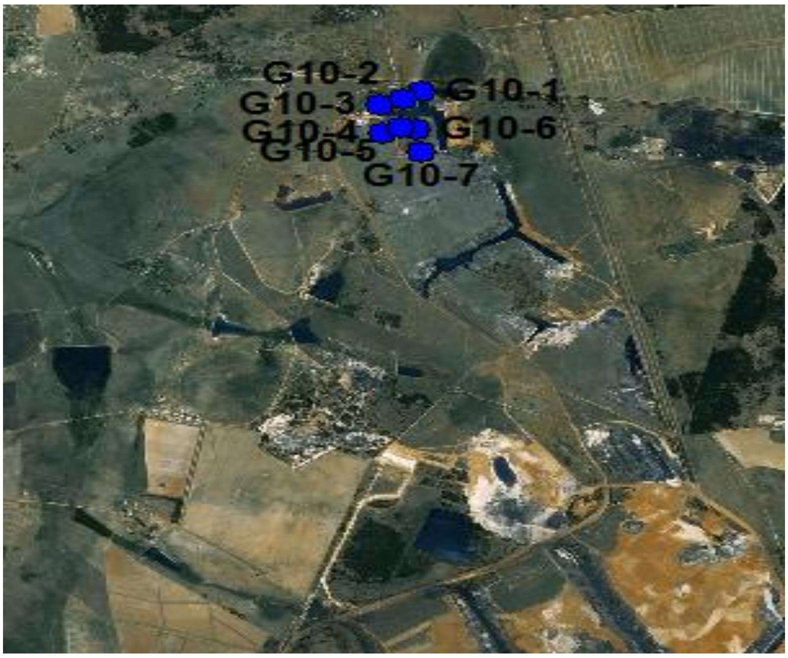


Figure 0-48 Location site for Goedehoop ramp 10

7 samples were analysed for Goedehoop ramp 10 (Figure 0-48)

Mineralogical analysis

Table 0-25 Mineralogical analysis of Goedehoop ramp 10 (left) and classification table (right)

Sample	Q	Kaol	Illite	Kvsp	Pyrite
G10-1	XX	XX	x	xx	<x
G10-2	XX	XX	x	<x	<x
G10-3	XX	XX	x	<x	<x
G10-4	XX	XX	xx	x	<x
G10-5	XX	XX	x	x	
G10-6	XX	XX	x	x	
G10-7	XX	XX	x	x	<x

Goedehoop ramp 10 mine consists predominantly of quartz and kaolinite with accessory components of illite, pyrite and K-Feldspar (Table 0-25).

Static results

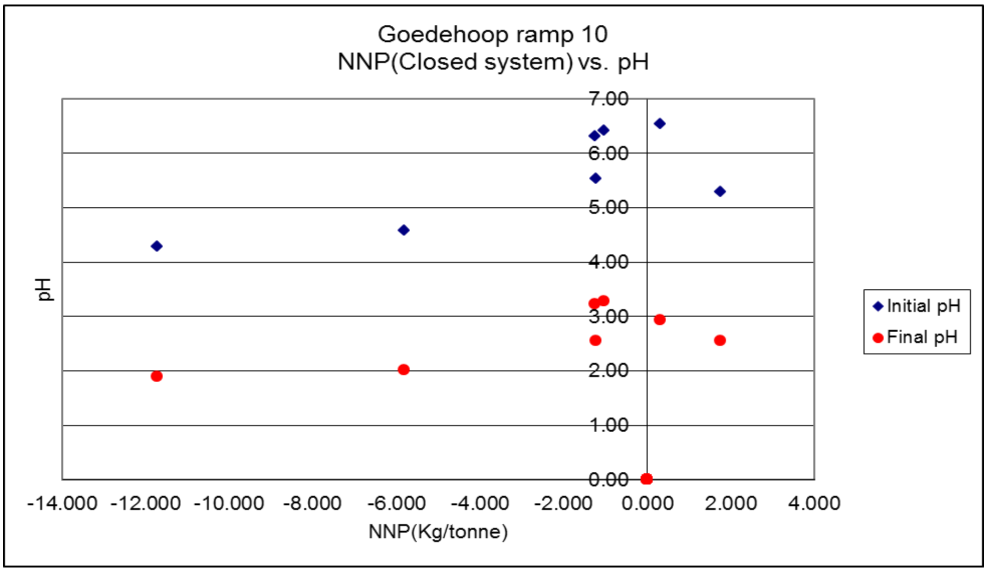


Figure 0-49NNP Goedehoop ramp 10 results

Goedehoop ramp 10 values of seven samples show a negative net neutralising potential therefore suggesting that the sample will likely produce AMD. Two samples show a positive Net Neutralising potential suggests that the samples would unlikely generate acidic conditions.

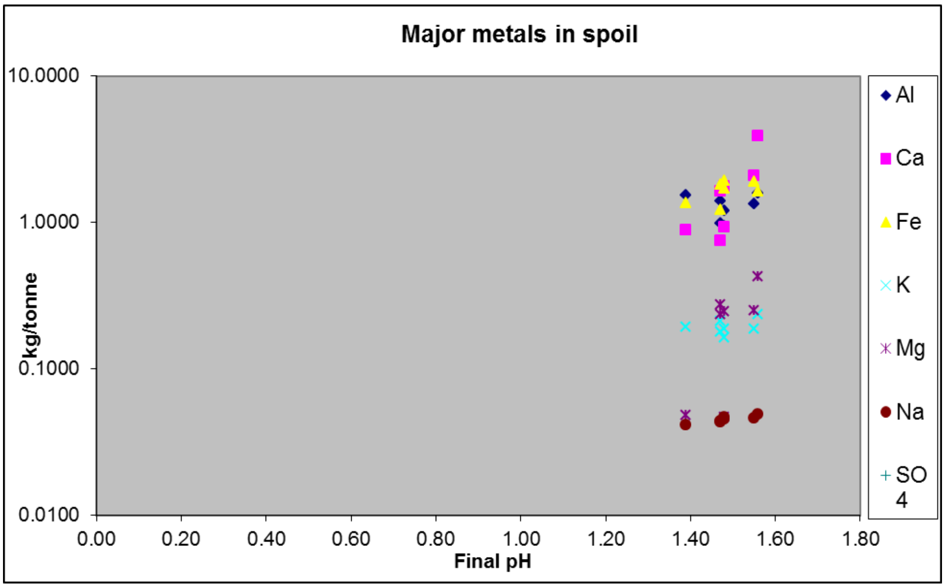


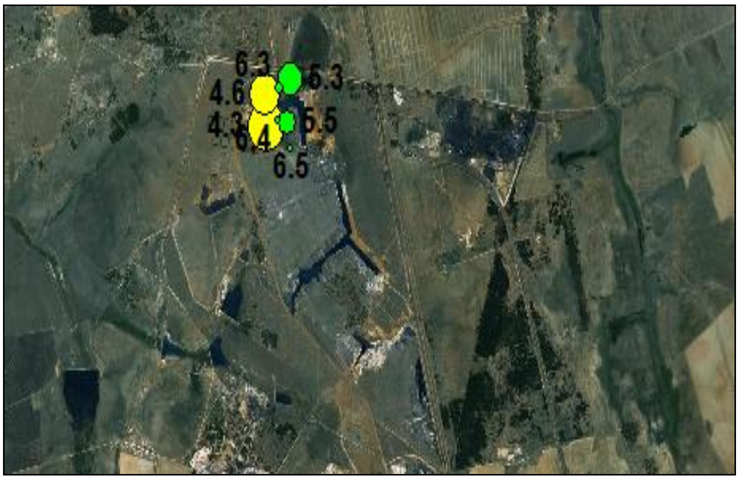
Figure 0-50 Major metal from the Goedehoop ramp 10 samples

Ca , $SO_4$and Fe have the highest values with Na as the lowest(Figure 0-50).

Table 0-26 Interpretation of ABA pH and NAG results for Goedehooop ramp 10

Site Name	Initial pH	Final pH	Interpretation
G10-1	5.29	2.56	Higher Risk Acid Generation
G10-2	6.31	3.23	Higher Risk Acid Generation
G10-3	4.58	2.02	Higher Risk Acid Generation
G10-4	4.29	1.89	Higher Risk Acid Generation
G10-5	6.42	3.29	Higher Risk Acid Generation
G10-6	5.54	2.56	Higher Risk Acid Generation
G10-7	6.55	2.94	Higher Risk Acid Generation

Some of the samples were already partly oxidised prior to the final pH method (Table 0-26). All the samples indicate that they have a higher risk of acid generation.



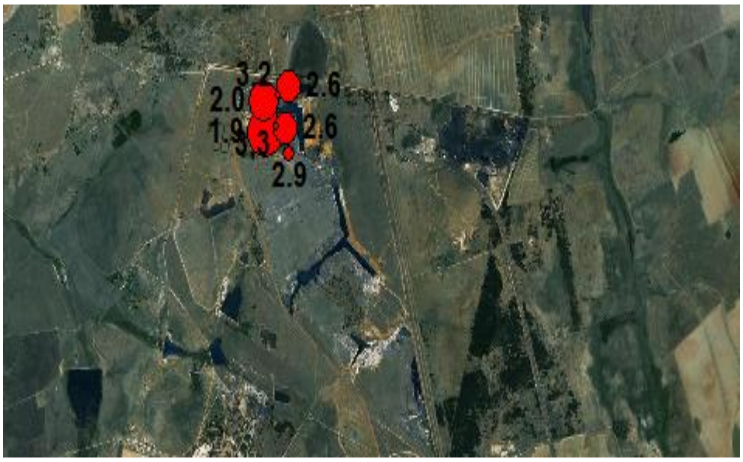


Figure 0-51Initial pH (top) and final pH (bottom) showing Goedehoop ramp 10 samples

An average initial pH value of 5.6 (Some of these samples are partly oxidized) and an average final pH is 2.6 (Figure 0-51) is calculated from the recorded values. The pH of all sampled dropped to values ranging 1-3, indicating a high risk of acid generation upon oxidation.

Table 0-27 Interpretation of ABA Net Neutralising Potential results.

Site Name	Net Neutralising Potential (Open)	Net Neutralising Potential (Closed)	Interpretation
G10-1	3.27	2.74	Verify with other tests
G10-2	4.80	4.70	Verify with other tests
G10-3	-0.37	-0.73	Verify with other tests
G10-4	-1.81	-3.62	Verify with other tests
G10-5	0.00	-0.27	Verify with other tests
G10-6	0.80	0.37	Verify with other tests
G10-7	1.33	0.95	Verify with other tests

The open and closed NNP is interpreted inTable 0-27where it indicates negative values as potential Acid generator and all samples need to be verified with Kinetic tests.

Table 0-28Interpretation and NP/AP ratios for Goedehoop 10.

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Interpretation Open System	Interpretation Closed System
G10-1	7.12	No Acid Potential	Acid under certain conditions
G10-2	48.96	No Acid Potential	No Acid Potential
G10-3	0.03	Likely Acid Generator	Likely Acid Generator
G10-4	0.01	Likely Acid Generator	Likely Acid Generator
G10-5	1.00	Acid under certain conditions	Likely Acid Generator
G10-6	2.87	Acid under certain conditions	Acid under certain conditions
G10-7	4.55	No Acid Potential	Acid under certain conditions

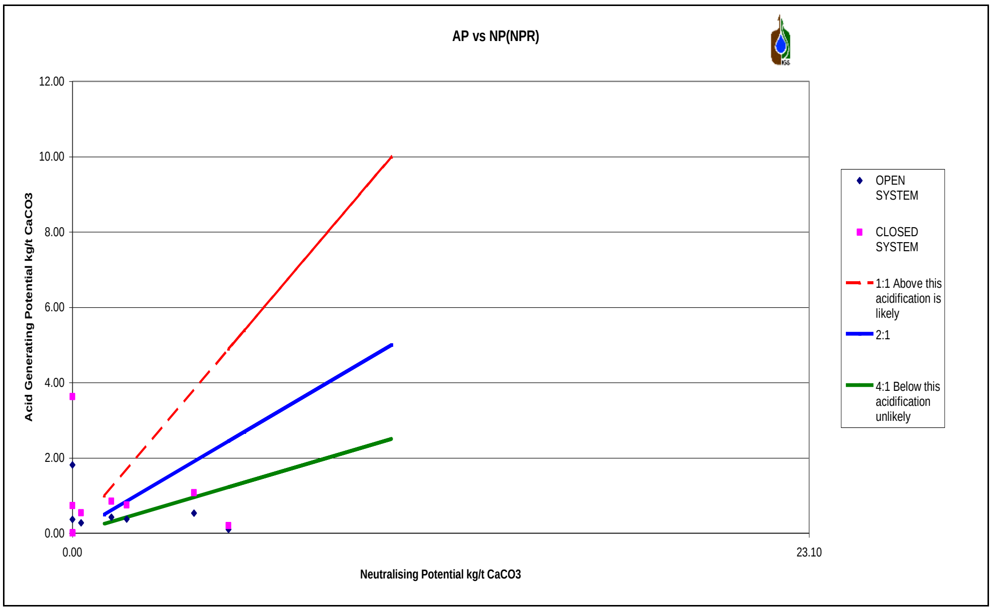
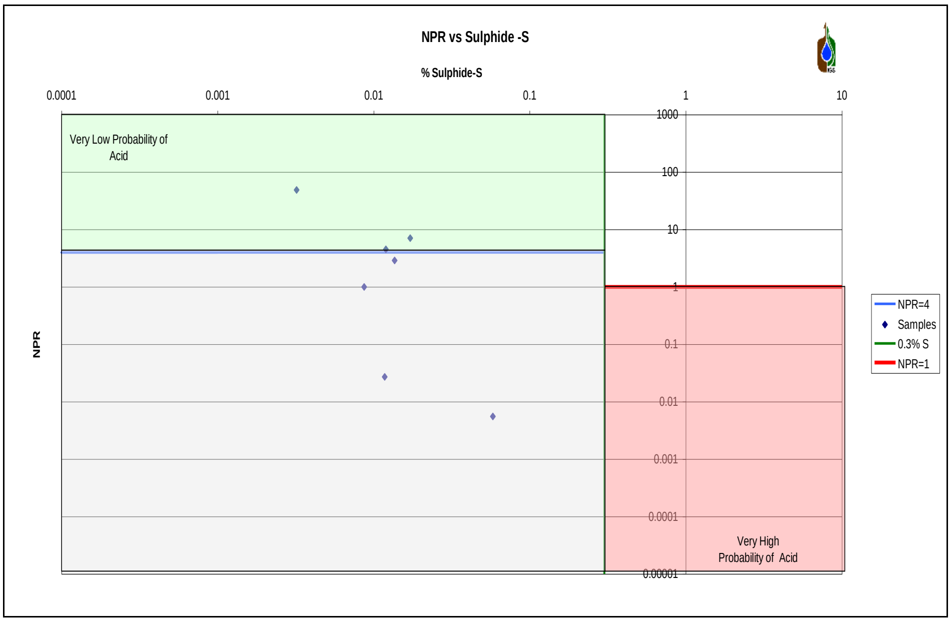


Figure 0-52 Graphical illustration of NPR results

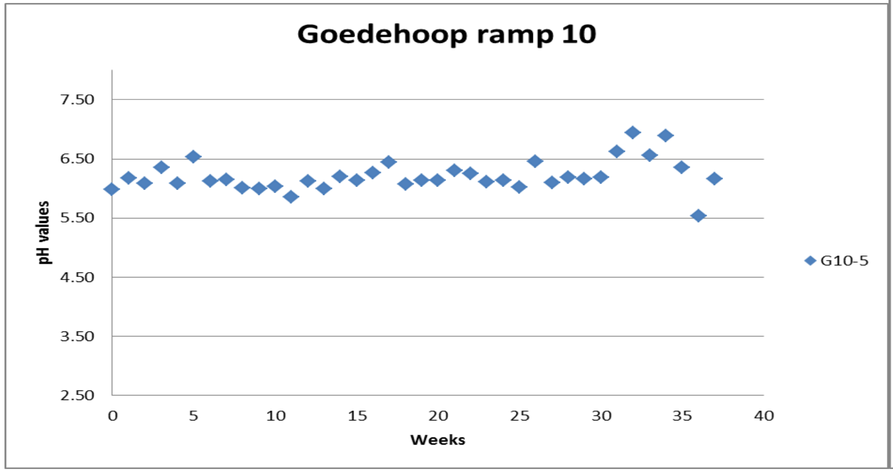
About two samples in both open and closed system illustrated the unlikelihood of acidification since it plotted under the green line, the rest of the samples are plotted along the y-axis therefore inconclusive (Figure 0-52).

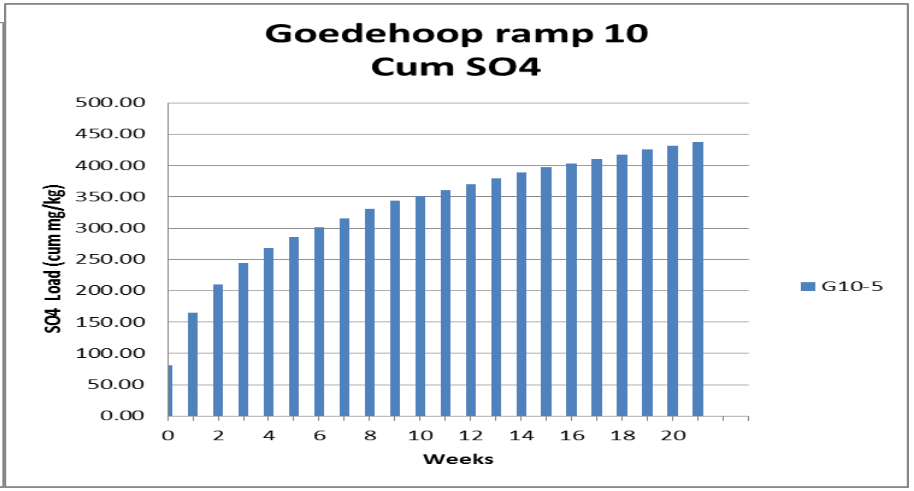


% S vs NPR for the Goedehoop ramp 10 samples

The percentage sulphur in the samples plotted against the NPR (Figure) indicates one sample that has an uncertain risk of acid production and another one having a high probability of acid generation plotting in the red, indicating a high risk of AMD.

Kinetic results

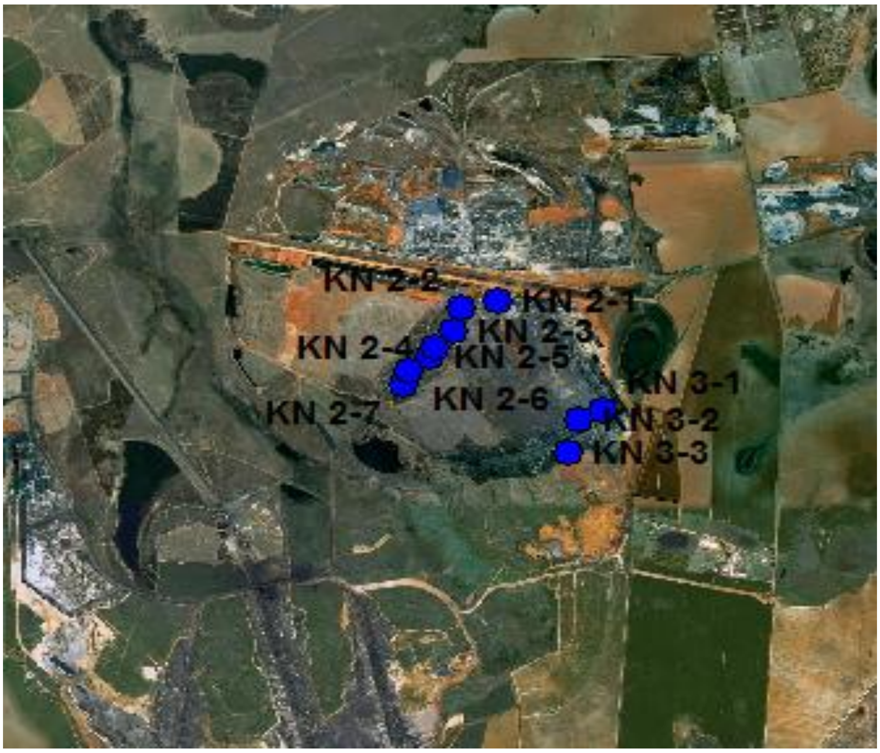




Kinetic cell pH value (left) with the Cumulative SO4 (right) of Goedehoop ramp 10 samples

G10-5show erratic measurements of the pH that is recorded and has a sulphate load of about 445 mg/kg/week .

4.5.4 Klipfontein North


KN 2-2
KN 2-1
KN 2-3
KN 2-4
KN 2-5
KN 2-7
KN 2-6
KN 3-1
KN 3-2
KN 3-3

Sampling point of Klipfontein North

10 samples were analysed for Klipfontein North (**Error! Reference source not found.**)

Mineralogical analysis

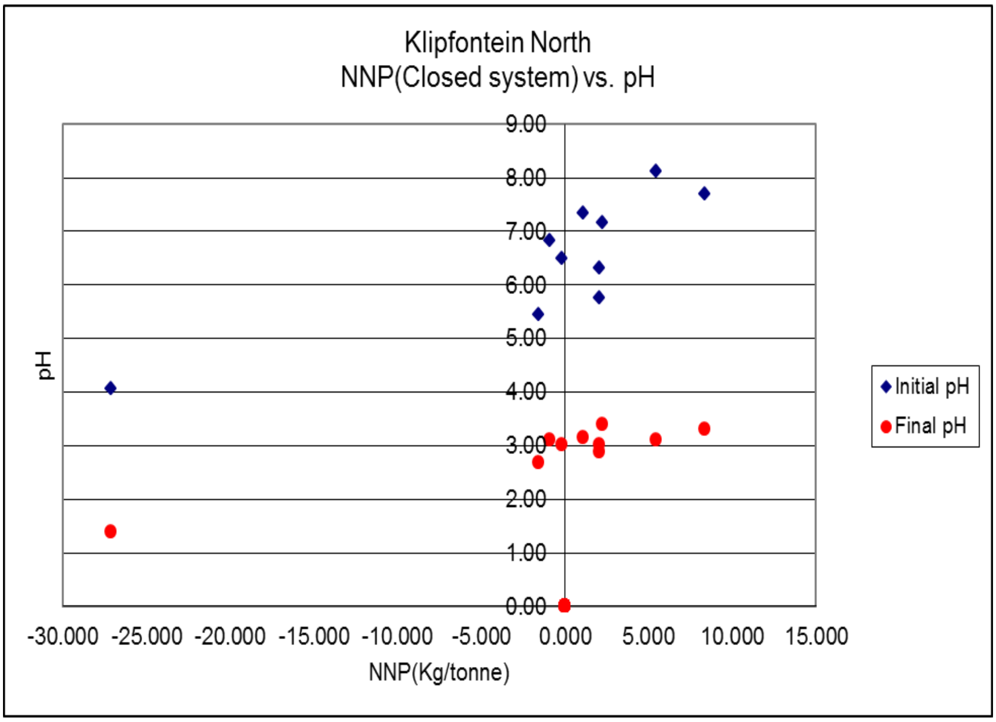
Table 0-29Mineralogical analysis of Klipfontein North (left) and classification table (bottom right)

Sample	Q	Kaol	Illite	Kvsp	Pyrite	Gyp
KN2-1	XX	XX	x	<x	<x	
KN2-2	XX	XX	xx	x		
KN2-3	XX	XX	xx	xx		
KN2-4	XX	XX	x	xx		
KN2-5	XX	XX	x	x		
KN2-6	XX	XX	x	x	<x	

KN2-7	XX	XX	x	x	<x	x
KN3-1	XX	XX	xx	x	<x	
KN3-2	XX	XX	x	x		
KN3-3	XX	XX	x	<x	<x	

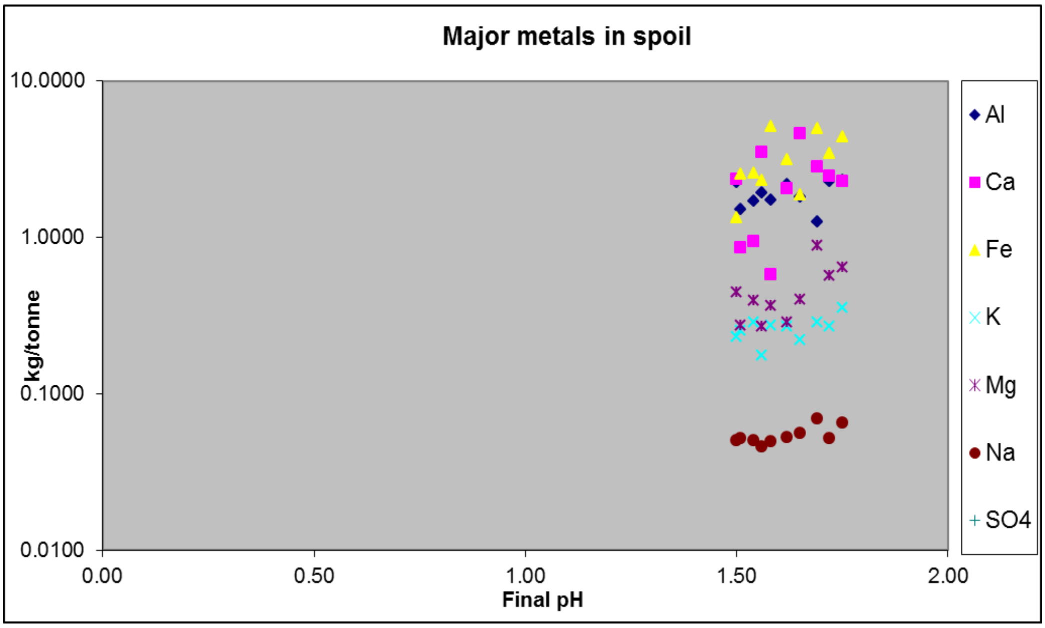
Klipfontein North mine consists (Table 0-29) predominantly of quartz and kaolinite with accessory components of pyrite, K-Feldspar and illite.

Static results



Klipfontein North results

Klipfontein values of four sample show a negative net neutralising potential therefore suggesting that the sample will likely produce AMD. Six samples show a positive Net Neutralising potential suggests that the samples would unlikely generate acidic conditions (**Error! Reference source not found.**).



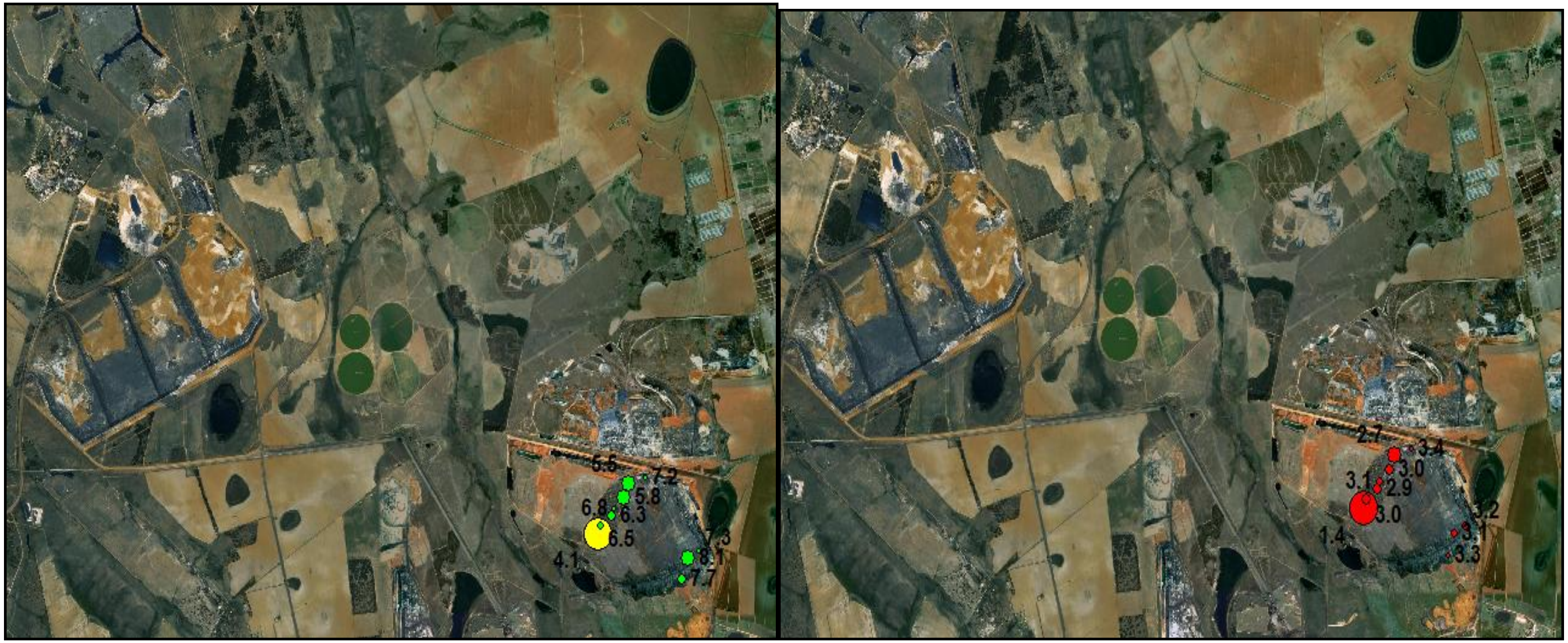
Major metal from the Klipfontein North samples

Ca , $SO_4$and Fe have the highest values with Na as the lowest.

Interpretation of ABA pH and NAG results for Klipfontein North samples

Site Name	Initial pH	Final pH	Interpretation
KN2-1	7.17	3.40	Higher Risk Acid Generation
KN2-2	5.46	2.68	Higher Risk Acid Generation
KN2-3	5.76	3.02	Higher Risk Acid Generation
KN2-4	6.84	3.12	Higher Risk Acid Generation
KN2-5	6.31	2.88	Higher Risk Acid Generation
KN2-6	6.49	3.02	Higher Risk Acid Generation
KN2-7	4.06	1.40	Higher Risk Acid Generation
KN3-1	7.35	3.16	Higher Risk Acid Generation
KN3-2	8.12	3.10	Higher Risk Acid Generation
KN3-3	7.71	3.30	Higher Risk Acid Generation

One of the samples was already partly oxidised prior to the final pH method (**Error! Reference source not found.**) the rest of the samples were slightly acidic or alkaline. All the samples indicate that they have a higher risk of acid generation.


5.5
7.2
5.8
6.8
6.3
6.5
7.3
4.1
8.1
7.7
2.7
3.4
3.0
3.1
2.9
3.0
3.2
1.4
3.1
3.3

Initial pH (top) and final pH (bottom) showing Klipfontein North samples

An average initial pH value of 6.5 (Some of these samples are partly oxidized) and an average final pH is 2.9 is calculated from the recorded values (**Error! Reference source not found.**). The pH of all sampled dropped to values ranging 1-3.4, indicating a high risk of acid generation upon oxidation.

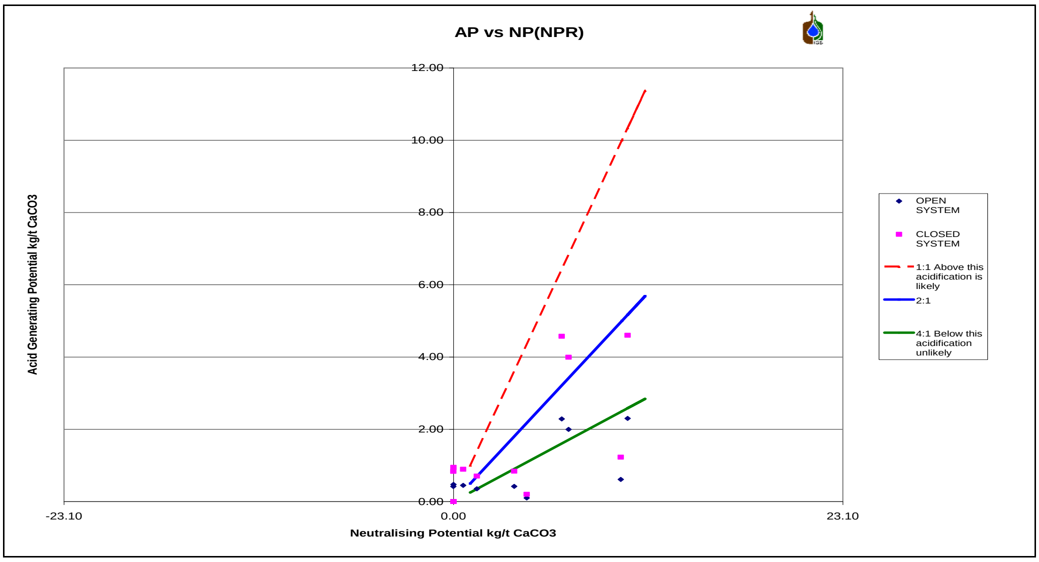
Interpretation of ABA Net Neutralising Potential results.

Site Name	Net Neutralising Potential (Open)	Net Neutralising Potential (Closed)	Interpretation
KN2-1	4.84	2.84	Verify with other tests
KN2-2	-0.42	-0.84	Verify with other tests
KN2-3	3.18	2.76	Verify with other tests
KN2-4	0.13	-0.32	Verify with other tests
KN2-5	4.35	4.35	Verify with other tests
KN2-6	1.04	0.69	Verify with other tests
KN2-7	-0.47	-0.95	Verify with other tests
KN3-1	4.14	1.85	Verify with other tests
KN3-2	8.04	5.73	Verify with other tests
KN3-3	9.31	8.70	Verify with other tests

The open and closed NNP is interpreted in **Error! Reference source not found.** where it indicates negative values as potential Acid generator and that all samples need to be verified with Kinetic tests.

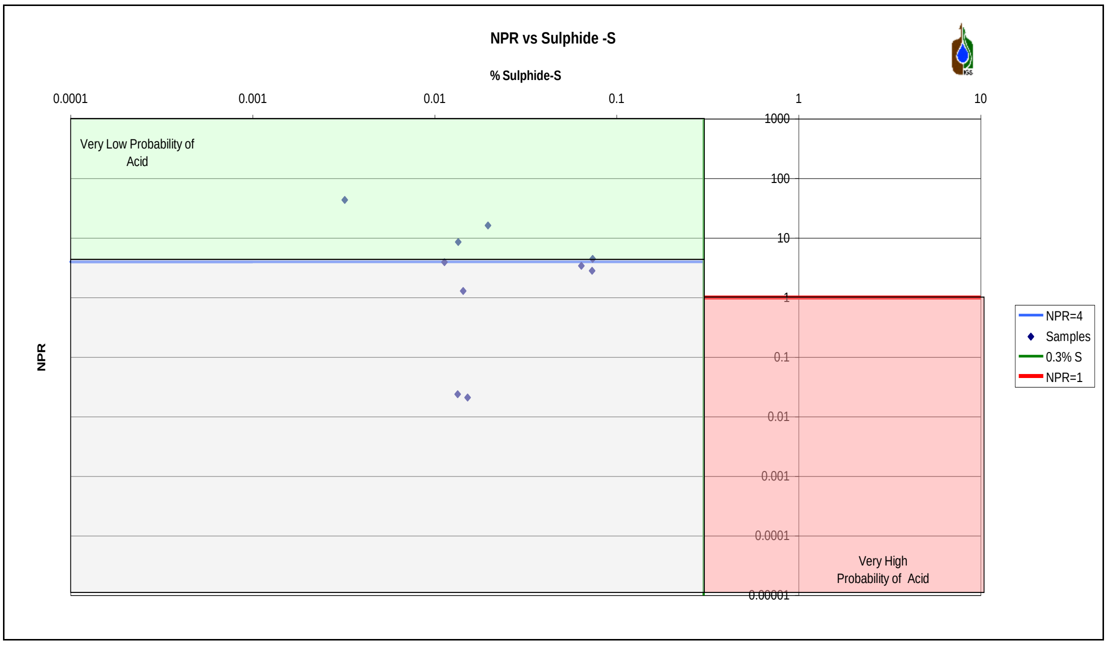
Interpretation and NP/AP ratios for Klipfontein North

Site Name	Neutralising Potential Ratio(NP/AP) for Open System	Interpretation Open System	Interpretation Closed System
KN2-1	3.42	Acid under certain conditions	Acid under certain conditions
KN2-2	0.02	Likely Acid Generator	Likely Acid Generator
KN2-3	8.57	No Acid Potential	No Acid Potential
KN2-4	1.29	Acid under certain conditions	Likely Acid Generator
KN2-5	43.51	No Acid Potential	No Acid Potential
KN2-6	3.95	Acid under certain conditions	Acid under certain conditions
KN2-7	0.02	Likely Acid Generator	Likely Acid Generator
KN3-1	2.81	Acid under certain conditions	Acid under certain conditions
KN3-2	4.49	No Acid Potential	Acid under certain conditions
KN3-3	16.17	No Acid Potential	No Acid Potential



Graphical presentation of NPR results for Klipfontein North

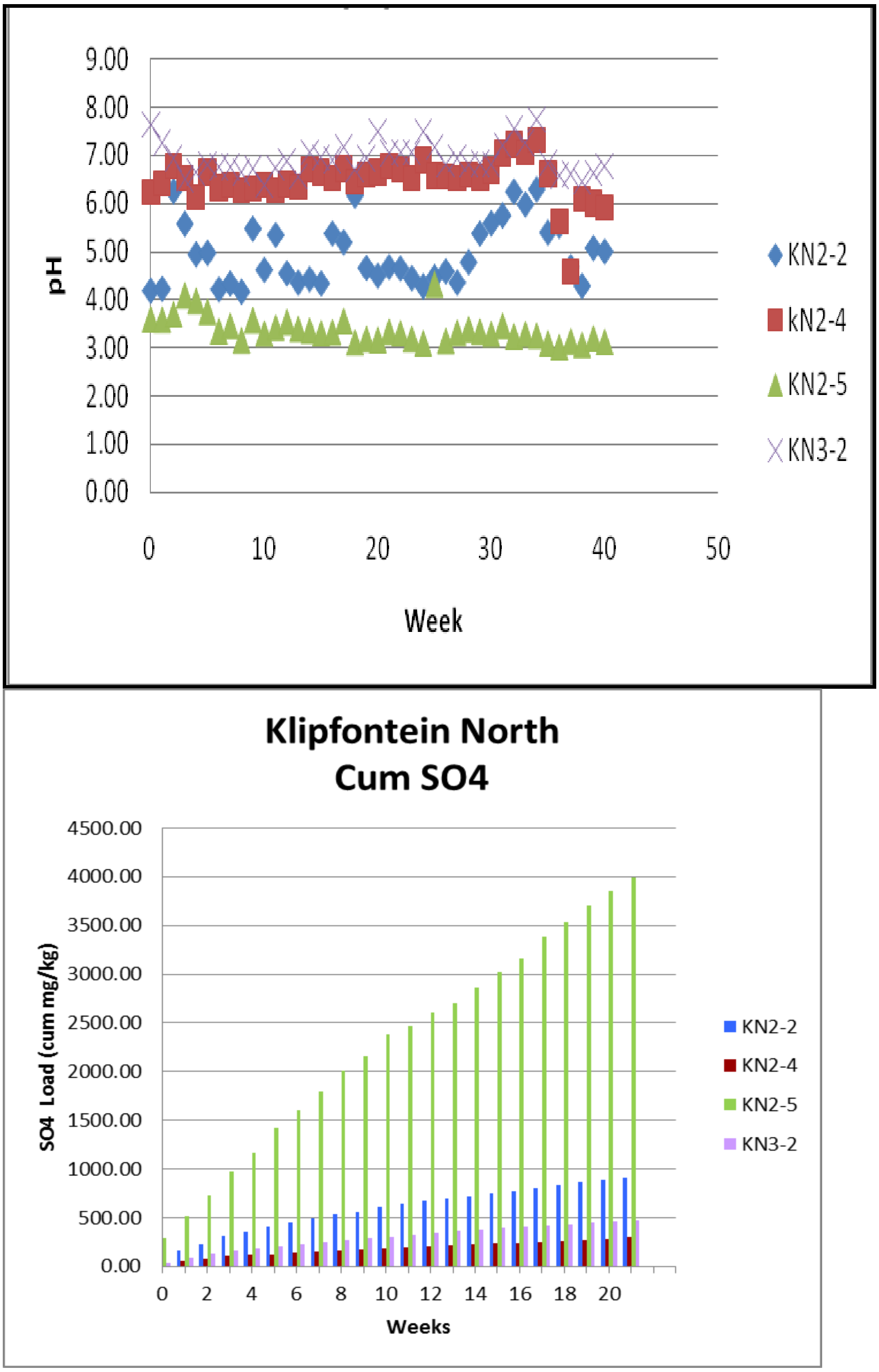
Majority of the samples in both an open and a closed system are uncertain or unlikely to acidify (**Error! Reference source not found.**).



% S vs NPR for the Klipfontein North

The percentage sulphur in the samples plotted against the NPR indicates 7 samples have an uncertain risk of acid production and the rest have a low probability of acid generation.

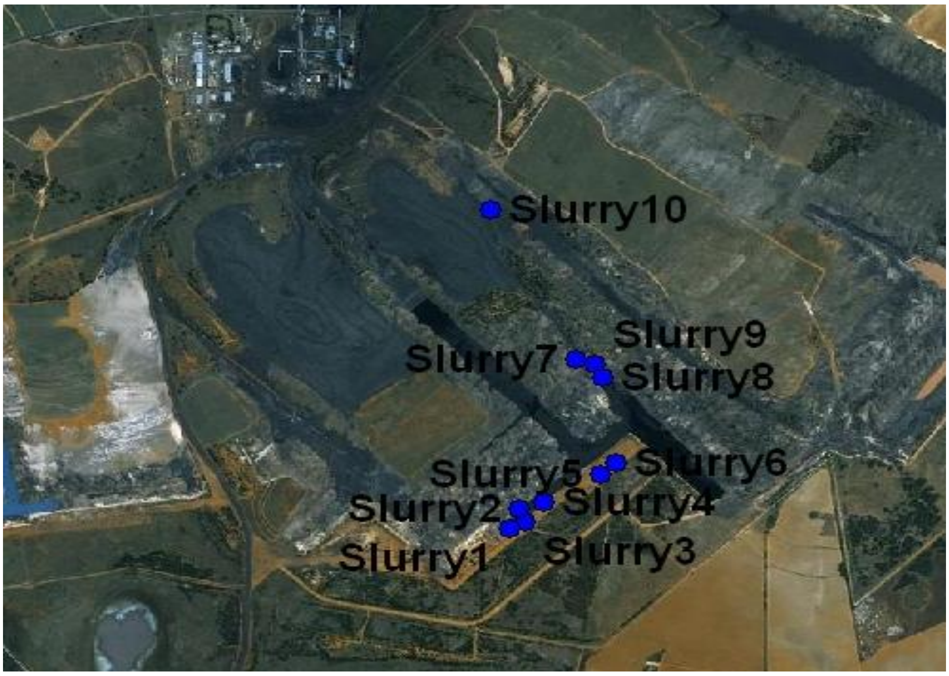
Kinetic results



Kinetic cell pH value (left) with the Cumulative SO4 (right) of the Klipfontein North samples

The lower the pH value the higher the SO4 load (i.e KN2-5) and visa versa (KN3-2). The only erratic pH shown is for KN2-2 sample which has the second highest SO4 load.

4.5.6 Slurry


Slurry10
Slurry9
Slurry7
Slurry8
Slurry6
Slurry5
Slurry2
Slurry4
Slurry1
Slurry3

Location site for the Slurry samples

10 were analysed for Slurry (**Error! Reference source not found.**)

Mineralogical analysis

Mineralogical analysis of slurry

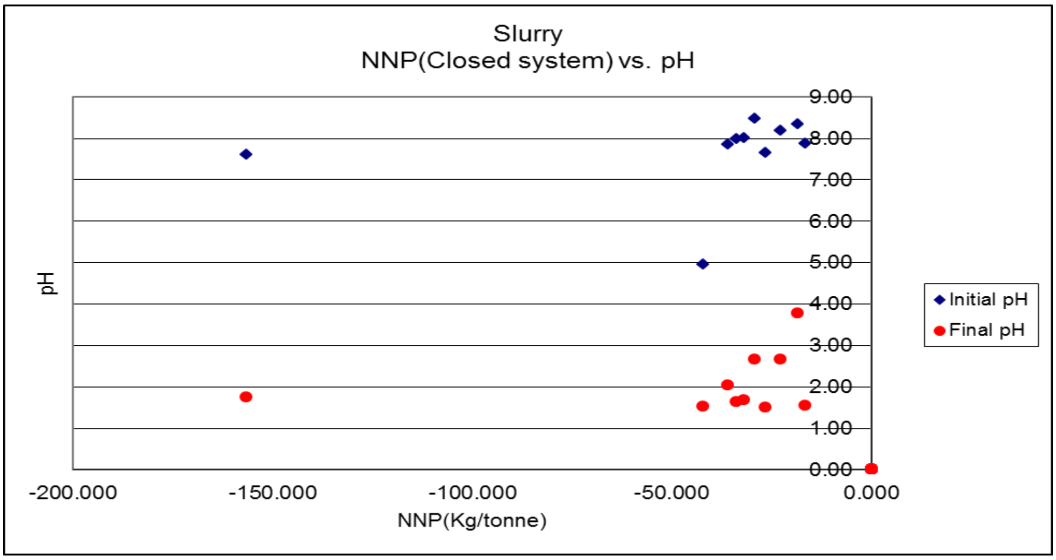
Sample	**Q**	**Kaol**	**Illite**	**Kvsp**	**Pyrite**	**Calcite**	**Montm**	**Gyp**	**Sid**	**Hem**	**Dol**
Slurry 1	XX	X	xx			x		x	<x		
Slurry 2	XX	X	<x	<x	<x	x		x	<x		<x
Slurry 3	XX	X				x		x			
Slurry 4	XX	X	<x	<x		xx		x			
Slurry 5	XX	X	<x	<x	<x	x		xx	x	x	
Slurry 6	XX	X					<x	xx		<x	
Slurry 7	XX	xx			<x	xx		xx		<x	
Slurry 8	XX	XX		<x	<x	x		xx		<x	
Slurry 9	XX	X		xx		x		xx	<x	<x	

Slurry 10	XX	X	<x	<x	<x	<x	<x	xx	<x	<x	

Classification of mineralogy

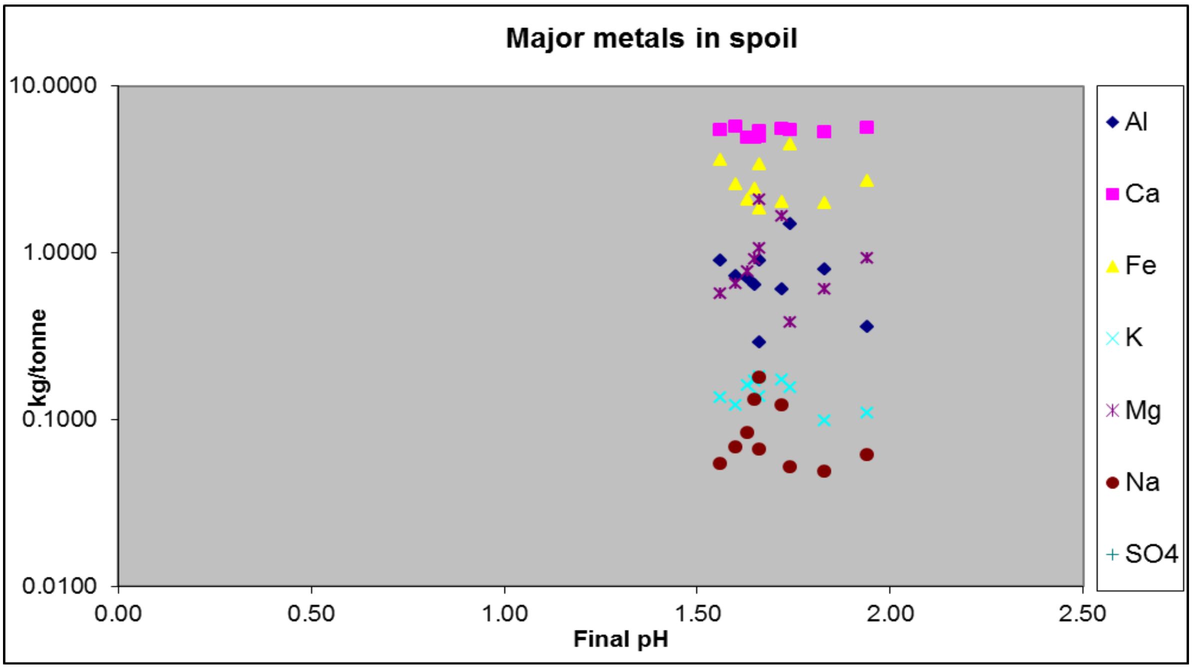
The Slurry consists predominantly of quartz and kaolinite with accessory components of pyrite, calcite, gypsum, Siderite and K-Feldspar .

Static results



NNP Slurry results

All the Slurry values show a negative net neutralising potential therefore suggesting that the sample will likely produce AMD.



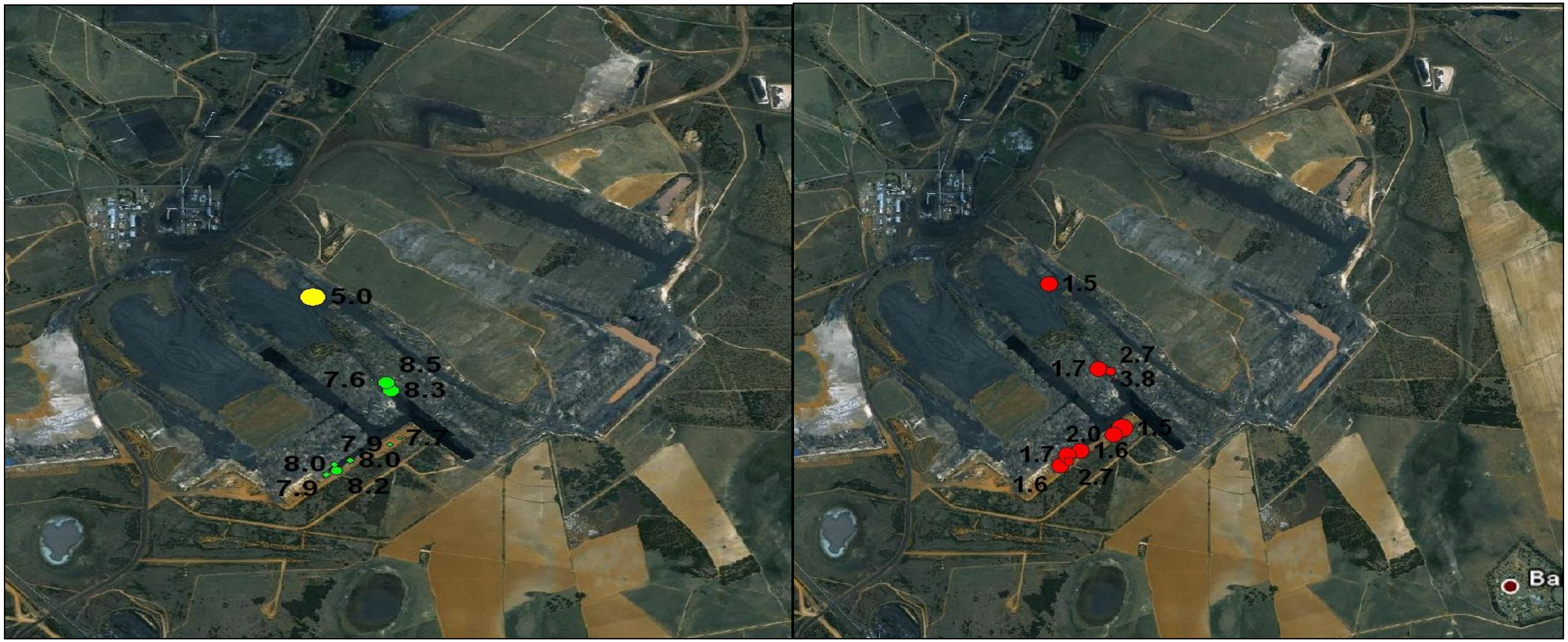
Major metal from the Slurry samples

Ca , $SO_4$and Fe have the highest values with Na as the lowest.

interpretation of ABA pH and NGA results for Slurry samples

Site Name	Initial pH	Final pH	Interpretation
Slurry 1	7.88	1.56	Higher Risk Acid Generation
Slurry 2	8.02	1.68	Higher Risk Acid Generation
Slurry 3	8.20	2.66	Higher Risk Acid Generation
Slurry 4	7.98	1.63	Higher Risk Acid Generation
Slurry 5	7.85	2.05	Higher Risk Acid Generation
Slurry 6	7.65	1.51	Higher Risk Acid Generation
Slurry 7	7.61	1.74	Higher Risk Acid Generation
Slurry 8	8.35	3.78	Medium Risk Acid Generation
Slurry 9	8.47	2.67	Higher Risk Acid Generation
Slurry 10	4.97	1.52	Higher Risk Acid Generation

Slurry 10 is the only sample that was already partly oxidised prior to the final pH method. All samples indicate that they have a high-medium risk of acid generation.


5.0
8.5
7.6
8.3
7.9
7.7
8.0
8.0
7.9
8.2
1.5
2.7
1.7
3.8
2.0
1.5
1.7
1.6
1.6
2.7
Ba

Initial pH (left) and final pH (right) showing Slurry samples

An average initial pH value of 7.7 (one sample was partly oxidized) and an average final pH is 2.1 is calculated from the recorded values. The pH of all sampled dropped to values ranging 1-3.8, indicating a high-medium risk of acid generation upon oxidation.

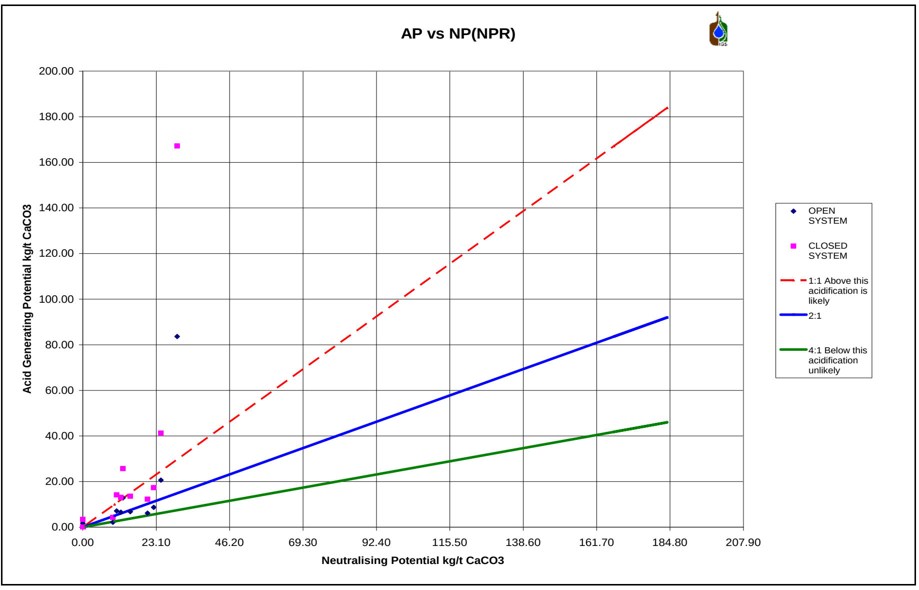
Interpretation of ABA Net Neutralising Potential results.

Site Name	Net Neutralising Potential (Open)	Net Neutralising Potential (Closed)	Interpretation
Slurry 1	7.31	5.17	Verify with other tests
Slurry 2	-0.18	-13.02	Verify with other tests
Slurry 3	8.15	1.38	Verify with other tests
Slurry 4	3.96	-16.67	Verify with other tests
Slurry 5	3.55	-3.54	Verify with other tests
Slurry 6	5.47	-1.07	Verify with other tests
Slurry 7	-53.89	-137.48	Potential Acid Generator
Slurry 8	13.67	5.00	Verify with other tests
Slurry 9	14.24	8.11	Verify with other tests
Slurry 10	-1.70	-3.40	Verify with other tests

The open and closed NNP is interpreted in **Error! Reference source not found.** where it indicates negative values as potential Acid generator and that all samples except for Slurry 7 need to be verified with Kinetic tests.

Interpretation and NP/AP ratios for Slurry

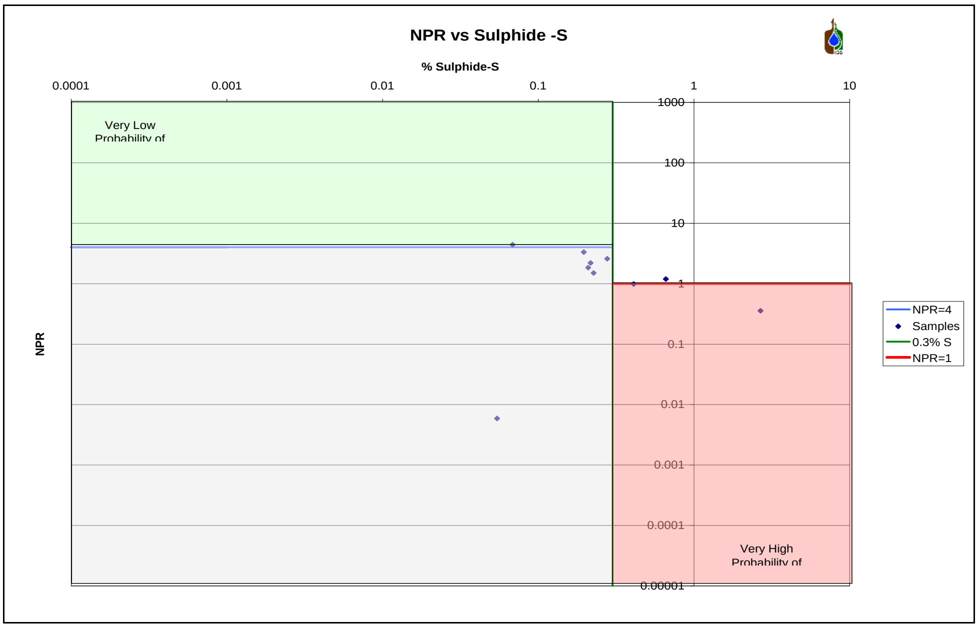
Site Name	Neutralising Potential Ratio (NP/AP) for Open System	Interpretation Open System	Interpretation Closed System
Slurry 1	4.42	No Acid Potential	Acid under certain conditions
Slurry 2	0.99	Likely Acid Generator	Likely Acid Generator
Slurry 3	2.20	Acid under certain conditions	Acid under certain conditions
Slurry 4	1.19	Acid under certain conditions	Likely Acid Generator
Slurry 5	1.50	Acid under certain conditions	Likely Acid Generator
Slurry 6	1.84	Acid under certain conditions	Likely Acid Generator
Slurry 7	0.36	Likely Acid Generator	Likely Acid Generator
Slurry 8	2.58	Acid under certain conditions	Acid under certain conditions
Slurry 9	3.32	Acid under certain conditions	Acid under certain conditions
Slurry 10	0.01	Likely Acid Generator	Likely Acid Generator



C

Graphical presentation of NPR results for Slurry samples

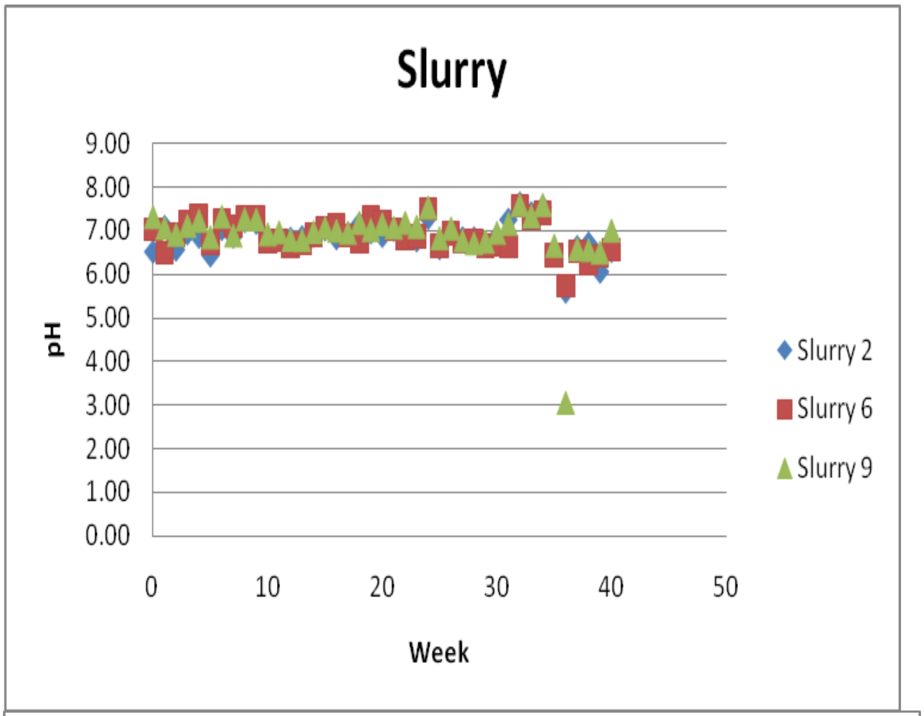
Majority of the samples in both an open and a closed system are uncertain or likely to acidify.

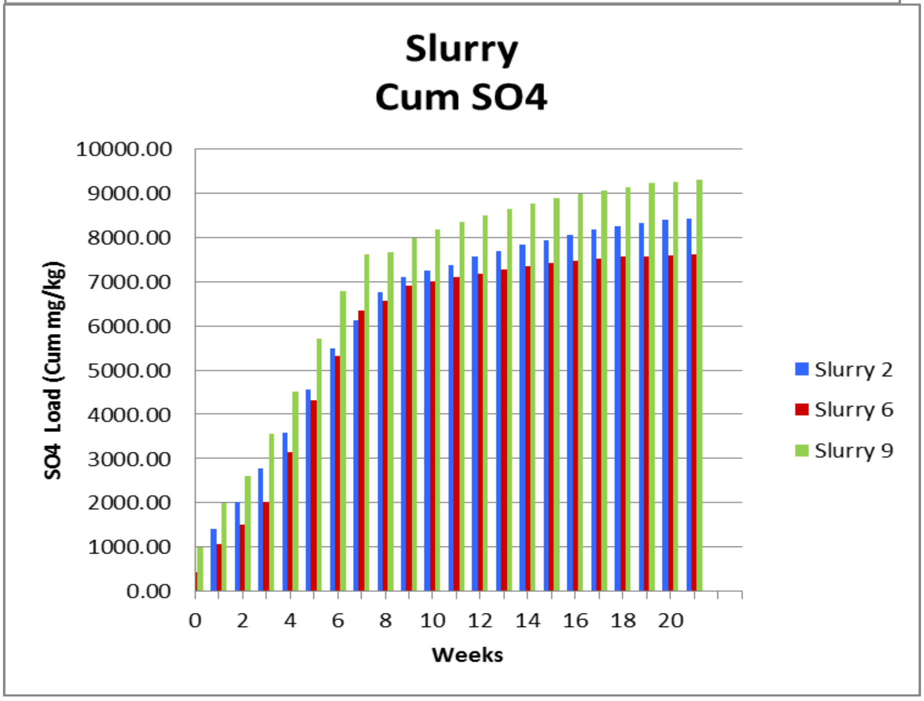


% S vs. NPR for the Slurry samples

The percentage sulphur in the samples plotted against the NPR indicates that the majority of the samples have an uncertain risk of acid production and two samples having a high probability of acid generation plotting in the red, indicating a high risk of AMD.

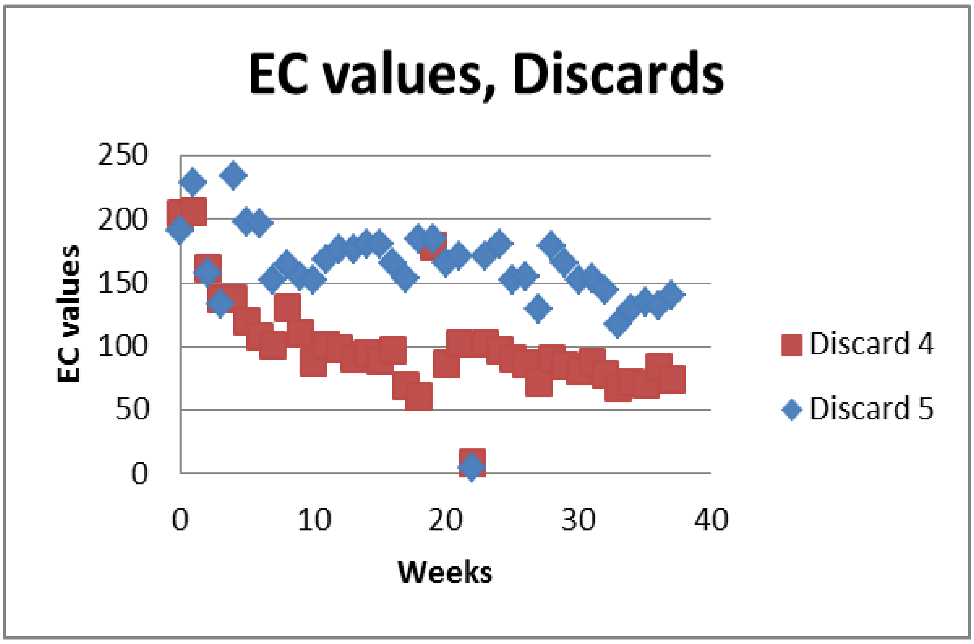
Kinetic results

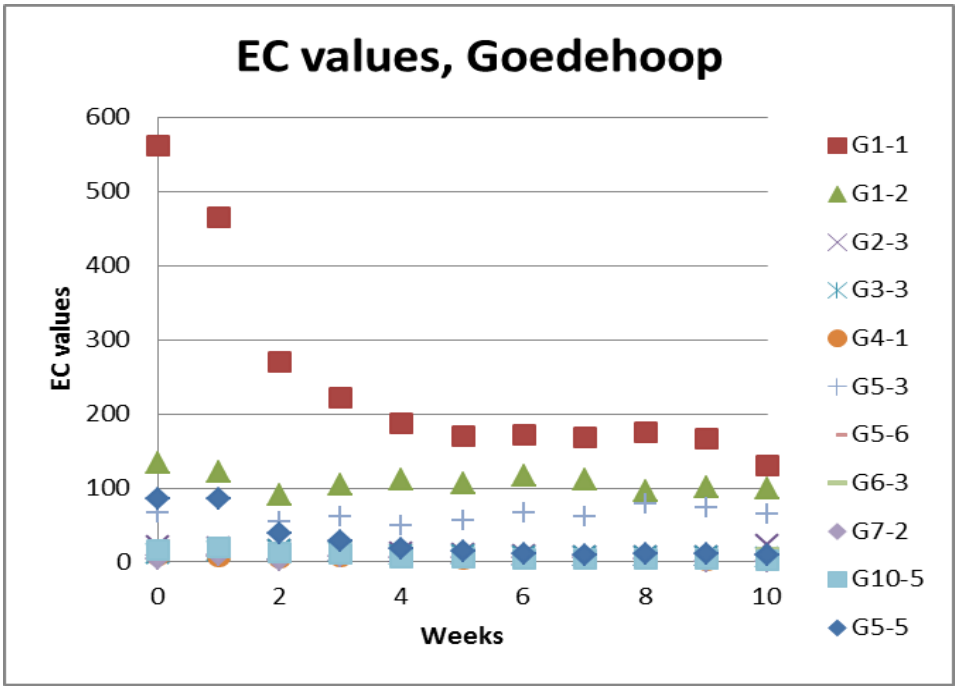


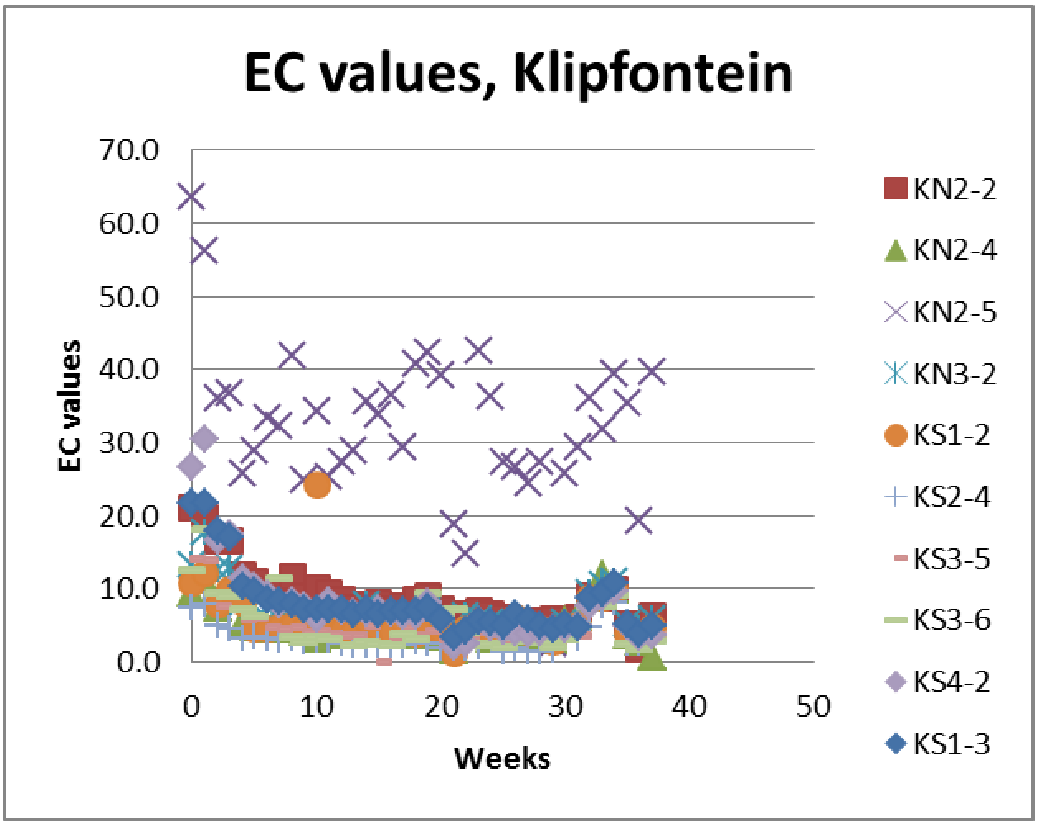


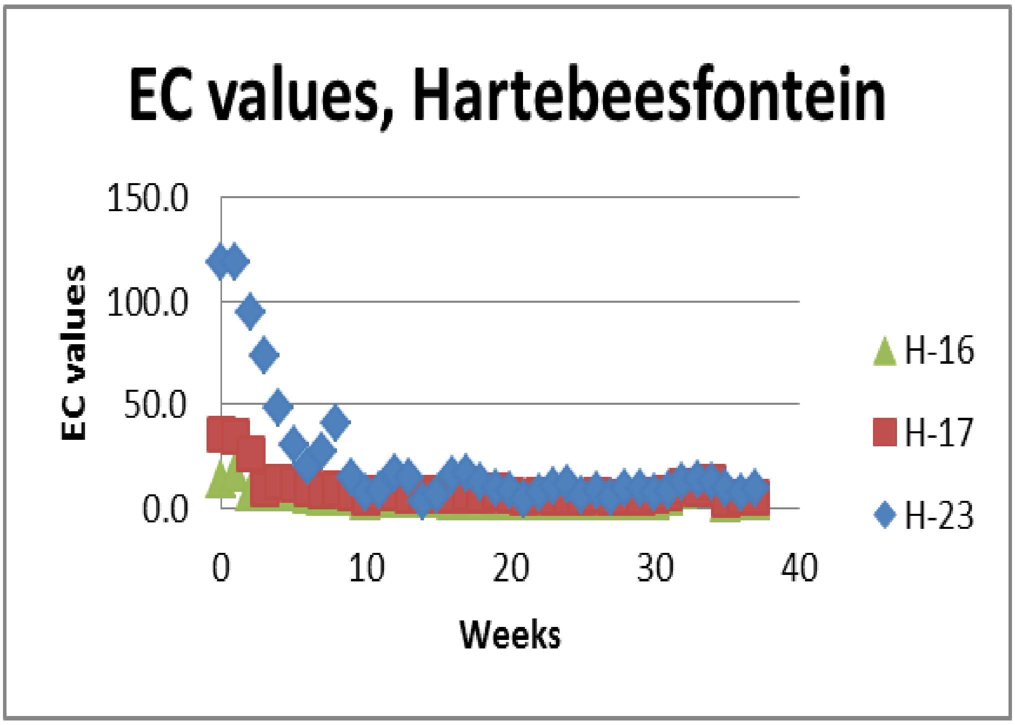
Kinetic cell pH value (left) with the Cumulative SO4 (right) of the Slurry samples

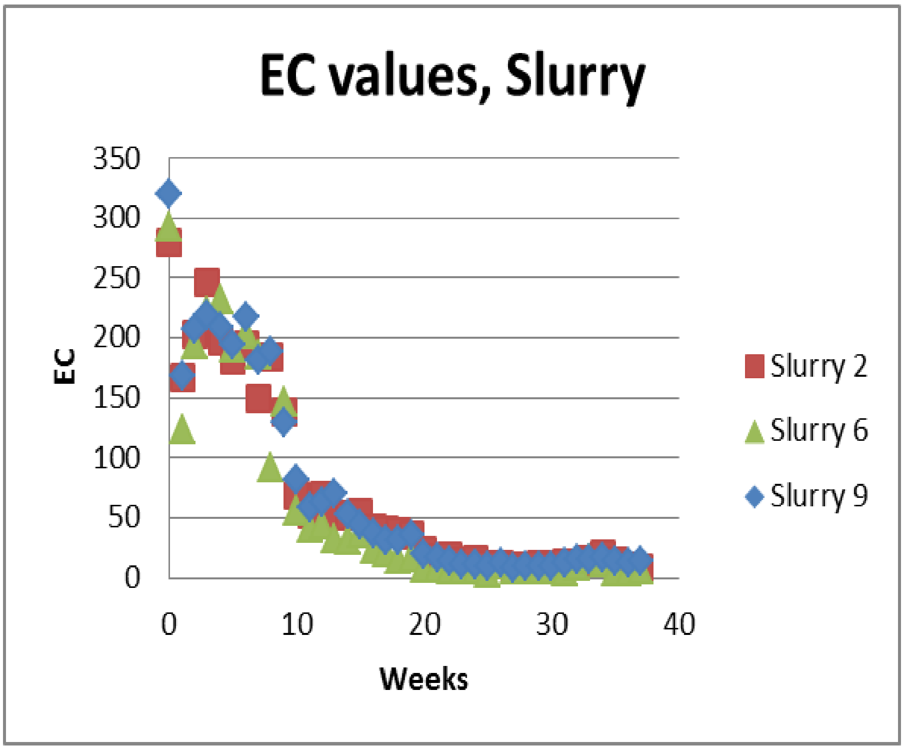
All the samples pH stays contant with a little erratic period before week 40. Slurry 9 has the high values of SO4 load with Slurry 6 showing a lowest SO4 load.


EC values, Discards
EC values
250
200
150
100
50
0
0
10
20
30
40
Weeks
Discard 4
Discard 5


EC values, Goedehoop
EC values
600
500
400
300
200
100
0
0
2
4
6
8
10
Weeks
G1-1
G1-2
G2-3
G3-3
G4-1
G5-3
G5-6
G6-3
G7-2
G10-5
G5-5


EC values, Klipfontein
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
EC values
0
10
20
30
40
50
Weeks
KN2-2
KN2-4
KN2-5
KN3-2
KS1-2
KS2-4
KS3-5
KS3-6
KS4-2
KS1-3


EC values, Hartebeesfontein
150.0
100.0
50.0
0.0
EC values
0
10
20
30
40
Weeks
H-16
H-17
H-23


EC values, Slurry
EC
350
300
250
200
150
100
50
0
0
10
20
30
40
Weeks
Slurry 2
Slurry 6
Slurry 9