UNIVERSITY OF CAPE TOWN
IYUNIVESITHI YASEKAPA • UNIVERSITEIT VAN KAAPSTAD

CHARACTERISING THE POTENTIAL ENVIRONMENTAL RISKS OF SOUTH AFRICAN COAL PROCESSING WASTES

Annah Moyo

February 2018

Dissertation submitted to the Faculty of Engineering and the Built Environment, University of Cape Town in fulfilment of the requirements of a degree in Master of Science in Chemical Engineering

University of Cape Town

The copyright of this thesis vests in the author. No quotation from it or information derived from it is to be published without full acknowledgement of the source. The thesis is to be used for private study or non-commercial research purposes only.

Published by the University of Cape Town (UCT) in terms of the non-exclusive license granted to UCT by the author.

University of Cape Town

DECLARATION

"I know the meaning of plagiarism and declare that all the work in the document, save for that which is properly acknowledged, is my own. This dissertation has been submitted to the Turnitin module (or equivalent similarity and originality checking software) and I confirm that my supervisor has seen my report and any concerns revealed by such have been resolved with my supervisor."

Annah Moyo

Signed by candidate

19 February 2018

SYNOPSIS

The environmental impacts of coal processing wastes are a challenge in South Africa as large amounts of coal wastes are produced annually, pegged at 60 million tons per year according to Eberhard (2011). Whilst the fossil fuel-based industry is in decline globally, coal is likely to remain the dominant source of power in South Africa. The major environmental impacts reported in several studies are water pollution and soil quality degradation due to acid rock drainage (ARD) and its associated elevated levels of elements and salts. Several studies have shown the environmental performance of the wastes to be dependent on the geochemical properties of the wastes. Owing to the complex nature of coal wastes, their characterisation using tools developed for hard rock ores is associated with inconsistency and uncertainty. As a result, the South African coal processing wastes are poorly characterized and the associated risks not well understood.

This study investigates the reliability of relevant characterisation techniques and interpretation of characterisation data in terms of the environmental risk potential of coal wastes. The outcomes of the study address some of the uncertainties and deficiencies arising from the current characterisation tools and evaluate potential environmental risks posed by coal processing wastes. Laboratory-scale characterisation of the physio-chemical properties and of ARD and elemental risk potential of two ultra-fine coal waste and one discard waste sample were conducted. Evaluation of accuracy and repeatability of selected analyses was conducted on a certified coal standard.

The selected analyses tested for accuracy and repeatability were total sulphur analysis by Leco and Eschka methods in addition to elemental analysis by wavelength dispersive x-ray fluorescence (WDXRF), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The ISO 157:1996 and ACARP C15034 protocols for assessment of sulphur forms were also compared and evaluated for precision using the coal standard and coal waste samples. Conversions of the sulphur species under static ARD tests were also studied to understand the sulphur species behaviour and implication on ARD potential. The mineralogy of the coal wastes was evaluated from a quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) and quantitative x-ray diffraction (QXRD) analysis. In addition, conventional net acid generating (NAG) and acid-base accounting (ABA) static tests were enhanced through extended boil NAG tests to assess the organic acids effect on the NAG capacity. The static tests were validated by theoretical ARD calculated from mineralogy as well as biokinetic shake flask tests which gave the time-related acid generating behaviour of the coal waste samples. Sequential chemical extractions combined with a simple score and ranking protocol were subsequently used to evaluate the potential water and soil-related risks associated with environmentally available elements and salts in the coal wastes.

The results showed both the Leco and Eschka methods to be highly precise (±0.01-0.03 % standard error) but the Leco was more accurate (±3.1 % compared to ±12.5 % relative standard error (RSE)). The total sulphur content of the coal processing waste was less than 2 %. The ISO157:1996 and ACARP C15034 protocols gave comparable and slightly different results but the latter was more precise in sulphate analysis. Furthermore, the ACARP protocol could differentiate the acid forming sulphates from the soluble sulphates giving a better theoretical maximum acid producing potential. The sulphur species from the two chemical methods and QEMSCAN mineralogy showed 52-61 %, 12-26 % and 21-43 % to be sulphide, sulphate and organic/low-risk sulphur respectively. The conversion of the sulphur species showed that partial solubilisation of sulphides in ANC and partial conversion of organic/low-risk sulphur under NAG tests can cause an over or underestimation of ARD potential.

The static ARD tests has shown the Witbank coal discards sample to be potentially acid forming (PAF) (9.2-25.9 kg H_2SO_4/Ton), Waterberg coal slurry to be non-acid forming (NAF) (-68.6 to -46.8 kg H_2SO_4/Ton) and Witbank coal slurry to be uncertain (-12.1 to 9.9 kg H_2SO_4/Ton). The extended boil NAG tests showed organic acids effect on the Witbank coal slurry likely caused an overestimation of the NAG capacity. Validation of the static tests by biokinetic tests and ARD calculated from mineralogy classified both Witbank samples as PAF and the Waterberg sample as NAF. The results also showed the net acid producing potential of the coal wastes to depend on the mineralogy of the samples. The elemental results showed WDXRF and LA-ICP-MS analysed most of the elements accurately within ±10 % RSE and that a combination of techniques provides more reliable and accurate results. The analyses showed the coal waste to contain significant amounts of environmentally sensitive elements like Cr, As, Mo, Sb, Se. The ranking and scoring of potentially available elements under oxidising leach conditions evaluated Fe in Waterberg coal slurry and Witbank coal discards to pose high risk in drinking water while S (as sulphate), Pb, Sb, Mn, As, Al and Hg in the three samples pose moderate risk.

This case study evaluated the accuracy and precision of commonly used analytical techniques and applicability of risk evaluation protocols for coal processing wastes. The research outcomes underlined some factors that cause uncertainty and inconsistency with the evaluation of ARD potential of coal wastes. The findings highlighted the need to validate and complement the characterisation data using various tools and risk evaluation protocols to overcome specific limitations. The results also indicated the coal wastes have the potential to cause environmental impacts from ARD and elevated concentration of elements and salts, thus providing a basis for designing and implementing waste management strategies which minimise these risks. The mineralogy and elemental composition of coal wastes showed enrichment of elements and presence of potentially usable and economically valuable constituencies for future studies on value recovery. Characterisation of coal processing wastes for air pollution impacts is recommended for future studies as well as a study of ARD behaviour under continuous flow systems to more closely represent the conditions in dump disposal scenario.

ACKNOWLEDGEMENTS

May I extend my warmest gratitude to the following:

- To my supervisors; Associate Professor Jennifer Broadhurst, Doctor Juarez Amaral-Filho and Professor Sue Harrison for giving "life" to this project.
- To Doctor Rosemond Henry and Doctor Nico Cloete for being my guardians, offering me your unwavering support and encouragement
- To all the staff in Chemical Engineering for giving me the support and opportunity in my studies. Special mention goes to Dr Megan Becker, Gaynor Yorath, Kirsten Corin, Lorraine Nkemba, Doctor Supratim Biswas, Tich Samkange, Emmanuel Ngoma, Dr Thanos Kostiopoulus, Stephanie Lagrange, Eunice Jacobs and Kathija
- To my colleagues in the Chemical Engineering Department for their support and companionship. Special mention goes to Michael Odidi, Leo Maritz, Tolbert Golela, Catherine Edwards, Thomas Hessler and Mehdi Ghadiri for their companionship
- To Doctor Takalani Theka in Chemistry Department for understanding and loaning me the heating mantle
- To Mareli Grobbelaar and Riana Rossouw at Stellenbosch University for all their effort and patience with the numerous analyses they conducted
- To Mcdonald Shilubane at ALS Global for all the assistance in sulphur and sulphur forms analyses
- To my family for their unconditional love
- Above all to God who gave me life, strength, motivation and endless love

Disclaimer

This work is based on research supported by: The Water Research Commission of South Africa. Any opinion, finding, conclusion or recommendation expressed in this material is that of the authors and the WRC does not accept any liability in this regard.

LIST OF PRESENTATIONS AND PUBLICATIONS

I. Moyo A, Filho J.A., Harrison S.T.L, Broadhurst J.L Project presentation at the Carbon Energy and the Environment National Student Colloquium 01 June 2016, North-West University
II. Moyo A, Filho J.A., Harrison S.T.L, Broadhurst J.L Poster presentation at the Centre for Bioprocess Research day, 31 August 2016, SUN hotel, Newlands Cape Town
III. Moyo A, Filho J.A., Harrison S.T.L, Broadhurst J.L Project presentation at Minerals to Metals symposium, 25 November 2016, Waterfront, Cape Town
IV. Moyo A, Filho J.A., Harrison S.T.L, Broadhurst J.L Project progress presentation at WRC meeting, University of Cape Town, 6 April 2017
V. Moyo A, Filho J.A., Harrison S.T.L, Broadhurst J.L SAIMM Minerals Research Showcase Conference presentation, Characterising the ARD potential of South African coal processing wastes by static and biokinetic tests, Philippi Village, Cape Town, 03 August 2017

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS

AAS	Atomic absorption spectrometry
ABA	Acid base accounting
ACARP	Australian Coal Association Research Program
ANC	Acid neutralizing capacity
AP	Acid generating potential
ARD	Acid rock drainage
ASTM	American Society for Testing Materials
BSI	British Standards Institution
CAF	Centre of Analytical Facilities
CMMA	Complete maceral and mineral analysis
CCSEM	Computer controlled scanning electron microscopy
CV	Calorific values
CVAAS	Cold vapour atomic absorption spectrometry
DME	Department of Minerals and Energy
DMS	Dense medium separation
EDXRF	Energy dispersive x-ray florescence
FAAS	Flame atomic absorption spectrometry
FC	Fixed carbon
HAAS	Hydride atomic absorption spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
IC	Ion chromatography
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
INNA	Instrumental neutron activation analysis

IR	Infrared spectroscopy
ISE	Ion-selective electrode
ISO	International Standards Organization
KZN	KwaZulu Natal
LA-ICP-MS	Laser ablation inductively coupled plasma mass spectrometry
MLA	Mineral liberation analyser
MM	Mineral matter
MPA	Maximum potential acidity
NAF	Non-acid-forming
NAG	Net acid generation
NAPP	Net acid-producing potential
NP	Neutralising potential
PAF	Potentially acid-forming
PIXE/PIGE	Particle induced R-ray/ γ-ray emission
PSD	Particle size distribution
QEMSCAN	Quantitative evaluation of minerals by scanning electron microscopy
ROM	Run of mine
RSD	Relative standard deviation
RSE	Relative standard error
SA	South Africa
SANS	South African National Standards
SCE	Sequential chemical extractions
SEM	Scanning electron microscopy
SUN	Stellenbosch University
SXRF	Synchrotron x-ray florescence
TDS	Total dissolved solids

UC	Uncertain
UCT	University of Cape Town
UV-VIS	Ultraviolet-visible spectroscopy
VM	Volatile matter
WDXRF	Wavelength dispersive x-ray florescence
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectra
XRD	X-ray diffraction
XRF	X-ray florescence

Units of Measurement

g	gram - unit of mass (1g = 1000 mg = 10^{-3} kg)
kg	kilogram - unit mass (1 kg = 1000 g = 10^{-3} Ton)
KW	kilowatts – units of power (1 kW = 1000 J/s)
L	litre - unit of volume (1 L = 1000 ml = $10^{-3}m^3$)
mg	milligram - unit of mass (1 mg = 10^{-3} kg)
MJ	Megajoules – unit of energy (1 MJ = 10^6 J = 10^6 Nm)
ml	millilitre - unit of volume (1 ml = 10^{-3} L)
nm	nanometres- unit of length (1 nm = 10^{-6} mm)
pH	measure of acid concentration (-log $[H^+]$)
ppb	parts per billion – unit of concentration (1 ppb = 10^{-3} ppm)
ppm	parts per million – unit of concentration (1 ppm = 1 g/ Ton = 1 mg/ kg = 1 mg/ L)
µL	microliter – unit of volume (1 µL = 10^{-3} ml)
µm	micrometre – unit of length (1 µm = 10^{-3} mm = 10^{-6} m)
Ton	Tonnes-unit of mass (1 Ton = 1000 kg)

CHAPTER 1

INTRODUCTION

Solid coal beneficiation wastes in South Africa, particularly the fine-coarse wastes, have limited published characterisation data and their potential environmental risks from acid rock drainage (ARD), mobilised toxic elements and salts are not assessed qualitatively and quantitatively. Based on a report by Eberhard (2011), wastes from coal processing plants in South Africa were being produced at a rate of 60 million Tonnes a year in 2010. Vast majorities of these wastes are being disposed of in dump deposits with no market value. Several researchers have reported these coal wastes to cause adverse environmental, health and socio-economic impacts when not managed properly despite institutionalised waste management practices and legislation (Bell et al., 2001; Department of Minerals and Energy, 2001; Eberhard, 2011; Pone et al., 2007; Reddick et al., 2007; Zhao, 2012). However, some of the coal wastes' constituencies such as residual coal, kaolinite, pyrite and limestone can be recovered and fed into other processes as a resource, but this is currently not being done to a significant extent (Belaid et al., 2013; Department of Minerals and Energy, 2001; Kazadi Mbamba et al., 2012; Belaid et al., 2013). Reliable characterisation data linking the coal wastes physio-chemical properties to their environmental impacts is necessary for coal waste management. A combination of the characterisation data, sustainable waste management policies and adequate technologies provides the basis to justify and implement interventions to mitigate the environmental impacts and improve value recovery.

This project focuses on the comparison, evaluation and application of commonly used techniques for assessment of the environmental risk potential of coal processing waste. Characterisation was done by applying and extending mineralogical, chemical and element risk analysis techniques together with sulphur speciation and Acid Rock Drainage (ARD) potential assessment tests on coal waste samples obtained from South African coal processing plants. The results can be used in the generation of consistent and reliable environmental risk potential data which enables design and implementation of strategies for impacts mitigation.

1.1. Background

1.1.1. South Africa Coal Production and Consumption: Overview

In 2016, South Africa (SA) was the 7th top producer of coal in the world with annual production averaging approximately 257 million Tonnes, which is 3.5% of the world's total coal production (International Energy Agency, 2017). The coal consumption in 2015 according to Eskom is illustrated

in Figure 1 (Eskom, 2016). SA's coal production feeds its various local industries, with 39.75% of the mined coal being used for electricity generation. A quarter of the produced coal is exported and 24.75 % is used by the petrochemicals industry. Metallurgical industries consume 9 % of the coal while the remainder 1.5 % is used for domestic purposes. Most of SA's coal is mined in the Highveld, Witbank and Ermelo coalfields located in Mpumalanga province. However, some studies claimed that the Waterberg coal reserves which amount to nearly half of the country's remaining reserves will be the major coal supplier in the future (Belaid et al., 2013; Eberhard, 2011; Hancox and Goetz, 2014).

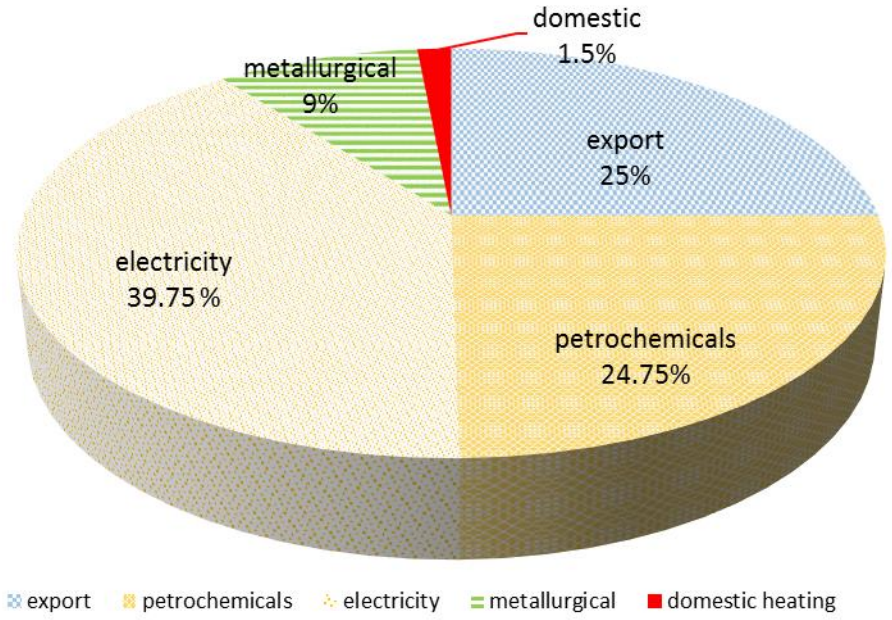

Figure 1 Coal consumption in South Africa (Eskom 2016 Fact Sheet)

The Eskom Fact Sheet of 2016, show coal as the major energy source in SA, providing 72.1 % of the energy while oil, nuclear and renewable sources provide 22 %, 3 % and 1 % respectively. Although there is an increase in energy contribution by renewable energy sources, future energy plans in SA still depend mainly on coal as shown by the 2010 Integrated Resource Plan and construction of the Medupi power plant which is fuelled by "clean coal" (Baker, 2011; Hall, 2013). Hence the SA Coal Roadmap of 2013 predicts the international coal demand of 3500 million tonnes reported in 2012 to increase by a quarter by 2020 (Hall, 2013). Thus, coal processing wastes generation is also anticipated to increase proportionally to the increasing demand and so will the need for consistent and reliable characterisation data of potential environmental risks posed by of the wastes.

1.1.2. Coal Preparation and Waste Generation

51 and 49 % of SA's run-of-mine (ROM) coal is excavated from underground and open cast mining respectively. The ROM coal has total sulphur contents between 0.15-1.8 %, high contents of moisture and extraneous mineral matter (often termed ash) typically 20-40 %. The extraneous mineral matter consists of dirt bands in the seam, shales, sandstones and rocks from the seam's roof and floor, pyrite

(the major form of sulphur), calcite and other minerals deposited in the coal seam after the coal formation. These materials on combustion will form ash, emit hazardous gases and particulate matter. As a result of the high extraneous mineral matter and moisture content, the ROM coal has low heating values; calorific values (CV). Thus the coal has to be beneficiated to lower the ash (to below 15%) and sulphur (to below 0.6 %) and increase CV (to above 24.7 MJ/kg) to comply with the international market product specifications (Eberhard, 2011). The ROM coal also contains elements which are often grouped based on their weight concentration into major elements if the concentration exceeds 0.1 %, minor elements if it ranges between 0.01-0.1 % or trace elements if it is below 0.01 % (Speight, 2005). The major, minor and trace elements may occur in both the organic and inorganic components of coal in concentrations that are toxic to flora and fauna. As the coal cleaning process removes most of the ash-forming minerals from the coal, so are the elements occurring in the ash-forming minerals removed, generating coal wastes with higher ash content and elemental concentration than the ROM coal. The elevated concentration of the elements in the coal waste increases the environmental risk posed by the coal wastes, therefore adequate analysis and evaluation techniques are required for routine element risk characterisation (Speight, 2005; Ward, 2002).

The coal preparation process to produce clean coal usually involves two major operation units, screening and beneficiation (generally termed washing). Screening is used for the separation of the coal particles of different sizes into groups of definite maximum and minimum size limits. The screened material can be directly sold or further processed by washing or beneficiation if the screening alone produces coal that does not meet the product specifications. A typical South African washing plant employs density medium separation (DMS) to beneficiate the coal from the undesirable and detrimental gangue (mainly sulphur and ash/extraneous mineral matter) based on the difference in specific gravities between coal (1.2 – 1.4) and mineral matter (2-5) (Speight, 2005; Ward, 2002). In addition to improving the environmental performance and CV of the "clean coal" washing also improves the caking properties of metallurgical coal and maintains a uniform size and composition in the coal.

According to Prevost (2010), generally, 60 % of the 312 Tonnes of crushed ROM coal produced in SA is washed while the remainder is screened (Figure 2). Only 68 % of the ROM coal fed to the washing process is deemed market suitable after washing, while the rest reports in the waste stream, On the other hand, over 97 % of the material fed to the screening process meets the specifications required for market coal. While the remainder of the material is classified as waste. Overall, the cleaning processes typically produce "clean" coal and coal wastes which are 80 % and 20 % respectively of the crushed ROM.

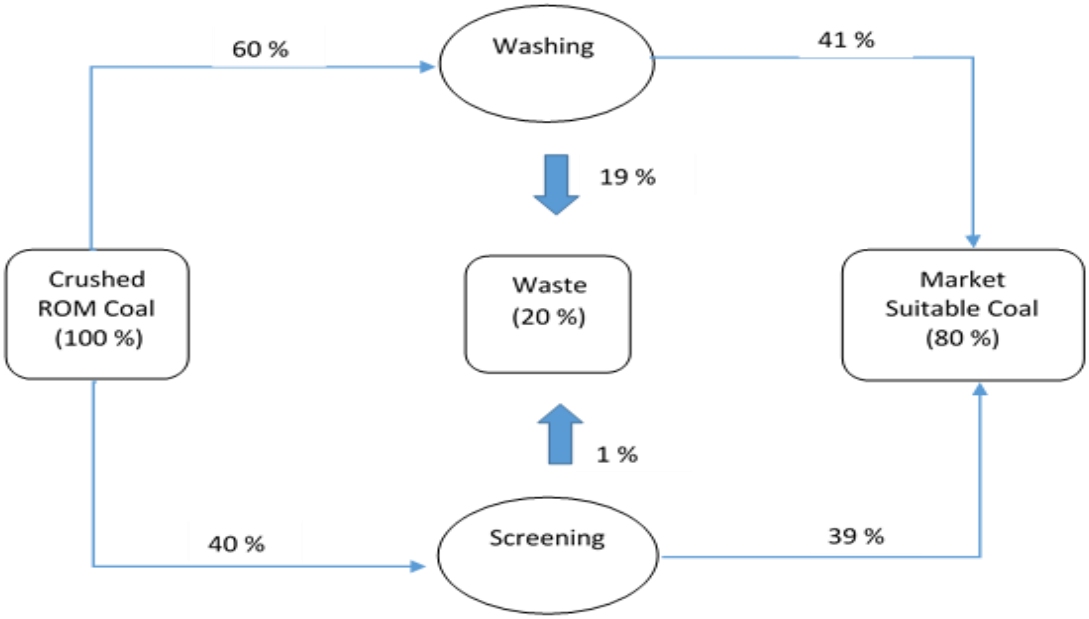

Figure 2 South African coal chain showing the distribution of mined coal processing (Prevost 2010)

The emergence of new technology, increase in demand for high-quality coal by the consumers, strict environment and waste management legislation and depletion of quality and reserves has changed the coal preparation methods over the years. A typical South African coal preparation process flowchart is shown in Figure 3 (Reddick, 2006). Due to near-density material in SA coals, coarse coal is washed by DMS technology such as the Wemco drum separators. Intermediate coal is typically washed in dense medium cyclones to separate the gangue and coal of different densities. On the other hand, spiral concentrators are commonly used for beneficiation of fine coal in SA following an increase in fines production because of mechanised mining (The South African Coal Processing Society, 2011). In the earlier coal processing days, froth floatation was only applied to Natal coking coal but some plants in different coalfields in SA now beneficiate ultra-fine coal through froth flotation. The high moisture content in beneficiated fines and ultra-fines is removed usually by thickening and/or complex dewatering and drying processes to produce clean, dry coal of high CV and recover process water (SACRM, 2011).

The waste from the coal preparation process is often termed “discards” but discards are commonly coal wastes generated by processing of coarse (> 25mm), intermediate /middling coal (1 -25 mm) and fines (0.15 – 1 mm). Waste from beneficiation of ultra-fine coals (<0.15 mm) is commonly termed slurry or ultra-fine coal waste instead of discards (Department of Minerals and Energy, 2001; Horsfall, 1980; Reddick et al., 2007). It is important to note that both discards and slurry from the washing process have typically high contents of the undesirable and detrimental ash and sulphur (refer to Table 1). While discards are compacted, piled into dumps which are then covered with soil and plant vegetation, ultra-fine coal wastes are either used as backfilling of underground mines or disposed of in slurry dams or together with discards in the dumps (SACRM, 2011).

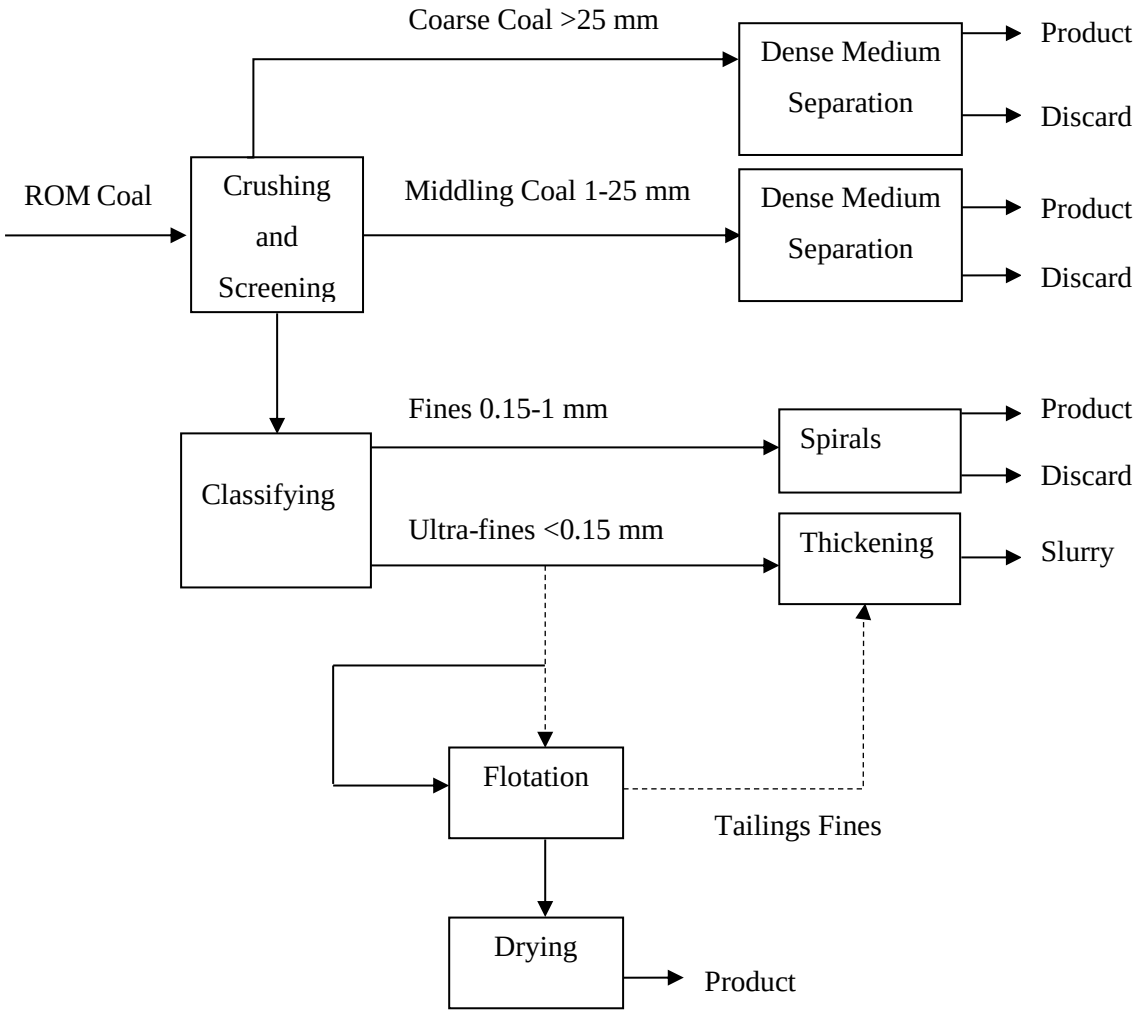

Figure 3 Typical coal preparation process in South Africa (adapted from Reddick (2006))

Table 1 Typical discards and ultra-fines quality as adapted from SA department of minerals and energy (DME) (2001)

	Discards	**Ultra-fine/ Slurry**
Ash	30-60 %	10-50%
Caloric Value	11-20 MJ/kg	20-27 MJ/kg
Fixed Carbon	18-42 %	41-56 %
Sulphur	1-5 %	2% and below
Volatile Matter	18- 24 %	17-27 %

Global requirements for sustainable waste management practices and restrictive waste management legislation operative in SA has prompted the recovery of part of the coal waste mainly for residual coal. In some plants in SA, discards and fines are re-processed and used for both local and international power generation (Department of Minerals and Energy, 2001; Eberhard, 2011). Coal waste dumps have been reported to be reclaimed in KwaZulu Natal Province for re-use in thermal, metallurgical and

construction purposes (Zhao 2012). However, value recovery of the major components of the coal processing waste has not been fully exploited. Such components include kaolinite, pyrite and limestone. They can be used as raw material in other processes such as in the formation of ceramics, molecular sieves, fertiliser and mineral wool manufacture (Department of Minerals and Energy, 2001; Fan et al., 2014).

1.1.3. Environmental Impacts of Coal Wastes

The disposed of wastes from coal processing have been shown by several researchers to pose environmental impact challenges when not managed properly (Bell et al., 2001; Department of Minerals and Energy, 2001; Eberhard, 2011; Pone et al., 2007; Reddick et al., 2007; Zhao, 2012).The potential environmental impacts associated with coal wastes have been highlighted by a number of previous researchers (Bell et al. 2001; Department of Minerals and Energy 2001; Kotelo 2013; McCarthy 2011; Opitz et al. 2015; Pone et al. 2007; Reddick et al. 2007; Zhao 2012). These impacts include disturbance of biodiversity, restriction on agriculture activities, degradation of water quality from acid rock drainage (ARD) toxic elements and salts, as well as air pollution resulting from burning of coal dumps and wind dispersed dust. According to Finkelman and Gross (1999), most of the impacts largely compromise human health through the mobilisation of toxic elements in the human system. The toxic elements are mobilised through various processes which include leaching into water bodies and combustion of waste piles (Finkelman, 1999).

Water Pollution from ARD

A major impact associated with coal mining is water pollution from ARD and its associated high levels of dissolved elements and salts (Munnik, 2010). Some researchers have shown discards in dumps (including rehabilitated dumps) also generate ARD, adding to the water pollution challenges SA is facing (Bell et al., 2001; Munnik, 2010; Zhao, 2012). According to Oelofse (2008), coal discard dumps and tailings are some of the biggest surface sources of ARD that pollutes water. The ARD and its associated toxic elements and salts from the coal waste in the dumps and the tailings dams can seep and pollute underground water sources (Oelofse, 2008). Coal mining activities including coal processing in the Witbank, Ermelo and Highveld coalfields contributes to water pollution reported in the Olifants and especially the Vaal River basins (Bell et al., 2001; Munnik, 2010; Oelofse, 2008). According to McCarthy (2011), the impact on these two water catchments is significant to the extent of being a great concern for SA's future generations. Thus, Eberhard (2011) states, "further developments of the coal industry are likely to cause permanent and costly water degradation in the central basin."

ARD occurs from the oxidation reaction of the coal wastes' pyritic sulphur in the presence of moisture resulting an increase in acidity (H^+) and production of $Fe(OH)_3$ and sulphates. Buffers like $MgCO_3$, $CaCO_3$, often present in coal discards neutralise the acid generated from the ARD reaction producing

salts ($CaSO_4$, $MgSO_4$ and $FeSO_4$) (Munnik, 2010). Owing to the acidity of the generated solution, inorganic elements and the salts are dissolved in surface water and can reach concentrations that are toxic to flora and fauna. The reported elements from ARD produced by coal wastes are Cd, Cu, Cr, Mn, Pb, As, Co, Fe, Al, Mg and U (Bell et al., 2001; Munnik, 2010). According to Oelofse (2008), lack of reliable data of ARD potential risks from coal mining activities (which include processing) exists and there is a need for risk evaluation and development of mitigation measures.

Air Pollution from Coal Waste Dumps

Air pollution impacts occur from toxic elements and fugitive emissions from the self-heating of the coal waste dump which occurs when coal, carbonaceous shales and pyrite are oxidised generating enough heat to enhance the combustion process. The spontaneous combustion can mobilise toxic elements such as As, Hg, Zn, Cu, Fe, Ge, Pb (Bell et al., 2001; Pone et al., 2007). The gases which form most of the emissions include CO and CO_2 which are infamous for causing the greenhouse effect which results from entrapment of solar radiation in the atmosphere leading to global warming challenges. Other gases emitted are SO_2 and NO_2 which on exposure to atmospheric humid air will react to form smog and acid rain on further oxidation and reaction with water vapour (Bell et al., 2001; Pone et al., 2007; Zhao, 2012). Another cause of air pollution besides spontaneous combustion is windblown coal waste dust as reported by Munnik (2010). The air pollution from coal waste can cause human health impacts in the form of respiratory disease such as asthma, pneumoconiosis and lung cancer (Weston, 2011).

Land Impact of Coal Waste Dumps

According to the Department of Minerals and Energy (DME) 2001 report, "the coal wastes have accumulated to over 1 billion Tonnes covering 4011 hectares, constraining the land from other beneficial uses such as agriculture." The report also shows the distribution of discard dumps to be concentrated in Mpumalanga and KwaZulu Natal (KZN). The disposed waste change the composition of the soil in the surrounding areas making the soils unsuitable for plant growth and a source of water pollution as rainwater percolates through it (Bell et al., 2001; Munnik, 2010). Soil quality degradation also occurs from the deposition of particulate matter from spontaneous combustion and dissolved solids in ARD solutions (Bell et al., 2001; Pone et al., 2007; Zhao, 2012). Characterising coal wastes for ARD potential, elements and salts deportment, and the physiochemical properties also provide data on soil pollution potential risk (Finkelman and Gross, 1999).

1.1.4. Characterisation Techniques for Coal Wastes

The characterisation methods used to evaluate the environmental risk for coal waste comprises of various tools and evaluation techniques which can be grouped into:

- Analytical methods
- Geochemical ARD tests
- Elements risk assessment tools

- Predictive modelling

There are many techniques and tools for analytical determinations, each having different advantages and disadvantages (Huggins, 2002; Pinetown et al., 2007; Speight, 2005). The analytical methods are used to determine the mineralogy, elemental composition, species and their occurrences and physical properties. The analytical data links the composition, geology and environmental behaviour of the ore or its waste. Preliminary characterisation of mineralogical and chemical properties of coal wastes at UCT by Kotelo (2013) and Opitz et al. (2015) was limited to two samples of ultra-fine slurry and did not include a full assessment of the concentration and potential risks associated with minor and trace elements. Furthermore, the study by Kotelo (2013) highlighted a number of shortcomings with respect to the reliability and accuracy of certain methods, particularly the speciation of sulphur, the mineralogical analysis of mineral matter content and the use of conventional static methods for classification of acid rock potential (Kotelo 2013).

Geochemical ARD tests basically screen the samples on their acid-producing capacity and acid neutralising capacity. These tests are either static or biokinetic, with the static tests conducted under worst-case chemical scenarios and biokinetic tests under laboratory conditions imitating disposal conditions. Although the static tests are short-term and inexpensive in contrast to biokinetic tests, their major disadvantages are over or underestimating the ARD potential (Parbhakar-fox and Lottermoser 2015; Smart et al. 2002). One of the reasons for this inaccuracy is the use of the total sulphur content which overestimates the maximum producing acidity (MPA) of the coal waste since not all sulphur species in the coal wastes are acid-forming as was shown by Kotelo (2013).Another reason could be the effect of organic acids on the net acid generation capacity (Miller, 2008; Stewart et al., 2009). In order to correctly classify the ARD potential from static tests, the MPA needs to be calculated from acid-producing sulphur species only and the acidity from organic acids taken into account (Kotelo, 2013; Miller, 2008).

Element risk assessment entails studying the availability, mobilisation and conditions at which the different elements within the ore or waste exist. The elements are ranked and scored against the environmentally allowed concentrations. The leaching behaviour of elements and salts under ARD leach tests in addition to appropriate sequential chemical extractions allow the assessment of the long-term environmental effects of coal waste minerals. From this assessment elements of environmental concern are identified and can be monitored (Broadhurst et al., 2009; Broadhurst and Petrie, 2010; Opitz et al., 2015). A study by Opitz et al. (2015) found Fe and Ca in two ultra-fine coal wastes to be mobilized under ARD tests but the study was limited to major elements and trace elements were not evaluated. The risk of the toxic elements deported under ARD was also not assessed.

Reliable characterisation data is necessary to design and implement adequate management strategies to minimize the environmental and human health risks posed by the coal waste. Insufficient and inadequate characterisation tools and evaluation techniques can lead one to underestimate or even overestimate contamination of water bodies and soil by ARD and associated toxic elements and salts, hence reducing the implementation of mitigation interventions (Miller, 2008; Oelofse, 2008). Several researchers have highlighted that incorrect assessment of the environmental risk potential results either exposure of the environment to the impacts or unnecessary implementation of impact mitigation measures (Belaid et al. 2013; Finkelman and Gross 1999; Jeffrey 2005; Mohring 2001; Pone et al. 2007; Stewart et al. 2009; Zhao 2012;).

1.2. Problem Statement

Coal processing wastes disposed of in dumps and slurry dams can cause adverse impacts on water, soil, air, human health and biodiversity. However, these wastes are generally poorly characterised and the associated risks not well understood. This is at least partly due to the current uncertainties and deficiencies associated with current characterisation tools, many of which have been developed for the characterisation of wastes from hard rock ores. Furthermore, little attention has been paid to the characterisation of potential element toxicity and salinization risks associated with coal processing wastes.

1.3. Project Objectives and Scope

The overarching objective of this project is to investigate the reliability of relevant characterisation techniques and interpretation of characterisation data in terms of the environmental risk potential of coal wastes. The project entailed laboratory-scale characterisation of the physio-chemical and acid generating properties of two ultra-fine coal waste and one discard waste sample. Selected analyses were also conducted on a certified coal standard to evaluate the accuracy and repeatability of analytical methods used in this study. Analytical data was subsequently used to evaluate the potential water and soil-related risks associated with environmentally available elements and salts in the coal processing wastes, using a simple score and ranking protocol.

It is envisaged that the characterisation and risk potential data generated through application of these techniques will facilitate the reliable prediction of environmental risks and liabilities associated with coal processing wastes, and ultimately the justification and selection of effective impact mitigation measures. In addition, the characterisation data and evaluated potential risks helps in designing and planning appropriate coal beneficiation circuits and environmentally sustainable waste management strategies. Reliable characterisation data can also help to identify opportunities for potential value recovery and provide a basis to formulate policies and regulations for environmental management. However, the evaluation of accuracy and repeatability of analyses in this project relates to the methods applied by selected analytical laboratories and should not be considered to be indicative of the reliability

of specific analytical techniques per se. Furthermore, the samples were grab samples at specific sites and are not necessarily representative of all coal processing waste generated in South Africa.

1.4. Dissertation Structure

The thesis is structured in six main sections (shown in Figure 4). Chapter 1 introduces the study, giving an overview of the problem, purpose of the study, background and context of the research. The second chapter contains critical literature review of related work in terms of achievements, findings and knowledge gaps, then formulate key questions to address the research problem. Then Chapter 3 entails the research approach, materials and methods to answer the research questions made from literature reviewing. After applying the methodology, the findings from the physiochemical characterisation are presented and discussed in Chapter 4, while the risk assessment results are presented and discussed in Chapter 5. The final chapter summarises the key results, outline their significance in the research context and make recommendations based on the findings.

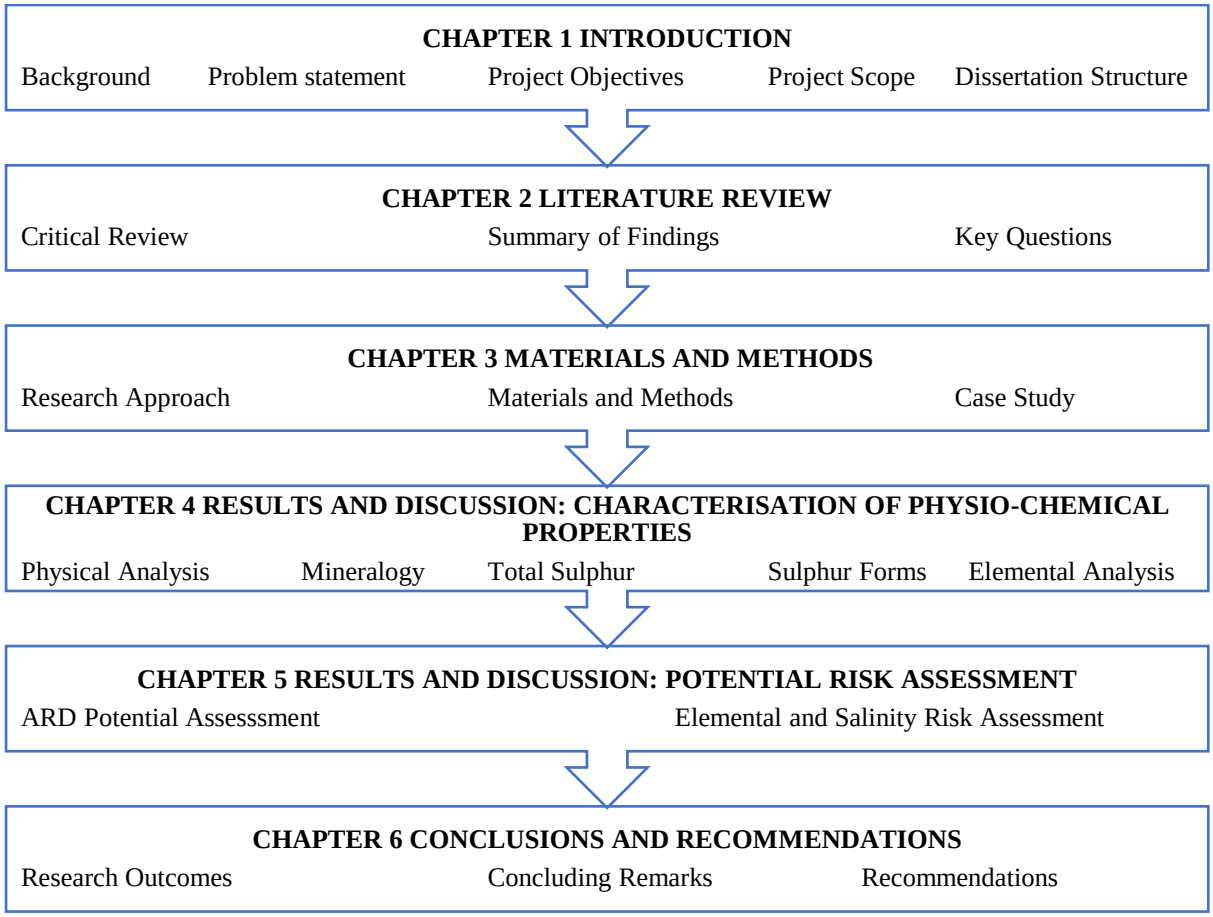

Figure 4 Schematic showing structure of thesis

CHAPTER 2

LITERATURE REVIEW

This chapter provides a detailed review and assessment on the currently available literature on the compositions and characteristics of coal and coal processing wastes; associated acid rock drainage and related environmental risks; as well as the relevant characterisation methods and techniques. From the literature, research keys questions are developed to address the identified knowledge gaps.

2.1. SA Coal Geology

The SA coal reserves are distributed in 19 coalfields (shown in Figure 5), which cover a total area of 9.7 million hectares. Most of the coal fields are located in the KZN, Mpumalanga, Limpopo and the Free State. The northern coalfields have coal of mixed Ecca and Beaufort group while rest of the coalfields are mainly of the Ecca group of Vryheid formation except the Molteno and Somkhele coalfields which are of Molteno formation. (Hancox and Goetz, 2014; Jeffrey, 2005). According to Jeffrey (2005), "Waterberg, Witbank, and Highveld coalfields contain about 70% of South African coal. Ermelo, Free State and Springbok Flats coalfields also contain significant quantities." (Jeffrey, 2005). The coal seams that are largely mined consist of both bright and dull coal of varying quality but mostly of bituminous rank. The coal seams are characterised by dolerite sills and dykes formed from molten igneous rocks intrusions, while the seam floors and roofs consist of sandstones, carbonaceous shale, siltstone as well as minor conglomerates (Hancox and Goetz, 2014; Pinetown et al., 2007). Due to depletion of higher quality coal reserves in the central Karoo basin, future exploitation is anticipated to be mainly in the Karoo age peripheral basins particularly the Waterberg coalfield. The Waterberg coalfield is characterised by narrow coal seams that are intimately mixed with mineral matter resulting low-grade coal with high mineral matter proportions which need to be removed through the beneficiation process (Hancox and Goetz, 2014; Pinetown et al., 2007).

2.2. Composition and Characteristics of Coal and Coal Processing Wastes

The maturity of SA coals rank from bituminous to anthracite with negligible quantities of sub-bituminous coal, and the rank increases with increasing igneous intrusions which supplied heat of metamorphosis during coal formation (Jeffrey, 2005). Higher rank signifies lower volatile matter and moisture content but higher fixed carbon and heating values. Low-rank bituminous coal is largely mined from the Free State coalfields, while higher rank bituminous coal is supplied by the Witbank coalfield. The coalfields in KZN supply anthracite coal of the highest rank in SA (Jeffrey, 2005; Pinetown et al., 2007). South African coals like the rest of the Southern hemisphere coals are generally characterised by high ash, low sulphide, chloride and trace elements (Wagner and Hlatshwayo, 2005). According to

Bergh (2013), the high ash content substantiates the environmental concerns for the total elemental content including sulphur in SA coals and the coal preparation wastes.

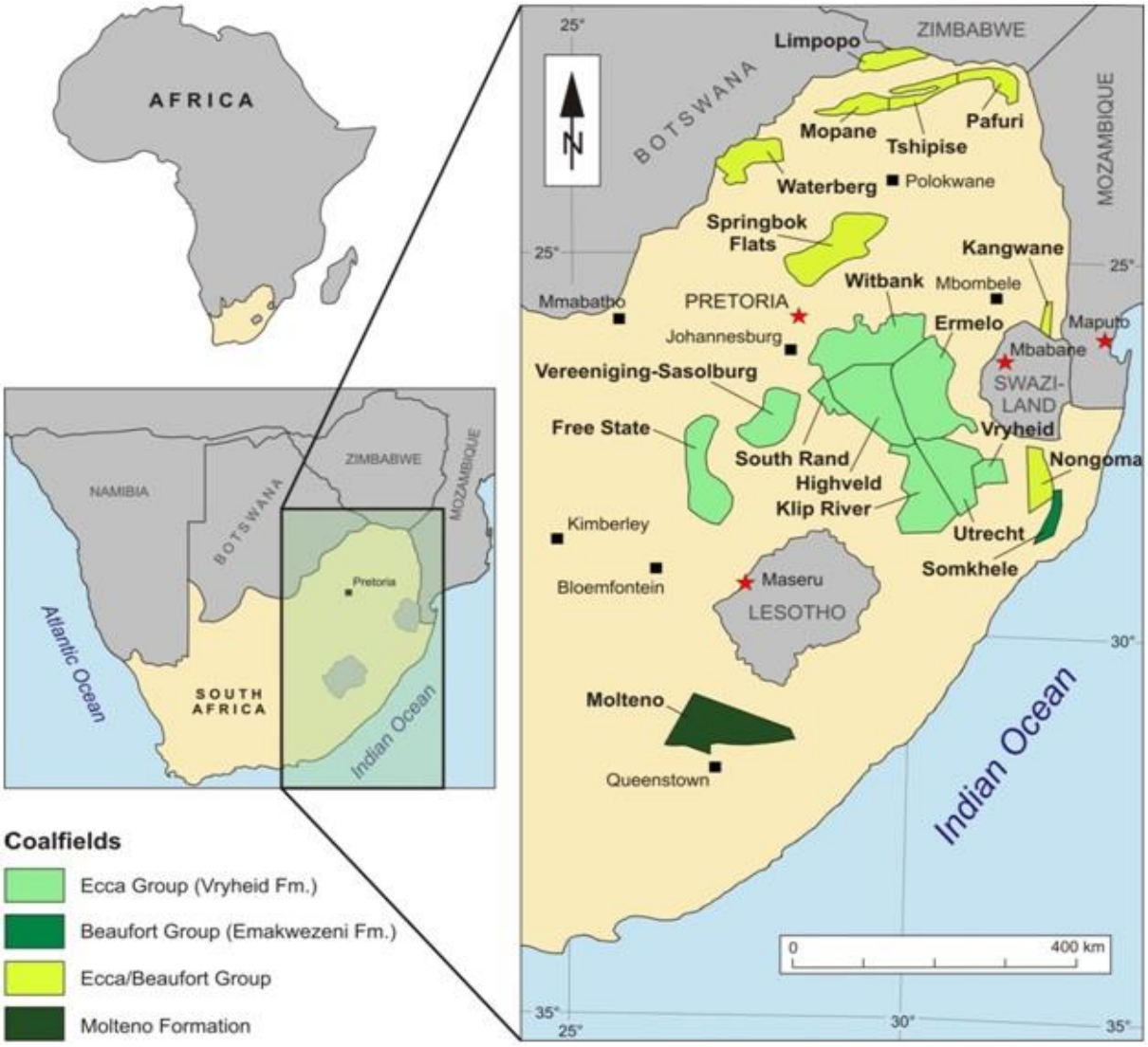

Figure 5 The South African coalfields (Hancox and Goetz, 2014)

2.2.1. Mineralogical Composition of Coal and Coal Processing Wastes

The SA coals have generally high ash in situ content (classified as extraneous coal if ash exceeds 60 wt. %, carbominerite if organic content is 40-80 wt. % and ash 20-60 wt. %, dull or bright coal if ash is less than 20 %) which has to be removed during the beneficiation process (van Alphen, 2007; Falcon and Ham 1988). According to Speight (2005) and Ward (2002), the mineral matter common in coals worldwide occurs in six distinct phases; aluminosilicates (clay), sulphides and sulphates, phosphates, carbonates, silicates and other mineral phases depending on deposition and maturity of coal (summarized in Table 2).

Pinetown et al. (2007), approximated the mineral matter content in Witbank and Highveld coal to be 8-35 % weight from XRD analysis. Eberhard (2011) reported the ash content of SA coals can be as high as 65%. The common aluminosilicates are kaolinite [{$Al_4Si_4O_{10}$ $(OH)_2.H_2O$} 20-70%] and illite [{$KAl_2(AlSi_3O_{10})(OH)_2$} <16%]. Quartz [{$SiO_2$} 20-30%] is also a common mineral, while other usual silicates are muscovite [$K_2Al_4(Si_6Al_2O_{20}$ $(OH)_4$] and microcline ($KAlSi_3O_8$) (Pinetown et al., 2007).

Table 2 Common mineral phases in coal from various sources (adapted from Ward (2002))

Silicates
- Quartz (SiO_2)
- Chalcedony (SiO_2)
- Muscovite [$K_2Al_4(Si_6Al_2O_{20}$ $(OH)_4$]
- Microcline ($KAlSi_3O_8$)

Aluminosilicates (Clays)
- Kaolinite ($Al_4Si_4O_{10}$ $(OH)_2.H_2O$)
- Illite ($KAl_2(AlSi_3O_{10})(OH)_{2)}$
- Smectite ($Na_{0.33}(Al_{1.67}Mg_{0.33})$ $Si_4O_{10}(OH)_2$
- Chlorite $(MgFeAl)_6(AlSi)_4O_{10}(OH)_8$
- Feldspar($KAlSi_3O_8$)
- Plagioclase ($NaAlSi_3O_8$)
- Anorthite ($CaAl_2Si_2O_8$)
- Tourmaline$(Na(MgFeMn)_3Al_6B_3Si_6O_{27}(OH)_4)$
- Analcime ($NaAlSi_2O_6.H_20$)
- Clinoptilolite ($(NaK)_6(SiAl)_{36}O_{72}.20H_20$)
- Heulandite ($CaAl_2Si_7O_{18}.6H_20$)

Phosphates
- Apatite ($Ca_5F(PO_4)_3$)
- Crandallite ($CaAl_3(PO_4)_2(OH)_5.H_20$)
- Gorceixite ($BaAl_3(PO_4)_2(OH)_5.H_20$)
- Goyazite ($SrAl_3(PO_4)_2(OH)_5.H_20$)
- Monazite $(Ce,La,Th,Nd)PO_4$)
- Xenotime $((Y, Er)PO_4)$

Sulphates
- Gypsum ($CaSO_4.2H_20$)
- Bassanite ($CaSO_4.1/2H_20$)
- Anhydrite ($CaSO_4$)
- Barite ($BaSO_4$)
- Coquimbite ($Fe_2(SO_4)_3.9H_20$)
- Rozenite ($FeSO_4.4H_20$)
- Szomolnokite ($FeSO_4.$ H_20)
- Natrojarosite $NaFe_3(OH)_6(SO_4)_2$
- Thenardite (Na_2SO_4)
- Glauberite $Na_2Ca(SO_4)_2$
- Hexahydrite ($MgSO_4.6H_20$)
- Tschermigite ($NH_4Al(SO_4)_2.12H_20$)
- Epsomite ($MgSO_4.7H_2O$)
- Melanterite ($FeSO_4.7H_2O$)
- Jarosite ($KFe_3(OH)_6(SO_4)_2$)
- Alunite ($KAl_3(SO_4)_2(OH)_6$

Carbonates
- Calcite ($CaCO_3$)
- Aragonite ($CaCO_3$)
- Dolomite ($CaMg(CO_3)_2$)
- Ankerite ($(Fe,Ca,Mg)CO_3$)
- Siderite($FeCO_3$)
- Dawsonite ($NaAlCO_3(OH)_3$)
- Strontianite ($SrCO_3$)
- Witherite ($BaCO_3$)
- AlsTonite ($BaCa(CO_3)_2$)

Sulphides
- Pyrite (FeS_2)
- Marcasite (FeS_2)
- Pyrrhotite ($Fe_{(1-x)}S$)
- Sphalerite (ZnS)
- Galena (PbS)
- Stibnite (SbS)
- Millerite (NiS)

Others
- Anatase (TiO_2)
- Rutile (TiO_2)
- Boehmite (Al.O.OH)
- Geothite ($Fe(OH)_3$)
- Crocoite ($PbCrO_4$)
- Chromite $(Fe,Mg)Cr_2O_4$)
- Clausthalite (PbSe)
- Zircon ($ZrSiO_4$)

Carbonates common in SA coals are calcite ($CaCO_3$) <2 %; dolomite {$CaMg(CO_3)_2$} <2 %; siderite {$FeCO_3$} <3 %}. Other common minerals are apatite, [$Ca_5(PO_4)_3$ (OH,F,Cl)], and rutile (TiO_2) (van Alphen, 2007; Hancox and Goetz, 2014; Pinetown et al., 2007; Wagner and Hlatshwayo, 2005). The mineral matter that occurs intimately with pure coal is termed intrinsic or inherent mineral matter and

seldom exceeds 1 % by weight (Speight, 2005). The inherent mineral matter is reportedly not easily removed by washing unlike the extraneous matter (Speight, 2005; Vassilev and Vassileva, 1997; Ward, 2002; Wagner and Hlatshwayo, 2005). The mineral matter in coal can be classified according to transportation and deposition during coal formation. The mineral matter deposited by wind and water in the peat is called allogenic or detrital and that which formed at the place, authigenic. According to Vassilev and Vassileva (1997), sulphides, sulphates, chlorites, carbonates, some phosphates and some clays (mostly kaolinite) are authigenic. On the other hand, the rock-forming minerals quartz and other silicates, feldspars, mica, Fe-oxyhydroxides and other oxyhydroxides and some clay minerals (mainly illite and montmorillonite) are detrital. Many of the coals trace elements have an affinity for organic matter and authigenic matter (Vassilev and Vassileva, 1997).

The mineralogical compositions in coal preparation wastes will reflect but vary in concentration to the parent coals depending on washability of the coal (Speight, 2005). The DME (2001) inventory showed the discards from dense medium separation and ultrafine tailings from floatation (see Figure 3 in Chapter 1) to which the majority of the gangue in the ROM coal will report, have higher ash forming minerals and sulphur concentration compared to the average reported in ROM coal. On the other hand, the ultrafine coal slurry which has not gone through floatation will be more representative of the ROM coal. Bergh (2013) also showed washing could remove 82 % of the ash and 6-75 % of some trace elements. However little is known in the publicly available literature about the mineralogical compositions of the waste generated from processing SA coals. Ash contents of coal processing wastes characterised in previous work at UCT shown in Table 4, confirm ash contents within the 10-50 % average range typical of SA coal waste reported by the DME (2001).

Table 3 Ash content of South African ultrafine coal wastes from collieries in Waterberg, Witbank (Iroala 2014) *and Middelburg* (Kotelo 2013) *compared to the national average from DME (2001).*

Mineral	**DME (2001) Average (%)**	**Ash content (mass % of whole coal)**		
	Ultrafine/ Slurry	**Waterberg**	**Witbank**	**Middelburg**
Ash	10-50	49.20	40.20	33.50–43.20

Mineral composition results from the previous characterisation by Kotelo (2013) and Iroala (2014) presented in Table 4, show kaolinite and quartz as the major phases of mineral matter in Waterberg and Middelburg ultrafine coal wastes. The same mineral phases which were reported to be also dominant in ROM coal in Section 2.2.1 (Pinetown et al., 2007).

Table 4 Mineralogical composition of South African ultrafine coal wastes from collieries in Waterberg (Iroala 2014) *and Middelburg* (Kotelo 2013)

Mineral	**Mineralogical composition (mass % of whole coal)**	
	Waterberg	Middelburg
Quartz	20.17	17.90-23.90
Kaolinite	18.69	19.80-24.90
Calcite	1.96	2.20-7.00
Dolomite	3.93	0.50-1.20
Siderite	<1.00	1.40-4.90
Pyrite	<1.00	2.60-7.90
Gypsum	2.46	1.00-2.00
Jarosite	<1.00	<1.00
Epsomite	<1.00	<1.00

2.2.2. Sulphur Content

According to Hancox and Goetz (2014), the common sulphur range of South African coals is 0.4 – 1.8 % but high values (up to 15 %) have been recorded. Pinetown et al. (2007) reported sulphur ranges between 0.15 and 8.0 % in Highveld and Witbank coals. Sulphur occurs in coal mainly in three forms, organically bound (usually less than 3 %), inorganic sulphides and sulphates and rarely occurs as free sulphur (Speight, 2005). The main sulphides are the dimorphs; pyrite (FeS_2) which has a fambroid structure and marcasite (FeS_2) which is orthorhombic crystalline. These sulphides are largely responsible for ARD in coal. Kalenga (2011) reported an average of 45 % of the total sulphur to be pyrite in six SA coals from Mpumalanga and Free State. Other usual inorganic sulphides occurring in small quantities in coal are pyrrhotite, sphalerite, galena and chalcopyrite.

The inorganic sulphates rarely exceed 0.1 % except in weathered coal samples (Speight, 2005). In fresh coal samples, the dominant sulphates are usually gypsum ($CaSO_4.2H_2O$), barite ($BaSO_4$), epsomite ($MgSO_4.7H_2O$) and melanterite ($FeSO_4.7H_2O$). The sulphates jarosite ($KFe_3(OH)_6(SO_4)_2$) and alunite ($KAl_3(SO_4)_2(OH)_6$) occur in trace amounts and are associated with weathered or oxidised coals. Elemental (free) sulphur is usually produced during coal weathering (Speight, 2005; Stewart et al., 2009). Organic sulphur compounds are generally grouped into thiophenes, mercaptans, disulphides and aliphatic and aryl sulphides. The organic sulphur is bound in the coal matrix during the formation period and therefore hard to remove during washing, while the inorganic sulphur deposited along cleats and cracks is easily washed off (Gluskoter, 1974; European Commision, 1998; Speight, 2005). The pyritic and organic sulphur in SA coal increases with increasing vitrinite from west to east geologically (Hancox and Goetz, 2014).

The previous characterisation carried at UCT (results presented in Table 5) found higher total sulphur contents in Waterberg and Witbank ultrafine coal wastes compared to the DME (2001) average range of 2 % and below but the Middelburg coal waste was within the average range. The sulphur speciation revealed pyrite as the major form of sulphur in ultrafine coal processing wastes forming 48-80 % of the

total sulphur. The characterisation also showed the presence of 4-30 % organic and 6-34 % sulphate sulphur, with gypsum, epsomite and jarosite being the common sulphates with contents varying with the degree of oxidation of the samples (Iroala, 2014; Kazadi Mbamba et al., 2012; Kotelo, 2013).

Table 5 Total sulphur and sulphur forms in South African ultrafine coal wastes from collieries in Waterberg, Witbank (Iroala, 2014) *and Middelburg* (Kazadi Mbamba *et al.*, 2012; Kotelo, 2013)

Sulphur Form	**Content (mass % of whole coal)**		
	Waterberg	Witbank	Middelburg
Total Sulphur	2.04	4.18	0.80 -1.10
Sulphide Sulphur	0.98	2.58	0.64-1.05
Organic Sulphur	0.56	0.16	0.25-0.51
Sulphate Sulphur	0.50	1.44	0.05-0.50

2.2.3. Elements Content in Coal and Coal Processing Wastes

As mentioned in Chapter 1; ROM coal also contains elements that are commonly called the major elements (>0.1 wt. %) minor (0.1-0.01 wt. %) and trace elements (<0.01 wt. %) (Vassilev and Vassileva, 1997; Speight 2005). The concentration of these elements differs between coals but the usual major elements are C, O, H, Si, Al, S, N and Fe, minor elements Ca, K, Mg, Ti, Na, P, Mn, Cl, Ba and St and trace elements As, Pb, Hg, Ni, V, Be, Cd, Cr, Cu, Mo, Zn, Se Rd, etc. Elements that concentrate in metallic iron are called siderophile elements (such as Sc, V, Cr, Ni, Co, Os and Ir), chalcophile elements concentrate in sulphides (e.g. Se, As, Zn and Cd) and lithophile elements concentrate in silicate phases, e.g Rb, Sr, Ba, Nb, Ta, Th, U and REE. Sulphides are the dominant carriers of trace elements in coal; thus, sulphides together with organic matter and clay minerals control the distribution of trace elements in coal. Quartz and feldspars are diluents of the concentration of the trace elements in coal (Vassilev and Vassileva, 1997). Although present in relatively low concentration levels, many of the (minor) and trace elements are highly toxic and will pose a risk to fauna and flora if released into the environment (Finkelman and Gross, 1999). Table 6 summarizes the typical concentrations ranges and modes of occurrence of environmentally sensitive elements in SA coals.

*Table 6 Environmentally Sensitive Elements Composition and Occurrences (Finkelman and Gross, 1999)*** in SA Coals (Highveld, Witbank and Waterberg Coal)(adapted from Bergh (2013)[*]) and Highveld Coals range (adapted from Wagner & Hlatshwayo (2005)[**])*

Element	SA Coals Range[*] (ppm)	Highveld Coals Range[**] (ppm)	***Modes of Occurrence
Antimony	n/a	<0.094-0.3	Organic association, pyrite and accessory sulphides
Arsenic	3.1-11.4	1.0-4.7	Pyrite
Barium	n/a	n/a	Barite and other Ba-bearing minerals
Beryllium	n/a	n/a	Organic association
Boron	n/a	n/a	Organic association
Cadmium	0.17-0.6	0.05-0.51	Sphalerite
Chlorine	599-839	n/a	Chloride ions in pore water or adsorbed onto macerals
Chromium	0-0.016	23.0-69.0	Organic association, illites, chromites
Cobalt	n/a	5.0-12.0	Multiple associations
Copper	n/a	9.0-16	Chalcopyrite, pyrite
Fluorine	297-302	n/a	Various minerals
Lead	7-76	4.2-11.0	Galena
Mercury	0.12-1.3	0.04-0.27	Pyrite
Manganese	n/a	84-117	Carbonates: siderite and ankerite
Molybdenum	n/a	0.4-<5	Accessory sulphides, organic association
Nickel	n/a	12.0-23.0	Multiple associations
Phosphorus	n/a	n/a	Phosphates
Selenium	0.8-3	<0.5-1.5	Organic association, pyrite, accessory selenides
Silver	n/a	n/a	Sulphides
Thallium	n/a	n/a	Pyrite
Thorium	7.5-15	n/a	Monazite, xenotime, zircon, clay
Tin	n/a	n/a	Oxides and sulphides
Vanadium	27-96	23.0-37	Clays and organic association
Uranium	2.6-4.7	n/a	Organic association, zircon silicates
Zinc	0-0.56	8.0-19.0	Sphalerite

Previous research has shown SA coals from Klipriver, Sasolburg, Witbank and Eastern Transvaal generally have lower trace elements content compared to coals from USA, Germany, Belgium and Australia (Cairncross, 2001; Dale, 2006; Pinetown et al. 2007). However, a comparison of international coals in an ACARP report showed high values of Hg (>0.1 mg/kg) in South African export coals (Dale, 2006). Highveld coals were found to have more Cr than in most typical international coals but lower Cd, Cu, As, Mo, Pb, Se, Sb and Zn compared to global coal averages (Wagner and Hlatshwayo, 2005). The As, Cd, Pb, Hg, Se, V, Cl, F, U and Th contents of Highveld, Witbank and Waterberg coals (shown in Table 6) are also lower compared to international contents (shown in Table 8).

As in the case of minerals, the concentrations of the elements in coal processing wastes will be a function of their concentrations and forms in ROM and the nature of the processing operations. However, there is limited data available in the literature on the elements concentration, particularly trace elements composition in SA coal processing wastes. Characterisation from previous studies at UCT only characterised the major and minor elements and the results are presented in Table 7.

Table 7 Elemental composition of South African ultrafine coal wastes from collieries in Waterberg, Witbank (Sanyika and Ngcobo, 2014; Opitz et al., 2015) *and Middelburg* (Kotelo, 2013)

Element	**Chemical composition (mass % of whole coal)**		
	Waterberg	Witbank	Middelburg
Al	4.84	4.29	3.74-3.95
Si	n/a	n/a	8.52
Fe	3.94	3.78	1.40-1.46
Ca	3.66	0.90	1.07-1.19
K	0.63	0.16	0.22-0.24
Mg	n/a	n/a	0.08
P	n/a	n/a	0.10

2.3. Acid Rock Drainage and Related Impacts and Risks of Coal Processing Wastes

Discussions in Chapter 1 indicated that ARD is one of the most significant issues associated with coal mining and processing. Whilst underground and surface mine workings are a major source of ARD, coal stockpiles and coal waste deposits have also been reported to give rise to ARD generation (Bell et al., 2001; Munnik, 2010). A characterisation study using static acid-base accounting (ABA) tests on overburden and inter-burden coal samples from Waterberg coalfield showed 35-50 % of the samples to have a high risk for acid generation, while 30-40 % were evaluated as potentially non-acid-forming and the rest were shown to possess medium risk potential to generate acid (Deysel and Vermeulen, 2015). Pinetown et al. (2007) also evaluated the ARD potential of coal-bearing successions in the Witbank and Highveld coalfields using static ABA tests. The results showed all the samples with the exception of the unit between No.1 and No. 2 coal seams to be potentially acid generating. Ultrafine coal processing wastes, one from Witbank, and another from Middelburg coalfields were shown to be potentially acid-forming (PAF) by a combination of static ABA, net acid generation (NAG) and biokinetic tests in previous studies carried at UCT (Kazadi Mbamba et al., 2012; Kotelo, 2013; Opitz et al., 2015). Contrastingly a thickener feed ultrafine sample from Waterberg coalfield was shown to be potentially non-acid generating using the same combination of tests (Opitz et al., 2015). These results indicated that the acid generating behaviour of coals and coal processing wastes can vary quite considerably, even within the same coal mining region

As highlighted in Chapter 1 and in the previous sections, ARD pollution is normally associated with high salinity and elevated concentrations of elements. The composition data also show that coal and hence coal wastes contain a number of elements in varying concentration levels, which may become mobilised under the low pH conditions associated with ARD formation. In order to characterise the ARD risks of coal processing waste, the mechanisms and factors governing ARD and its associated elevated levels of salts and elements should be understood. Hence this section focuses on the mechanisms involved in ARD generation and the associated mobilisation of salts and elements.

2.3.1. ARD Formation

Pyrite is the major source of ARD formed from coal and coal processing wastes (Ahern et al., 2004). In ARD formation pyrite (FeS_2) oxidizes in the presence of water to ferrous ions (Fe^{2+}), acidic ion (H^+) and sulphates (SO_4^{2-}) as shown in equation 1. The ferrous is subsequently oxidized to ferric (Fe^{3+}) (equation 2), and acidity increases. At pH below 4.5, the solubility of ferric is more favourable which promotes oxidation of more pyrite according to the reaction shown in equation 3 (Ahern et al., 2004). The cyclic oxidation of pyrite and generation of ferric ions can continue for decades producing more acid and sulphates which can contaminate water bodies if not contained. However, if pH increases to above 3, the Fe^{3+} hydrolysis forms hydroxide precipitates and more acidity ions (equations 4 and 5) (Ahern et al., 2004; Parbhakar-fox and Lottermoser, 2015).

$$FeS_2 + {}^{7}/_{2}\,O_2 + H_2O \rightarrow Fe^{2+} + 2{SO_4}^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + {}^{1}/_{4}\,O_2 + H^+ \rightarrow Fe^{3+} + {}^{1}/_{2}\,H_2O \quad (2)$$

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

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

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+ \quad (5)$$

Although pyrite is the acid-producing sulphide with the highest capacity in coal and coal wastes, other sulphides such as galena, pyrrhotite, arsenopyrite and chalcopyrite are also acid-producing (as shown in equations 6-11) but with low capacity. Reactivity is in the order pyrrhotite> galena- sphalerite> pyrite-arsenopyrite> chalcopyrite if galvanic and biological interactions are not considered (Hansford and Vargas 2001; Nemati and Webb, 1997; Rohwerder et al., 2003; Yahya and Johnson, 2002).

$$(Fe_{(1-x)}S + ({}^{2-x}/_{2})O_2 + xH_2O \rightarrow (1-x)Fe^{2+} + {SO_4}^{2-} + 2xH^+ \quad (6)$$

$$FeAsS + {}^{7}/_{2}\,O_2 + 6H_2O \rightarrow Fe(OH)_3 + {SO_4}^{2-} + H_2AsO_4{}^{-} + 3H^+ \quad (7)$$

$$2CuFeS_2 + {}^{17}/_{2}\,O_2 + 5H_2O \rightarrow 2Cu^{2+} + 2Fe(OH)_3 + 4{SO_4}^{2-} + 4H^+ \quad (8)$$

$$ZnS + 2O_2 \rightarrow Zn^{2+} + {SO_4}^{2-} \quad (9)$$

$$PbS + 2O_2 \rightarrow Pb^{2+} + {SO_4}^{2-} \quad (10)$$

$$2MeS + 4Fe^{3+} + 3O_2 + 2H_2O \rightarrow 2Me^{2+} + 4Fe^{2+} + 2SO_4{}^{2-} + 4H^+ \quad (11)$$

Owing to a larger surface area compared to orthorhombic marcasite, the framboid form of pyrite is more prone to oxidation than its counterpart (Parbhakar-fox and Lottermoser, 2015; Parbhakar-fox et al., 2011; Smart et al., 2002; Stewart et al., 2009). As shown by Kotelo (2013), fine particle sizes (below 75 µm) have higher pyrite content, thus higher ARD generation capacity compared to coarser particles of the same sample. In natural disposal systems the ARD reactions are catalysed by acidophiles such as *Acidothiobacillus ferrooxidans* (Fe and S oxidizer), *Acidothiobacillus thiooxidans* (S oxidizer) and *Leptospirillum ferrooxidans* (Fe oxidizer) (Parbhakar-fox and Lottermoser, 2015).

The organic sulphur is presumed to be non-acid-forming in ARD reactions as well as commonly available sulphates in coal and coal wastes i.e. gypsum and epsomite (Miller, 2008). Alunite ($KAl_3(SO_4)_2(OH)_6$) and melanterite ($FeSO_4.7H_2O$) are some acid-forming soluble sulphates. Some secondary sulphates such as jarosite ($KFe_3(OH)_6(SO_4)_2$), and schwertmannite $Fe_8O_8(OH)_6(SO_4).nH_2O$ often found in oxidizing environments and weathered coal samples and can also produce acidity by direct precipitation and dissolution producing Fe hydroxides and oxides as shown in the equations 12-14 for jarosite (Parbhakar-fox and Lottermoser, 2015):

$$Fe^{3+} + K + 2SO_4{}^{2-} + 6H_2O \leftrightarrow KFe_3(SO_4)_2(OH)_6 + 6H^+ \quad (12)$$

$$KFe_3(SO_4)_2(OH)_6 + 3H_2O \rightarrow Fe(OH)_3 + K^+ + 3H^+2SO_4{}^{2-} \quad (13)$$

$$jarosite \rightarrow geothite: KFe_3(SO_4)_2(OH)_6 \rightarrow 3FeO(OH) + K^+ + 3H^+2SO_4{}^{2-} \quad (14)$$

Most studies of the bioleaching process identify two pathways depending on the acid solubility of the sulphide; thiosulphate pathway for the acid insoluble (such as FeS_2, MoS_2 and WS_2) and polysulphide pathway for acid soluble (such as ZnS, PbS, FeAsS, $CuFeS_2$ and MnS_2) (Ahmadi et al., 2015; Johnson et al., 2012; Yahya and Johnson 2002). FeS_2 being the most abundant sulphide mineral on earth has been studied extensively in bioleaching process which occurs in two simultaneous steps (cooperative bioleaching) as shown in Figure 6 (Liu et al., 2011). In the first step, (the contact step) the cell attaches to the sulphide surface and the hexi-hydrated Fe^{3+} contained in the extracellular exopolymer starts the indirect attack of the sulphide and the intermediate thiosulphate further reacts to produce sulphate. Step 2 (non-contact): microorganisms (iron oxidisers) oxidise the dissolved Fe^{2+} to Fe^{3+} thus renewing the leaching agent while the sulphur oxidisers oxidise the primary sulphur in the reaction. The bioleaching is governed by redox, pH, microorganism growth kinetics and the culture type (Liu et al., 2011).

Redox potential indicates the oxidation state of the dissolved iron ions, i.e. the Fe^{3+} / Fe^{2+} ratio which is related to pH (Hansford and Vargas, 2001; Johnson et al., 2012; Rodriguez et al., 2003). Cell population growth is dependent on the availability of appropriate physiochemical environments such as the substrate, pH, elements, temperature and dissolved oxygen. Acidophiles have a wide metabolic diversity and can utilize both organic and inorganic sources of energy but their pH optimum range,

between 1 and 3, is narrow. The Fe^{2+} oxidising bacteria has been shown by several researchers to accelerates the rate of Fe^{2+} oxidation by up to 10^6 times faster than just chemical oxidation (Ahmadi et al., 2015; Boon and Heijnen, 1998; Nemati and Webb, 1997; Rawlings et al., 1999). Key acidophilic mesophiles (30 – 40 ^oC) identified in bio-oxidation of pyrite are *Acidothiobacillus ferrooxidans, Acidothiobacillus thioxidans* and *Leptospirillum ferrooxidans.* However the new genera of moderately thermophilic (45 – 50 ^oC) bacteria such as *Acidothiobacillus caldus, Sulfobacillus thermosulfidooxidans, Sulfobacillus acidophilus* and extremely thermophilic (65 – 85 ^oC) bacteria of the genera *Sulfolobus, Acidianus, Metallosphaera and Sulfurisphaera* are becoming reputable (Olson et al., 2003; Rawlings et al., 1999; Rohwerder et al., 2003; Yahya and Johnson, 2002).

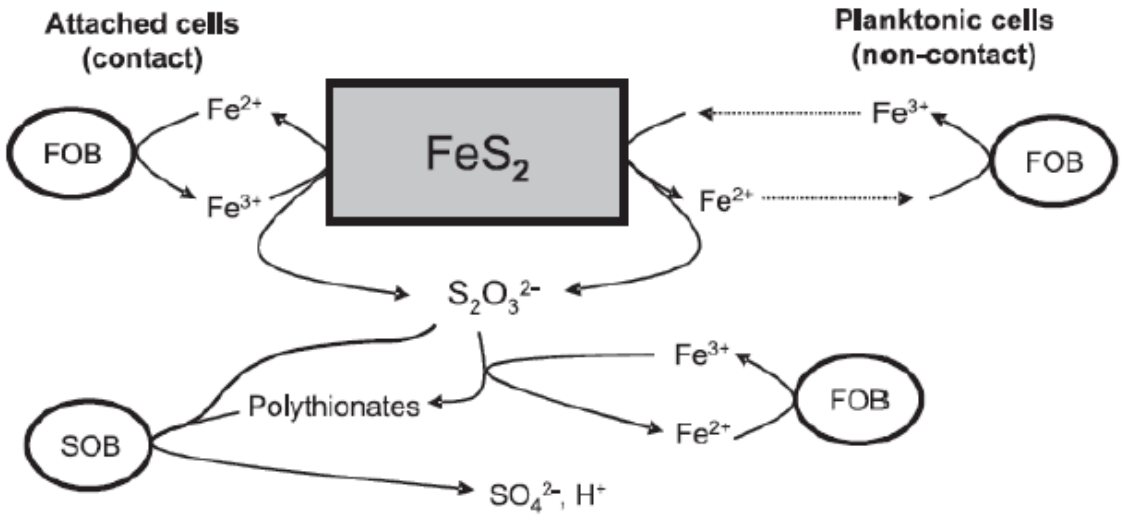

Figure 6 Bio-kinetic tests mechanism for pyrite leaching by Fe oxidising and S oxidising acidophiles (Bryan, 2006)

2.3.2. ARD Neutralisation

The acid produced from the oxidation of pyrite, other sulphides and sulphates is neutralized by gangue material such as carbonates, silicates, and clay minerals. According to Lapakko (2002), "different neutralizing minerals have varying neutralization potentials (NP) based on their dissolution rates and reaction environment pH ranges." The carbonate with the highest neutralizing capacity is calcite (equations 15 at pH below 6.4, equation 16 at pH above 6.4 and equation 17 for overall reaction with pyrite) as it displays the most rapid dissolution. Other neutralizing carbonates are magnesite, dolomite and ankerite (Lapakko, 2002). Some neutralising minerals such as the silicates forsterite (shown in equation 20), olivine, wollastonite and serpentine have slower dissolution rates and lower neutralising capacities compared to carbonates. The degree of acid neutralization by silicates is affected by the surface area available for the reaction. Clay minerals e.g. Plagioclase-feldspar, anorthite (shown in equation 19 and 20) too have a net acid neutralizing capacity which is negligible compared to carbonates (Miller et al., 2010; Parbhakar-fox and Lottermoser, 2015; Schumann et al., 2012; Stewart et al., 2009).

$$CaCO_3 + H^+ \rightarrow HCO^{3-} + Ca^{2+} \quad (15)$$

$$CaCO_3 + 2H^+ \rightarrow H_2CO_3 + Ca^{2+} \quad (16)$$

$$FeS_2 + 2CaCO_3 + 3.75O_2 + 15H_2O \rightarrow Fe(OH)_3 + 2SO_4{}^{2-} + 2Ca^{2+} + 2CO_2 \quad (17)$$

$$CaMg(CO_3)_2 + 2H_2SO_4 \rightarrow CaSO_4 + MgSO_4 + 2CO_2 + 2H_2O \quad (18)$$

$$CaAl_2Si_2O_8 + 2H^+ + H_2O \rightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4 \quad (19)$$

$$Mg_2SiO_4 + 4H^+ \rightarrow 2Mg^{2+} + H_4SiO_4 \quad (20)$$

According to Lapakko (2002), "the rate of dissolution, and therefore of neutralization potentials of dolomite (equation 18) and magnetite are slower than calcite by one and four orders of magnitude, respectively." Siderite and manganese carbonates have no net acid neutralizing capacity as the oxidation reaction that is acid-consuming is counteracted by a subsequent hydrolysis reaction that is acid-forming (Lapakko, 2002).

2.3.4. Salinization and Mobilisation of Elements

In fresh coal waste, initially, the fast mobile phases such as Cl^-, SO_4^{2-} and Na^+ are released by ionic exchange of the ions with infiltrating water under alkaline and neutral conditions (Szczepanska and Twardowska, 1999). On depletion of these mobile ions, the leachate composition is governed by the dynamics of the sulphides oxidation and acid neutralisation reactions of carbonates. The ions mobilized in the leachates are largely Mg^{2+}, Ca^{2+}, $SO_4^{2-}$and trace elements mobile under the relative pH and redox. Exhaustion of the ions from carbonates and other acid neutralizing minerals results in acidification of the leachates (Szczepanska and Twardowska, 1999). The acidic leaching in ARD increases solubility, mobility and bioavailability of elements such as Cd, Cu, Cr, Mn and Pb in the coal waste. Acid leaching dissolves more ions into the leachate than they would in the absence of the acid (Deysel and Vermeulen, 2015; Munnik, 2010).

The direct solubilisation of sulphide minerals and soluble sulphates, and the subsequent neutralisation reactions give rise to high level of dissolved salts, mainly in the form of sulphates of Fe, Ca, Al and Mg, and in less acidic waters carbonates. Other salts that can accumulate are chlorides and phosphates. The high salinity levels resulting from ARD can contaminate soils and water sources which constrain their uses (McCarthy, 2011; Munnik, 2010). The salts that are usually associated with SA coals and coal processing wastes form from sulphates such as jarosite, alunite and gypsum (Munnik, 2010; Pinetown et al., 2007). The secondary salts precipitate from the ARD reactions can form in streams, run-off, pore waters, and re-mobilise with time, forming a secondary source of contaminating elements such as Pb, As, Zn, Cu, Al, Mn and Ni (Finkelman and Gross, 1999). The dissolved ions increase ionic strength and conductivity of ARD solutions increasing the mobility of soluble ions such as As, Co, Fe, Mg and U (Munnik, 2010). The attenuated contaminants include elements which are toxic to animals and most plants (Finkelman and Gross, 1999).

Water sources can be contaminated from seepage of ARD solutions containing high levels of toxic elements. These elements reportedly affect the environment, plants, human and animal health depending on their toxicity, concentration and availability (Misz-Kennan and Fabianska, 2011; Swaine, 2000; Zhang et al., 2004). According to Swaine (2000), 26 of the elements found in coal which are considered to be of environmental concern are grouped with decreasing importance from I-III as shown together with their concentration ranges (in ppm) for most coals in Table 8. The reported elements from ARD produced by coal mining in South Africa are Cd, Cu, Cr, Mn, Pb, As, Co, Fe, Al, Mg and U (Bell et al., 2001; Munnik, 2010). Again, there are limited comprehensive studies on the elemental risk associated specifically with coal processing wastes thus the elemental risk potential of coal processing wastes is largely unknown.

Table 8 Elements of environmental concern grouped I-III with decreasing importance, found in most coals and their typical concentration ranges in ppm adapted from Swaine (2000)

I (High)	II (Moderate)	III (Low)
As (0.5-80)	**B** (5-400)	**Ba** (20-1000)
Cd (0.1-3.0)	**Cl** (50-2000)	**Co** (0.5-30)
Cr (0.5-60)	**F** (20-500)	**I** (0.5-15)
Hg (0.02-1)	**Mn** (5-300)	**Ra** (1 in 10^6)
Pb (2-80**)**	**Mo** (0.1-10)	**Sb** (0.05-10)
Se (0.2-10)	**Ni** (0.5-50)	**Sn** (1-10)
	Be (0.1-15)	**Tl** (<0.2-1)
	Cu (0.5-50)	
	P (10-3000)	
	Th (0.5-10)	
	U (0.5-10)	
	V (2-100)	
	Zn (5-300)	

2.4. Analytical Characterisation Methods

Standard analytical techniques were developed for testing coal properties to monitor the coal quality and performance. Various testing standards were developed by organisations such the South African National Standards (SANS), American Society for Testing Materials (ASTM), British Standards (BS) Institution and the International Standards Organization (ISO) (Speight, 2005; Zhu, 2014). Standard chemical analytical methods include ultimate analysis to determine elements (C, H, N, S and O) that are in the organic matter and proximate analysis to test for inherent moisture, ash, volatile matter and fixed carbon. Standards developed for physical analytical methods include density, abrasiveness, porosity, particle size distribution and moisture content as well as grindability, washability, and coking tests to monitor performance (Speight, 2005).

Over the years, faster instrumental methods have replaced some of the standard analytical techniques which use wet chemical methods. Many of these standard analytical procedures and methods have been

updated as analytical techniques have advanced, with instrumental methods replacing some of the more time-consuming wet chemical methods. To address the previously outlined challenges posed by coal preparation wastes, a toolbox with some of the protocols developed at UCT which aims to provide adequate and reliable data and information on the environmentally significant properties and characteristics of solid mineral wastes. The toolbox (shown in Figure 7) for characterising potential environmental risks consist of analytical tools, geochemical ARD tests, elemental risk analysing tools and geochemical models. Various tools are available in each of the four characterising techniques.

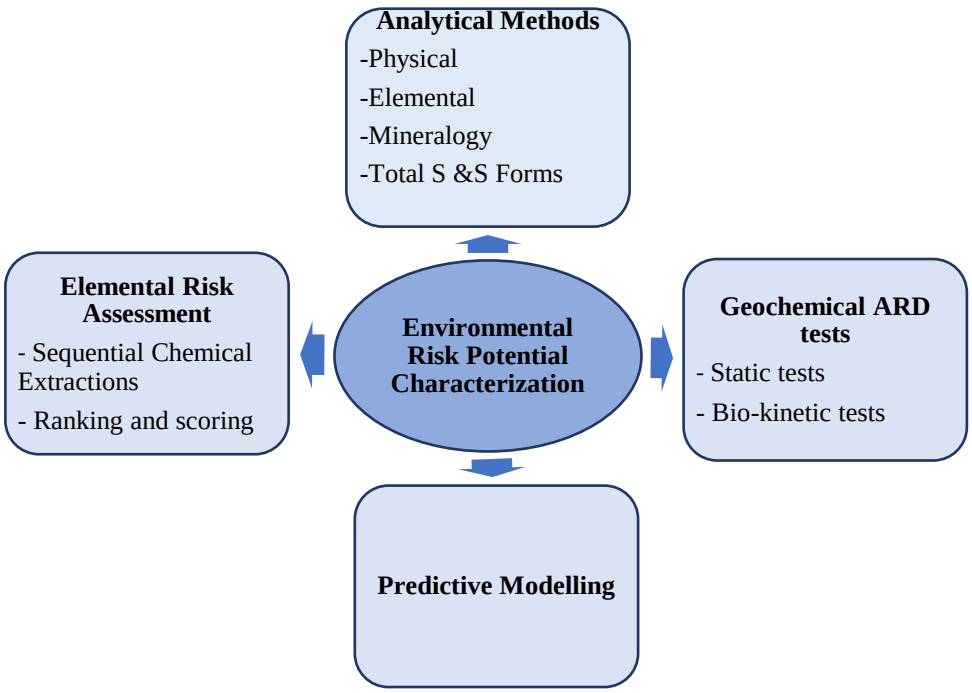

Figure 7 Toolbox used for characterising the environmental risk potential of coal processing wastes

2.4.1. Physical Analysis –Particle Size Distribution

Particle size distribution (PSD) shows the proportions of particles of different sizes which make up your coal waste sample. PSD is important since size also affects the environmental impacts of coal processing waste (such as ARD and dust impacts) and each characterising technique has its required particle sizes for good results. Sieving of samples partitions fine-coarse particles of 25µm-45 mm diameter but micro sieving can separate particles of diameter as low as 5 µm (Richardson and Harker, 2002). Although cyclosizing based on hydraulic principles can separate particles of diameters less than 75 µm, it is only applicable to ultrafine sizes (Richardson and Harker, 2002). On the other hand, sizing using Laser techniques is only useful in supplying the PSD and particle shape data but does not partition the particles into different portions for analysis. By virtue of being less expensive, simple to apply and interpret, sieving is a favoured technique for PSD (Richardson and Harker, 2002).

2.4.2. Mineralogy Analysis

Mineralogy is useful in coal exploration, mining, preparation, use, environmental and process behaviour of coal, its by-products and waste streams. The mineralogy analyses give information on occurrence, texture, concentration, speciation of the mineral constituents of the coal samples. Various methods of different merits and limitations are available for selection when characterising a sample's mineralogy (van Alphen, 2007; Huggins, 2002; Ward, 2002). Huggins (2002) listed four distinct techniques for mineralogy analysis as X-ray diffraction (XRD), infrared (IR) spectroscopy, chemical analysis (normative calculation) and optical and scanning electron microscopy (SEM). IR spectroscopy is not a commonly used technique because of complications in analysing inorganic coal constituencies but is useful in analysis major elements of ash after combustion. Petrography, XRD and SEM remain the commonly used tools for mineralogy analysis (Huggins, 2002).

Calculation from Chemical Analysis

The mineral matter percentage is calculated from the ash yield of coal and other key inorganic constituents in the coal which are retained in the ash such as inorganic carbon, chlorine, pyritic and sulphate sulphur. The common method for this type of mineralogy analysis is the Parr method which is mostly used in the USA (ASTM D-388) (Speight, 2005; Ward, 2002). The Parr formula uses ash (A) and sulphur (S) wt. % to calculate mineral matter (MM) percentage assuming all sulphur is pyritic with a weight loss correction factor of 0.55 when it burns to Fe_2O_3 and hydration water of the minerals to be 8 %. The formula expression is:

$$\% MM = 1.08\, A + 0.55S \qquad (21)$$

Another approach is using chemical analysis of the inorganic elements of the coal sample to calculate the total mineral matter percentage. This approach is not precise in estimating the actual mineral matter content since it assumes the nature of the minerals (Huggins, 2002; Ward, 2002). Acid digestion of coal using HCl and HF has been used to quantify the mineral matter from the weight loss of the sample following acid digestion. Selective element extraction using sequential acid digestion (HF, HCl, HNO_3 etc) and analysing the leachates has been used by several researchers to study the different mineral matter phases and associations in coal and ash samples. The disadvantage of this method as discussed by several researchers is overlapping of mineral phases extracted and incomplete dissolution which can cause underestimation of contents (Huggins, 2002; Kalenga, 2011; Laban and Atkin, 2000; Pinetown et al., 2007; Wagner and Hlatshwayo 2005).

X-Ray Diffraction (XRD)

According to Huggins (2002), "XRD is a fast way, requiring no special sample preparation (except fine grinding) that is widely used to characterise ores and their by-products (coal waste in this context), track their behaviour and to optimize metallurgical performance." Minerals and their phases are evaluated both qualitatively and quantitatively by comparing measured diffraction patterns against a database

comprising of known diffraction patterns. Calibration of the diffractometer with an internal standard is a prerequisite in XRD analysis (van Alphen, 2007). Previous studies have reported reduced accuracy and precision due to distortion of peak intensities from preferred mineral orientation and micro-absorption effects (Lapakko, 2002). Another limitation of XRD is the failure to detect mineral phases below 1 % by weight as well as the amorphous phases like coal unless an internal standard is used (van Alphen, 2007). Some researchers have indicated that amorphous macerals in coal produce an XRD pattern of high background continuum that can mask peaks of crystalline phases (van Alphen, 2007; French and Ward, 2009; Pinetown et al., 2007).

Recent developments in XRD included the incorporation of cluster analysis into the XRD software which allowed quick identification and comparison of samples. In addition, unidentified phases (of significant amounts) structure and phases or minerals in a mixture can now be found following the introduction of the Rietveld method (van Alphen, 2007). The method allows mineral phases to be identified more precisely by fitting the experimental XRD pattern on to a calculated one. Recent developments in computer software programs such as SIROQUANT, which was developed in Australia by CSIRO Energy Technology now allows the refinement of the Rietveld method parameters. The refined parameters include phase preferred orientation, phase scales and line asymmetry to improve XRD as a fast, precise and accurate tool in mineralogy analysis (Zhu, 2014). Application of the SIROQUANT program on XRD by Pinetown et al. (2007) on low-temperature ashes of SA coal standards SARM 18, 19 and 20 gave results that correlated well with the chemical analytical results.

Optical and Scanning Electron Microscopy (SEM)

Optical Microscopy is based on transmitted or reflected light for the detailed microscopy analysis of minerals on polished or thin sections of coal. To identify the mineral type, the optical properties; morphology, reflectance, refractive index and anisotropy are used (Huggins, 2002; Speight, 2005). A combination of automated SEM methods and optical reflected light microscopy gives a complete maceral and mineral analysis (CMMA) which provides better results than individual methods (van Alphen, 2007; Ward, 2002). Computer controlled SEM (CCSEM) is usually combined with image analysers to evaluate the mineral nature and distribution. Two automated SEM methods that were developed for identifying composition, association, abundance and nature of minerals in whole coal or ash are the quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) and the mineral liberation analyser (MLA). In addition to mineralogical analysis, the techniques show images as well as physical and chemical properties of the samples which can allow modelling the quantitative and qualitative output potential of coal beneficiation in a dense medium separation plant (van Alphen, 2007; Ward, 2002) and the ARD generation potential of coal processing wastes (Kotelo 2013). However, application of SEM to coal processing wastes remains limited.

Representative samples appropriately prepared to give a flat surface which is conductive are fundamental to achieving good results using CCSEM According to van Alphen (2007), carnauba wax is preferred to iodoform-doped epoxy resin as the mounting medium for polished block preparation because it is suitable to use with liquid epoxy and its molecular weight matches that of coal. However carnauba wax is not easy to polish and recently samples are prepared by mixing the coal sample with carnauba wax followed by setting the sample face down in epoxy resin for better polishing and reflective surfaces (Zhu, 2014). To reduce segregation of sample and touching of particles, only a small amount of coal (0.2 g) is used to prepare blocks for analysis. According to Kotelo (2013), segregation as a result of varying settling rates of particles during sample preparation caused a disparity between QEMSCAN assays and chemical assays. Since no standard reference materials are available for quality control in automated SEM, assay reconciliation between SEM and other chemical assays like ICP-OES is essential for data validation (van Alphen, 2007; Kotelo, 2013; Ward, 2002). According to Ward's (2002) study, a general low reproducibility, particularly for clays, was found in several CCSEM techniques including QEMSCAN, thus the development of calibrating standards should be prioritised. Neither CCSEM nor XRD methods could provide information on inorganic matter dispersed in the organic matrix (Ward, 2002).

Petrography

Petrography uses light reflected by polished surfaces of coal specimens to determine the coal's rank and maceral composition. The petrographic characterisation supplies information on the coal's formation, quality and predicted performance. Developments in petrography have enabled visual characterisation of the coal's rank and type from colour images of high resolution. (Misz-Kennan and Fabianska, 2011; O'Brien et al., 2003). Although petrography can quantify the major mineral groups, the emphasis of this method is on organic constituencies and mineral matter evaluation is not reliable and accurate for coals with low mineral matter content (Ward, 2002).

2.4.3. Elemental Analysis

Coal, its products and wastes which includes processing wastes have been shown in the previous sections to contain major, minor and trace elements occurring in association with various mineral phases. Some of the elements are of environmental concern and in order to quantify the risk they pose; many analytical techniques have been developed to measure their concentrations. The elemental analysis techniques according to Huggins (2002), can be divided into four major groups; instrumental X-ray/ γ-ray emission techniques, optical absorption/ emission techniques, mass spectrometric methods and miscellaneous methods.

Comparison of Elemental Analysing Techniques

Generally the most used techniques for coal and its products elemental analysis are the inductively coupled plasma (ICP), atomic absorption spectrometry (AAS) and X-ray fluorescence (XRF) methods

(Iwashita et al., 2007; Misz-Kennan and Fabianska, 2011; Parbhakar-fox and Lottermoser, 2015; Rodushkin et al., 2000; Wagner and Hlatshwayo, 2005; Wang et al., 2004; Zhang et al., 2004). For the analysis of major and minor elements in coal energy-dispersive X-ray fluorescence (EDXRF) has been evaluated to be the best technique (Huggins, 2002). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) also known as inductively coupled plasma optical emission spectroscopy (ICP-OES) and variations of AAS are the commonly used methods to analyse minor and trace elements, but each technique generally has each advantages and disadvantages summarised in Table 9 (Tyler, no date). For the halogens, ion chromatography (IC) or ion-selective electrode (ISE) are the best methods for determination (Huggins, 2002). Most researchers recommend a combination of techniques on both coal and ash for a complete analysis of all elements (Iwashita et al., 2007; Finkelman, 1999; Finkelman and Gross, 1999; Rodushkin et al., 2000; Vassilev and Vassileva, 1997; Wagner and Hlatshwayo, 2005; Zhang et al., 2004).

Table 9 Summarised generic comparison of ICP-MS, ICP-OES, FAAS and GFAAS adapted from Tyler, (no date)

	ICP-MS	**ICP-OES**	**FAAS**	**GFAAS**
Detection limits	Excellent for most elements	Very good for most elements	Very good for most elements	Excellent for most elements
Sample Throughput	All elements 2-6 min	5-30 elements / min	15 seconds/ element	4 min / element
Linear dynamic range	10^5 (10^8 with range extension)	10^4 - 10^8	10^3	10^2
Precision:				
Short-term (in-run)	1 – 3 %	0.3 – 1 %	0.1 – 1 %	1 – 5 %
Long-term (4 hrs)	< 5 %	< 3 %		
Isotopes	Yes	No	No	No
Dissolved solids max concentration	0.1 – 0.4	1 - 30	0.5 - 3	>30
No. of elements	>75	>75	>68	>50
Sample usage	low	low	Very high	Very low
Semi-quantitative analysis	Yes	Yes	No	No
Routine analysis	Yes	No	No	No
Method development	Skill required	Skill required	Easy	Skill required
Operating cost	High	High	Low	Medium
Capital cost	Very high	High	Low	Medium / high

Instrumental X-Ray/ γ-ray Emission Techniques

The oldest techniques under this category are the X-ray fluorescence (XRF) and Instrumental neutron activation analysis (INAA). From these two methods synchrotron XRF (SXRF) and particle-induced X-ray/γ-ray emission (PIXE/PIGE) evolved. The INAA identifies elements (isotopes) from the γ-ray energy and half-life, and measures concentration from the intensity, of γ-ray emitted by an element following irradiation of the material with thermal neutrons. INAA although having a high sensitivity of 0.1-10 ppm and highly precise (within 1 % of the relative standard deviation) for analysis of a wide

range of elements, it is not commonly used because of its turnaround time of 10-12 weeks (Baedecker, 1987).

X-Ray Fluorescence (XRF) Analysis

The XRF method has been used extensively for analysing major and minor elements; Si, Al, Fe, Ca, K, Mg, Ti, Na, P, Mn, Ba and Cr in coal and coal ash and commonly determining them as oxides. The elements absorb the radiation from an x-ray tube and emit low energy x-rays which are characteristic of individual elements. X-ray excitation and absorption vary uniformly with atomic number and the method has poor sensitivity for low atomic numbers and elements in low (ppm) concentration. Therefore, elements in low concentration need pre-concentration. Technically for the method, the lower detection limit is 2-10 ppm for most elements and the upper detection limit is 100 % (Baedecker, 1987; Huggins, 2002).

For precise and accurate detections, a wavelength-dispersive (WDXRF) detector is used, in which the x-ray energies are determined individually in a sequence. Whilst for speed and throughput in elemental quantification an energy-dispersive (EDXRF) spectrometer is ideal since it measures the elements simultaneously. Samples for XRF analysis are prepared by either fluxing samples into glass discs or pressing the sample powder into pellets. Fusing the coal ash or coal powder with flux (usually $Li_2B_4O_7$) homogenizes the sample and improves the precision of major elements determination. The spectral interferences together with matrix absorption and enhancement effects in addition to sample inhomogeneity affect the precision, sensitivity and accuracy of the technique. The reproducibility of within ±1 % relative error is commonly observed, as well as an accuracy of ±5 % relative error for above detection limit concentration. The recent improvement in XRF was the use of polarized incident radiation for determining trace elements with EDXRF. Usually, the two detection methods are used together for a wider range of major and trace elements (Baedecker, 1987; Huggins, 2002).

Advantages of the XRF reported by Huggins (2002), are simple non-destructive sample preparation, infrequent calibration and the spectrometers can be of wavelength or energy variation. The wavelength dispersive X-ray fluorescence (WDXRF) spectrometer operates at a higher resolution than the energy dispersive X-ray fluorescence (EDXRF) spectrometer. As a result, WDXRF is less prone to spectral interferences, has better detection limits and sensitivity compared to EDXRF (Huggins, 2002). On the other hand, EDXRF by having stationary and fewer components is more efficient and cheaper than WDXRF. Furthermore, EDXRF can simultaneously detect many elements in short time unlike WDXRF (Huggins, 2002). Other variations of the XRF are the SXRF and PIXE/PIGE spectrometry which uses synchrotron and accelerated particles respectively as a source of radiation. SXRF is more precise and has lower detection limits than conventional XRF but not as readily available. In addition to being more precise and sensitive, the other merits of PIXE/PIGE over conventional XRF are it is more rapid, can

determine more elements including trace elements (up to 75 elements) and is ideal for analysing samples existing in small quantities as layers (e.g. dust) (Huggins, 2002).

Optical Absorption / Emission Techniques

Although emission is the older of the two optical techniques, it is now more common than absorption techniques following the introduction of inductively coupled plasma (ICP) as the excitation source. The commonly used ICP excitation source gives stronger excitation energy hence more accurate results, better detection limits and faster analysis rates compared to direct current excitation which was used prior to ICP (Baedecker, 1987; Huggins, 2002).

Inductively Coupled Plasma Atomic (or Optical) Emission Spectroscopy (ICP-AES/ ICP-OES)

In ICP-OES/ ICP-AES a high-temperature plasma excites the elements in the solution aerosols introduced at the base of the plasma. Detection can be sequential or simultaneous, up to 44 elements can be simultaneously determined semi-quantitatively according to Baedecker (1987). The throughput is between 2-6 minutes per sample depending if the analysis is sequential or simultaneous (Tyler, no date). The technique is capable of analysing most elements including those available in trace concentration, but appropriate dissolution is a prerequisite. According to Baedecker, "ICP-OES/ ICP-AES analysis does not usually determine elements in the fluxes and H, C, N, O, F, Cl, Br, S and I because of their presence in the air and the reagents used for dissolution." The application of the technique is also limited for refractory elements which require more energy to be excited (e.g. Nb, Mo, Ta, W, Re, Zr, Hf, Ti, V and Cr) and elements with low concentration unless they are pre-concentrated (Baedecker, 1987).

The ICP-AES detection limits for elements in silicate rocks is 0.1 – 100 ppm. The technique is highly precise, mostly in the range ±5-10 % RSD with the optimal limit of 1 - 2 % RSD for concentrations well above detection limits (Baedecker, 1987). Precision is affected by errors encountered during sampling, incomplete solubilisation during sample preparation and spectrometer calibration. Matrix effects are kept to a minimum by the heat from the plasma torch hence for most samples the technique is highly as accurate as it is precise (Baedecker, 1987).

Atomic Absorption Spectrometry (AAS)

In this method, resonant absorption of elements occurs when a flame is placed in the pathway of a strong stable light source to excite the valence electrons of elements in the flame. Four variations of excitation give four major classes of AAS; flame AAS (FAAS), electro-thermal/graphite-furnace AAS (EAAS / GFAAS), hydride AAS (HAAS) and cold vapour AAS (CVAAS). The coal or ash for AAS analysis is prepared by total solubilisation by digestion with acids such as HF, HNO_3, HCl, $HClO_4$ and H_2SO_4. Of the four methods, FAAS which usually uses an air-acetylene torch is the simplest and is sensitive for as many as 70 elements but its sensitivity is relatively low in the (0.28 -10 000 for elements in silicate rocks) ppm region (Baedecker, 1987; Huggins, 2002). EAAS/GFAAS is the most sensitive at 0.0005-5

ppm for silicate rock elements and can determine all the elements, except for refractory elements, (that FAAS can determine) and therefore is most suitable for trace elements. HAAS has a relatively high sensitivity (0.03-0.1 ppm in silicate rocks) and is usually applied to analyse elements that form stable hydrides when reduced by $NaBH_4$ such as As, Bi, Pb, Sb, Sn and Te. CVAAS is used particularly for determining Hg from a gold or silver amalgamation with a detection limit of 0.02 ppm and ±10 % RSD precision. HAAS and CVAAS in some laboratories are replaced by atomic fluorescence spectroscopy for the determination of As, Hg, and Se (Baedecker, 1987; Huggins, 2002).

A combination of the four AAS variations is routinely used for the determination of major, minor and trace elements with the exception of refractory elements which require more excitation heat than the instrument can provide (Huggins, 2002). Geologic materials are analysed by AAS with a precision in the 1-10 % RSD range; with FAAS having relatively good short-term precision of 0.1 -1 % (but long-term precision is lower) and GFAAS 0.5-5 % RSD. GFAAS typical throughput is 3-4 minutes per sample per element for duplicate analysis whereas FAAS is 15 seconds per element (Tyler, no date; Baedecker, 1987). The AAS techniques are generally susceptible to all interferences except spectral interferences thus Huggins (2002), recommended minimisation of the interferences for accurate results (Huggins, 2002).

Mass Spectrometric (MS) Methods

In this category, mass resolution detection is used to analyse the elements. The differences are in ion generation mechanisms. Variations include old methods such as secondary ion mass spectrometry (SIMS), accelerator mass spectrometry (AMS), spark source mass spectrometry (SSMS) and newer techniques such as ICP mass spectrometry (ICP-MS), laser ablation ICP mass spectrometry (LA-ICP-MS) and glow discharge mass spectrometry (GDMS). The commonly used mass spectrometry method currently is the ICP-MS **o**wing to its superior sensitivity relative to the older techniques (Huggins, 2002).

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The method has been used extensively in analysing almost all periodic table elements in fly ash and solid coal after ashing and solubilizing by acid digestion. Due to contamination problems, MS analysis of elements with high abundance in the earth's crust such as Si, Al, Fe, Ca, Na, K, Mn, and Ti are usually compromised (Becker and Dietze, 2003). He, C, N, O, F and Ne are not measurable by ICP-MS, while H, Po, At, Rn, Fr, Ra, Ac, Pm, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No and Lr do not have naturally occurring isotopes from which to identify and quantify the elements. For semi-quantitative analysis 80 elements can be analysed in 3 minutes (PerkinElmer Inc., 2004).While according to Tyler (no date), the throughput of ICP-MS is 5 minutes per sample for all trace elements analysis with high selectivity and few isotopic interferences. On coal analysis, the detection limits of ICP-MS on many trace elements was between 5-100 ppb (Becker and Dietze, 2003). The general precision of ICP-MS is

1-3 % but for coal precision (in the order of ±20%) and accuracy seemed to be affected by sample homogeneity (Becker and Dietze, 2003).

The main drawback of ICP-MS is systematic errors on the analyte signal which is affected by plasma nebulizer flow and radio frequency power supply. In order to avoid loss of volatiles by ashing, recent work has attempted at analysing coal instead of ash. One such method is combining laser ablation with ICP-MS (LA-ICP-MS). Other variations of ICP-MS in literature are flow injection (FI-ICP-MS) for Se, Cd and Hg analysis and hydride generation (HG-ICP-MS) for Se analysis because they provide separation of the matrix from the sample in addition to pre-concentration (Huggins, 2002; Rodushkin et al., 2000; Tyler, no date; Wang et al., 2006)

The coal for LA-ICP-MS analysis is finely ground and pressed into pellets which are ablated with pulsed laser forming very fine particles for elemental analysis. Results from Rodushkin et al. (2000) showed that this method has lower precision compared to ICP-MS analysis of microwave acid digested and fused samples but higher than ICP-MS analysis of samples prepared in slurry nebulization. The merits of this method are reliability, moderate-high to very high sensitivity (0.1-1 ppb for most elements). The precision of quantitative trace element determination is mostly between 2 and 5% RSD (Becker and Dietze, 2003). Sample preparation is inexpensive and fast (can analyse trace elements from the same fusion beads used for XRF major elements analysis) but operational costs are high. The absence of standard reference material (SRM) for sample matrix matching still causes problems and the SRM commonly used have no certified values for certain elements (Becker and Dietze, 2003). LA-ICP-MS technique is not as commonly used as ICP-MS which uses both SRMs and standard liquid solutions for calibration.

Miscellaneous Methods

For highly volatile elements such as the halogens, individual analytical methods were developed such as the ion-selective electrode (ISE), ion chromatography (IC) and chemical analysis methods. In ISE an anion selective electrode determines the concentration of a stable anion in aqueous solutions such as F- and Cl-. Alkali fusion, oxygen bomb digestion or pyro-hydrolysis pre-treatment is done to concentrate and/or separate the elements before analysis. Ion chromatography column separations coupled with detectors like conductivity, amperometric and indirect photometric detectors are used to determine anions of F, Cl, S, Br, P and N in solutions. (Huggins, 2002; Watkins et al., 1995). Chemical methods combined with modern analytical techniques such as XRF, AAS, ICP-AES and ICP-MS are now approved standard methods (Huggins, 2002; Speight, 2005; Wagner and Hlatshwayo, 2005):

- ASTM D 6414-99, D-6722 and D-3684 uses CVAAS to determine Hg as vapour following acid digestion, gold amalgamation and bomb combustion respectively
- ASTM D-4606As and Se are determined by AAS as gaseous hydride of each element

- ASTM D-2361 ASTM D-4208 Cl amount determined by either a modified Volhard or by a potentiometric titration with $AgNO_3$ in ASTM D-2361and with an ion-selective electrode by the standard addition method ASTM D-4208
- Other elements ASTM D-3682, ASTM D-3683 ASTM D-6349 and ASTM D-6357 for major and minor and trace elements from high-temperature ash (HTA) fused within $Li_2B_4O_7$ followed by dissolution in either dilute HCl or dilute HNO_3 then the solution is analysed by AAS/ emission spectroscopy for applicable major and minor elements. Or the ash is solubilised by a mixture of HF, HNO_3, HCl and solution analysed by ICP-AES ICP-MS and GFAAS for traces

Comparison of Sample Preparation Procedures for Elemental Analysis

A wide variety of sample preparation procedures have been used by many researchers for elemental analysis of coal and its products. The most elemental analysis reported was done on coal after ashing and little on coal directly (Huggins, 2002; Wagner and Hlatshwayo, 2005). Typically, coals are ashed at high temperatures (450-750 ^{O}C) to remove the organic fraction and the remaining inorganic fraction dissolved in acid(s) and or fusion with a flux such as $Li_2B_4O_7$. However, some volatiles (As, Se, Hg, B and halogens) are lost as gases during ashing and the ash does not correctly represent the mineral matter of the coal as the mineral matter undergo changes during ashing. To avoid problems associated with ashing and dissolution of coal or ash, samples can be directly introduced in the plasma as suspended solids, slurries or pulverized solids (Huggins, 2002; Speight, 2005; Ward, 2002; Wagner and Hlatshwayo, 2005).

Although coal dissolution is not as easy as ash, direct coal digestion methods such as the popular microwave-oven acid digestion and using various combinations and proportions of acids have given acceptable results but in most cases, are not easily repeatable. The most widely-used acid combination is (3-10 ml of 60-70 %) HNO_3 with (0.1-1 ml of 40-55 %) HF and (1-2 ml of 30 %) H_2O_2 (Baffi et al., 2002; Huggins, 2002; Iwashita et al., 2006; Rodushkin et al., 2000; Wagner and Hlatshwayo, 2005; Wang et al., 2004; Watkins et al., 1995). Some researchers replace H_2O_2 with $HClO_4$ or HCl or H_2SO_4. However HF, HCl, $HClO_4$ and H_2SO_4 have major drawbacks of negative effects on instruments parts (HF and H_2SO_4), on operators health and safety (HF is toxic and $HClO_4$ is explosive), matrix effects (H_2SO_4 and H_3BO_3) and spectral interferences (Cl based acids and H_2SO_4) on ICP-MS (Huggins, 2002). Usually, the HF is removed by either boric acid or evaporation. The addition of high concentration of boric acid can contaminate the torch and other parts of the ICP instruments (Wagner and Hlatshwayo, 2005).

HF addition in the acid mix has been reported by several researchers to ensure complete dissolution of the coal and/or ash and better trace element recoveries (90-103 %) (Iwashita et al., 2006; Wagner and Hlatshwayo, 2005; Wang et al., 2004; Watkins et al., 1995). Some researchers noted suppression of Al, Ca and Mg when HF was added in the acid mix, owing to the formation of insoluble fluorides (Wang

et al., 2004, 2006; Xu et al., 2005). This type of digestion is reported by several studies to be under investigation for optimization (Huggins, 2002; Iwashita et al., 2006; Wagner and Hlatshwayo, 2005; Wang et al., 2004, 2006; Xu et al., 2005). On the other hand, sequential leaching using a variety of acid combinations such as ammonium acetate ($NH_4CH_3CO_2$) with HCl and HNO_3 was found to incompletely solubilise coal giving highly variable and unreliable results. Other limitations of this sequential acid digestion are time consumption and high risk of contamination (Huggins, 2002; Rodushkin et al., 2000; Wagner and Hlatshwayo, 2005).

Use of a flux such as Lithium tetra/meta-borate ($LiBO_2$ / $Li_2B_4O_{7)}$, with and without acid digestion was found to give good results of more than 50 elements on coal without ashing. The problem with this type of digestion is hydrolysis of refractory elements (e.g. Ta and W) if HF is not used and low solubilities of fluoride salts of Y, Pb, Ca, U and Th. (Rodushkin et al., 2000). Furthermore, $LiBO_2$ / $Li_2B_4O_7$ does not allow analysis of Li or B but is suitable for silicon analysis in the samples. On the other hand, the method of injecting coal slurry in ICP was found to be reliable for almost half the elements in SARM 19 by Wagner and Hlatshwayo (2005). However further research is required to standardize the method (Wagner and Hlatshwayo, 2005). Other research works that have achieved good results with slurry nebulization are recorded by Rodushkin et al. (2000) and Huggins (2002) but poor results for Al, Se, Cd, Sb, U and some other elements are noted. The drawback of this method also noted by these researchers is the time taken for sample grinding to 5-10 µm which can be as long as 24 hours.

2.4.4. Sulphur and Sulphur Forms Analysis

In chapter 1 it was shown that in coal processing some of the sulphur reports in the products and in the waste streams and it is necessary to determine the amount of sulphur in each stream to evaluate the cleaning process, the environmental implications and suitability for certain use of the waste. Estimating acid-producing potential in ARD based on total sulphur is likely to overestimate the acid-producing potential since organic sulphur and some sulphates are non-acid-forming. This makes it necessary to study the sulphur occurrences of coal processing wastes (Kotelo, 2013; Miller, 2008; Schumann et al., 2012).

Total Sulphur Determination

The widely used traditional methods for total sulphur determination are the Eschka, bomb washing and high-temperature combustion. All the three traditional methods are based on combustion of the sulphur in the material to sulphate which is then measured gravimetrically or volumetrically. Wet chemical analytical methods have also gained popularity as methods for total sulphur determination in recent years.

Eschka Method (ASTM D-3177; ISO 334:1992; SANS 334:1992)

A certain amount of sample is mixed with the Eschka mixture (a combination of 2 parts by weight of light calcined MgO with 1 part of anhydrous Na_2CO_3) then completely burnt at 800 ± 25 ^{O}C in a muffled

furnace. The products from sulphur oxidation react with MgO and Na_2CO_3 producing $MgSO_4$ and Na_2SO_4which is then extracted and determined gravimetrically as a $BaSO_4$ precipitate. If material adsorbed to the $BaSO_4$ precipitate is not adequately washed off, it will cause too high results. The distinct advantage of the Eschka method is that it takes only two days to carry out the analysis using relatively simple equipment and employs commonly available analytical techniques. (European Commision, 1998; Kalenga, 2011; Speight, 2005; Vontorová et al., 2013)

Bomb Washing Method (ASTM D-2015 and ASTM D-3286)

Although the standard methods have been discontinued, many laboratories still use them. The sulphur is analysed gravimetrically from the washings from the oxygen bomb colorimeter after precipitation with $BaCl_2$. The bomb method is favourable particularly when the calorific value of the coal needs evaluation but this method is advantageous provided there is no sulphur loss during the process (Speight, 2005).

High-Temperature Combustion Test Methods (ASTM D-4239, Sub-methods A, B and C; SABS Method 931)

The high-temperature combustion test methods may be almost completely automated and may take less than three minutes for the analysis giving accurate results. In the combustion tests, a sample of known mass undergoes complete combustion in a tube furnace at a temperature from 1350 ^{O}C and above allowing all the sulphur compounds in the sample to oxidise mainly to SO_2 in a reproducible way. The SO_2 produced is quantitatively measured by acid-base titration, iodometric titration or infrared (IR) radiation- Leco method. The common used being the Leco method which is empirical and standard reference material with sulphur content in the range as the sample analysed should be used to calibrate the instrument. The LECO (LECO Corporation of Michigan, USA) Company designed the sulphur analyser Leco Model SC-132 which was purposed for determination of total sulphur in soils and sediments. The results obtained by this instrument agreed with those by other methods used then for determination of total S in such materials (Speight, 2005).

Instrumental Methods for Total Sulphur

Sulphur has been accurately and precisely determined by different methods such as ICP-AES/ OES, ICP-MS, Ultraviolet–Visible Spectroscopy (UV–VIS) and chromatography. All the methods sample preparations were done using microwave acid digestion for complete digestion of the samples. The sample preparation was shown to affect the performance of the analytical methods by several researchers (Baysal and Akman, 2011; Caroli et al., 1988; European Commision, 1998; Kalenga, 2011; Laban and Atkin, 2000; Mior et al., 2013; Vontorová et al., 2013). According to Laban and Atkin (2000) and the report by the European Commission (1998), XRF analysis for total sulphur was low in precision and accuracy for some coals even after using the fusion method to overcome the loss of volatile sulphur during grinding.

Comparison of Total Sulphur Analytical Methods

Several researchers have reported all methods used to determine sulphur as precise and accurate and the results deviated a little (Baysal and Akman, 2011; European Commision, 1998; Kalenga, 2011; Mior et al., 2013; Vontorová et al., 2013). The results from a study by Vontorová et al. (2013) have shown the combustion method results to be comparable but slightly higher than the gravimetric method. They recommended the use of combustion techniques due to its speed of measurement instead of the gravimetric analysis or chemical methods. However, the results of total sulphur in coal, determined by the Eschka method can be inconsistent due to the instability of the organic matter (European Commision, 1998).

Sulphur Speciation Methods

The commonly used tool to determine sulphur forms in coal/coal wastes is the ISO 157:1996 protocol. Another protocol for analysing sulphur forms was developed by Australian Coal Industry's Research Program (ACARP) Project C15034 method (Miller, 2008). This protocol was also used in previous UCT work by Kotelo (2013) to determine the sulphur forms in the Middelburg ultrafine coal waste.

ISO 157:1996 Protocol

This protocol involves a two-stage sequential acid leach to determine sulphate sulphur and pyritic sulphur (Speight, 2005). In the first leach step dilute HCl is used to selectively dissolve the sulphate minerals, and the leachate analysed for sulphate using the gravimetric $BaCl_2$ method. In the second step, HNO_3 is used to selectively solubilise the pyritic Fe in the residue from HCl digestion, and the leachate subsequently analysed for iron by means of AAS, titration or colorimetric methods. Organic sulphur is then calculated by subtracting the sulphate sulphur and pyritic sulphur from the total sulphur value, as determined by Leco analysis (see Section 2.4.4.1.). The standard test method is based on many assumptions, one being sulphate minerals are dissolved in the HCl leach step, while sulphide minerals and organic sulphur are not. The other assumption is dilute HNO_3 acid only dissolves pyritic Fe and this pyrite accounts for 100 % of the sulphide sulphur in the sample (Speight, 2005). Then all the unaccounted sulphur is assumed to be organic sulphur which is calculated as:

$$Organic\ S = Total\ S\ - (Pyrite\ S\ + Sulphate\ S) \qquad (22)$$

The calculation of organic sulphur using the standard method is affected by the errors accumulating from the total sulphur, pyritic sulphur and sulphate sulphur analysis, thus direct organic sulphur analysis is better (European Commision, 1998; Kalenga, 2011). The inaccuracy of the standard method also results from assuming that all the iron sulphides in coal are pyritic and not accounting for other sulphides contribution to pyritic sulphur (European Commision, 1998). Iron from the dissolution of iron silicates or iron oxides can cause overestimation of pyritic sulphur in the standard method. Incomplete extraction of pyritic sulphur by HNO_3 can result in lower values (Laban and Atkin, 2000). Elemental sulphur presence in the sample causes overestimation of the organic sulphur because it is not extracted by either

HCl or HNO_3 (Miller, 2008). The presence of jarosite species causes overestimation of pyritic sulphur and underestimation of sulphate sulphur because jarosite poorly dissolves in HCl and 86 % was reported to be removed by HNO_3 (European Commision, 1998). High levels of Ca or Ba may result in the formation of insoluble $BaSO_4$ or slightly soluble $CaSO_4$ thus lowering sulphate sulphur values (Speight, 2005).

ACARP C15034 Protocol

A research project supported by the Australian Coal Association Research Program (ACARP) C15034, developed sulphur speciation method that claimed to overcome the challenges of using the ISO157:1996 method (Miller, 2008; Stewart et al., 2009). The protocol is specifically for determining sulphur species in coal "washery" wastes to enable a reliable determination of the acid-producing potential of the wastes in ABA tests (Miller, 2008).The ACARP protocol aim is to distinguish the sulphur into pyritic sulphur, non-acid-forming sulphates (such as gypsum and epsomite), acid-forming sulphates (such as melanterite and alunite) and low-risk sulphur (organic sulphur and jarosite). Although steps have been developed to separately determine elemental sulphur and to distinguish between organic sulphur and jarosite, these steps are seldom applied as the jarosite and elemental sulphur contents are low, and the jarosite method was deemed insufficiently robust (Miller, 2008; Stewart et al., 2009). Furthermore, jarosite although being an acid-forming sulphate it only produces acid at slow rates and the acid production capacity is not as high as pyrite or the other acid-forming sulphates (Miller et al., 2010). Hence the final protocol opted to not determine the proportion of jarosite but group it as the low-risk sulphur together with organic sulphur.

For routine determination of sulphur species in coal processing wastes, the protocol is performed in three stages using representative samples for each stage as shown in Figure 8. In the first stage, Total sulphur is determined using the standard Leco method (see Section 2.4.4.1.). In the next stage, the chromium reducible sulphur (CRS) method is used to determine the pyritic sulphur content. In this method inorganic (pyritic) sulphur and elemental sulphur are selectively reduced by chromium to form H_2S which can be trapped in zinc acetate solution as ZnS. Although an acetone extraction step can be included to selectively remove and determine elemental sulphur (Tuttle et al, 2003), this is usually not necessary as coal processing wastes usually have trace amounts of elemental sulphur (Miller, 2008). In the third stage, all sulphates (except jarosite) are selectively dissolved in KCl solution and the filtrate separated into two portions. One portion is used to determine total sulphate, using the gravimetric $BaCl_2$ method, and the other to determine soluble acid-forming sulphates through back-titration with NaOH (Miller, 2008; Stewart et al., 2009; Tuttle et al., 2003). Low-risk sulphur (i.e. organic and jarosite S) is then calculated by difference. The sulphur proportions and their determining are summarised in equation 23-26.

$$Pyritic\ S = CRS \qquad (23)$$

$$Acid\ Sulphate\ S = S\ equivalent\ to\ acidity\ of\ KCl\ extract \quad (24)$$

$$Non - acid\ Sulphate\ S = KCl\ S - Acid\ Sulphate\ S \quad (25)$$

$$Low\ Risk\ S\ = Total\ S - (CRS - KCl\ S) \quad (26)$$

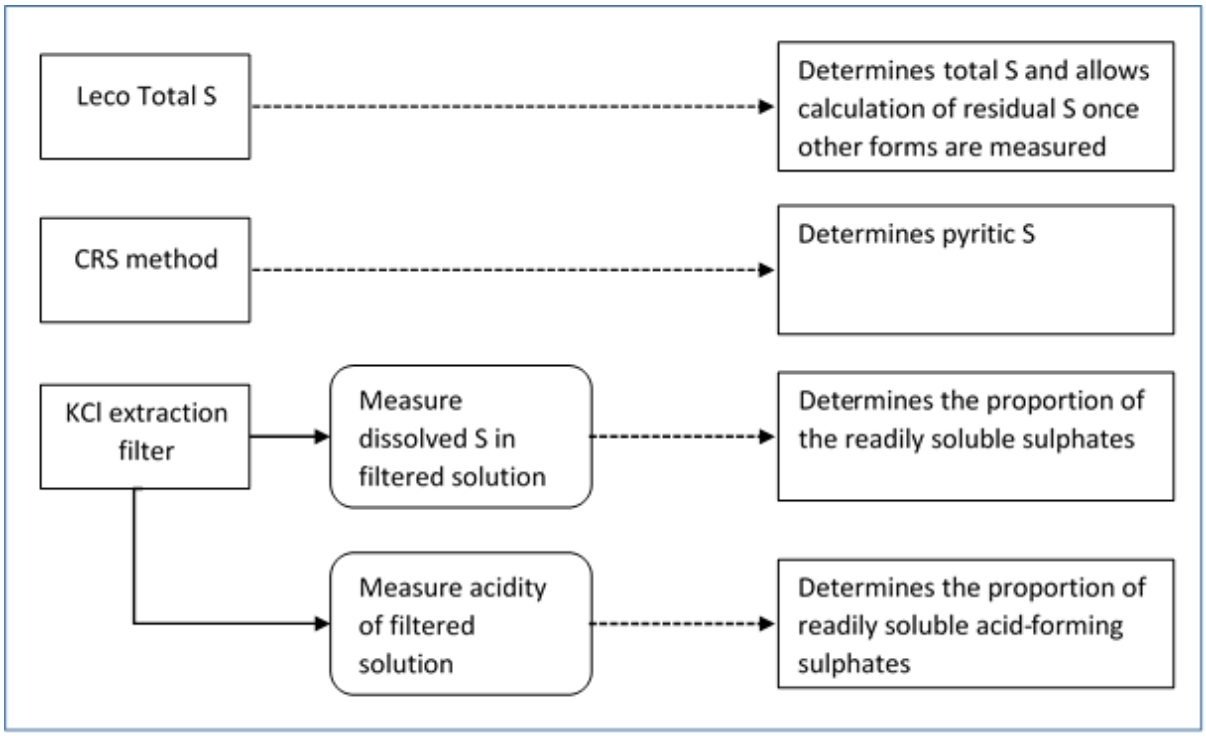

Figure 8 The ACARP C15034 protocol for routine determination of sulphur forms in coal "washery" wastes (Miller, 2008)

The ACARP protocol was developed on the basis of previous studies by Tuttle et al. (2003) and Ahern et al. (2004). The studies by Tuttle et al. (2003) showed that all the sulphates, including high concentrations of gypsum (exceeding 8 wt. %) are soluble in 1 M KCl at room temperature. Contrastingly pyrite, organic sulphur, elemental sulphur and jarosite are not soluble in KCl at room temperature in the extraction period of 1 hour (Tuttle et al., 2003). The method proposed by Ahern et al. (2004) showed that that inorganic (pyritic) sulphur and elemental sulphur are selectively reduced by chromium to form H_2S, and whilst the organic sulphur was determined to be neither extracted by KCl nor reduced by the CRS method (Ahern et al., 2004).

In the application of the KCl extraction method on melanterite/quartz mixture by Miller (2008), 80 ml of 1 M KCl was demonstrated to completely and reliably extract all the sulphates. Titration results of KCl extracted sulphates showed acidity measured by titrating to pH 7 was between 100-110 % of the expected acidity. The results also showed CRS method on synthetic sulphur mineral samples to completely extract pyrite with or without the acetone extraction (Miller, 2008). Application of both methods on coal and coal process wastes from Queensland, New South Wales and Indonesia in the

same study by Miller (2008) showed good reliability on Leco analysis (on all 125 samples). The repeatability of determination of acid-forming and non-acid sulphates on 22 samples was found to be "reasonable". However the results showed the CRS method on the selected 22 samples of coal and coal wastes to be of "reasonable reliability but a significant variance was observed on two samples" (Miller, 2008).

The ACARP C15034 protocol was applied by Kotelo (2013) on ultrafine coal slurry waste from a Middelburg colliery in South Africa. The study showed the protocol evaluated higher values of sulphate sulphur than the ISO protocol and was not precise with percentage standard deviation in excess of ±30 % for sulphate and calculated low-risk sulphur. Kotelo (2013) attributed the poor results to inadequate sample preparation and recommended further evaluation of these protocols. Reliable determination of low-risk sulphur will depend on the accuracy of the Leco analysis to determine total sulphur as well as the accuracy of CRS and KCl methods (Miller, 2008).

Miscellaneous Methods for Sulphur Forms analysis

Complex techniques are now being used to overcome the shortcomings of the standard method used to determine sulphur species. One such method is SEM with energy dispersive X-ray analysis (SEM-EDX) to determine non-pyritic sulphur. SEM / QEMSCAN technique is currently used extensively as a tool to characterize heterogeneous organic and inorganic compounds of coal. In addition to measuring the components on a nanometre to micrometre scale, it gives the 3-dimensional images of the samples (Huggins, 2002). X-ray absorption spectra (XAS) combined with X-ray absorption near edge structure (XANES), can greatly determine the organic species and total sulphur in coal (European Commision, 1998). Gas chromatography is another method used in identifying sulphur forms in coal after solubilisation. Despite the challenges of the standard sulphur speciation method it is still widely used because it is a well-tested method and several studies observed accurate results. Furthermore, the other techniques are more expensive, widely unavailable and require specialized personnel to operate them (European Commision 1998; Laban and Atkin 2000; Speight 2005).

2.5. Laboratory-scale Methods for ARD Characterisation

ARD characterisation is generally for prediction, rehabilitation and management of acid rock drainage associated with mining activities and mine wastes (Parbhakar-fox and Lottermoser, 2015). Several tests have been developed for field and laboratory ARD characterisation and they can be geochemical or mineralogical. Laboratory-scale tests characterise the acid generating behaviour and potential of a sample, providing a first-order estimate of the associated acid generating risks and liabilities. The tests do not predict the actual time-related generation of acid under disposal conditions. Such predictions would require consideration of site-specific disposal conditions and influencing factors.

The commonly used tools for characterising the ARD potential at laboratory scale are the two relatively fast, cost-effective, "worst case scenario" chemical static tests; acid-base accounting (ABA) and net

acid generation (NAG) tests. These tests neither account for the effect of microorganisms on ARD formation nor the rate of acid neutralization or acid production. They are used as the initial screening tools for assessing ARD potential (Smart et al., 2002).The more expensive and longer geochemical kinetic tests i.e. humidity cells and column leach tests are used as follow up tests to assess the relative rates of ARD acid formation and neutralization reactions, elements solubility and leaching behaviour of samples (Morin and Hutt, 1998). Biokinetic shake flask tests were developed at UCT to give time-related behaviour of waste samples incorporating microbial activity in ARD generation but are cheaper and relatively faster than the humidity cells and column leach tests (Hesketh et al., 2010). Bulk mineralogy is also used to evaluate ARD potential from acid-producing minerals and acid neutralising minerals (Lapakko, 2002; Parbhakar-fox and Lottermoser, 2015).

2.5.1. The ARD Static Tests

Routine methods for predicting the ARD potential are based on the net acid production potential NAPP determined in ABA tests and net acid generation capacity determined in NAG tests. Each of the tests has its own ARD classification criteria and limitations to reliably characterise the ARD potential. Very often the classification of the ARD potential uses a combination of both the static tests to better define the ARD potential and to highlight if there is a need for further testing using kinetic tests such as column leach tests or shake flask tests (Smart et al., 2002). The static tests are discussed in detail in the following sections.

Acid-Base Accounting (ABA) Tests

In ABA the net acid-producing potential (NAPP) is calculated as the difference between maximum potential acidity (MPA) and acid neutralising capacity (ANC). There are many methods to test ANC but previous work evaluated the modified Sobek and Skousen method with incremental H_2O_2 as suitable for samples with high silicates and carbonates such as coal wastes (Dyantyi, 2014).

Acid Neutralizing Capacity (ANC)

The ANC tests quantify the acid neutralizing capacity of a sample and the quantity expressed as kg H_2SO_4/Ton. The sample is reacted with a standard solution HCl to dissolve the acid neutralising minerals, and the acid consumed determined through back-titration with NaOH. Siderite correction is necessary during titration to avoid the error of quantifying siderite as acid neutralising because siderite has no net buffering effect (Smart et al., 2002).In conducting the ANC tests, it is assumed only acid neutralizing minerals react with the added HCl and the sulphur species will remain unchanged. However, due to the lack of selectivity some acid soluble sulphides or sulphates can be partially oxidised or solubilised (Dold, 2017), thus potentially under-estimating the ANC of a sample. The tests also assume all the neutralizing minerals are carbonates which will all react with the HCl at the same rate producing the same amount of neutralizing capacity (Paktunc, 1999).

The assumptions made in ANC testing are misleading as several studies have shown mine waste samples to have several acid neutralising minerals e.g. carbonates, amphiboles and silicates which have different acid neutralizing rates and capacities due to their reactivities (Miller, 2008). Carbonates such as dolomite, calcite and ankerite are fast dissolving and have higher acid neutralizing capacity compared to other acid buffers like amphiboles and silicates (see Section 2.2.3). Studies by Dyantyi (2014) showed slow weathering silicates such as mica reacted under the aggressive conditions of the modified Sobek method (Dyantyi, 2014). Although the silicates are acid neutralisers under field conditions the degree of dissolution and reactivity will be perhaps 2 magnitudes lower than in the Sobek and modified Sobek tests; hence the ABA Sobek tests can over-estimate the ANC capacity of samples (Lawrence and Scheske, 1996). Thus the assumption in ABA that all the neutralization is from calcite and using the factor of 49 to calculate the ANC in kg H_2SO_4/Ton is likely to over-estimate the ANC of coal wastes as some of the acid buffering is from silicates and other buffers (Dold, 2017). Furthermore, the tests conditions of vigorous boiling are worst-case scenarios that do not naturally exist under disposal conditions (Lawrence and Scheske, 1996; Paktunc, 1999).

Maximum Potential Acidity (MPA)

It is assumed in standard ABA tests that the MPA of a sample is from all the sulphur in the sample which is assumed to be pyrite. The MPA is assumed to be generated in the reaction:

$$FeS_2 + {}^{15}/_4 O_2 + {}^{7}/_2 H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4 \qquad (27)$$

From the stoichiometry of the reaction, the MPA derived from 1% of sulphur is 30.6 kg H_2SO_4/Ton (Smart et al., 2002). As a result, MPA is calculated from the equation:

$$MPA\ (kg\ H_2SO_4/ton) = Total\ S(\%) * 30.6 \qquad (28)$$

The assumptions have been reported to over-estimate the MPA of coal waste samples as not all total sulphur is pyrite and organic sulphur and some sulphates are non-acid-forming (Kotelo, 2013; Miller et al., 2008; Stewart et al., 2009). Furthermore, some sulphides in the coal wastes such as sphalerite and galena produce less acidity compared to pyrite and multiplying with the same factor of 30.6 will over-estimate MPA (Miller et al., 2010; Schumann et al., 2012; Stewart et al., 2009). According to Paktunc (1999), if a sample contains both pyrite and pyrrhotite, the overestimation of the MPA can be as high as 1.5 times. Overestimation is very prominent in weathered coal waste samples that contain more sulphates, particularly non-acid-forming sulphates than in fresh samples (Schumann et al., 2012). Instead several researchers propose that pyritic sulphur be used instead to calculate MPA, consequently methods such as chromium reducible sulphur (CRS) method were developed to measure the sulphide sulphur (Schumann et al., 2012; Smart et al., 2002; Stewart et al., 2009; Tuttle et al., 2003).

Net Acid-producing Potential (NAPP)

The NAPP is calculated from the equation:

$$NAPP = MPA - ANC \quad (29)$$

The NAPP value is used to classify the ARD potential of the samples. A positive NAPP indicates the sample does not have enough acid neutralizing capacity to counteract the acid the sample can generate. While negative NAPP indicates the sample has the potential produce enough acid neutralization to nullify the sample can produce.

Net Acid Generation (NAG) Tests

In NAG tests the acidity is quantified after reacting usually 2.5 g of the sample with 250 ml of H_2O_2 overnight allowing simultaneous acid generation and acid neutralizing reactions of the sample. The net acidity produced is obtained from titration of the sample solution after boiling, cooling and filtration. The after boiling pH (NAG pH), the acid consumption to pH 4.5 and pH 7 gives an indication of the acidity strength and nature (free acidity at pH 4.5 and elemental effect acidity pH 7). NAG pH above 4.5 and classifies the sample as NAF, while pH below 4.5 and NAG capacity above 5 kg H_2SO_4/Ton classifies the sample as NAF otherwise the sample is classified as uncertain (Smart et al., 2002). Misleading results by NAG can be as a result of high pyritic sulphur (> 0.7-1 %) which decomposes the H_2O_2 before complete oxidation of the sample. In such samples, a sequence of the NAG tests is repeated until complete oxidation occurs. In samples with high organic contents (>5%), the H_2O_2 can cause partial oxidation of the carbonaceous material in coal waste forming organic acids which contribute to net acidity causing an overestimation of the sample acidity potential (Miller, 2008; Smart et al., 2002).

The extended boil protocol developed in Australia under the ACARP C15034 program validates the effects of organic acid on NAG tests performed on coal processing wastes (Miller, 2008). The method involves performing the NAG test but without titration then boiling part of the leachate rigorously for 3-4 hours. The extended boiling is meant to eliminate the acidity derived from organic acids during NAG digestion. In the event that organic acids were dissolved during the leach period, the extended boiling will cause an increase of the leachate pH as the organic acids dissociate (Miller, 2008; Stewart et al., 2009). Application of the extended boil NAG protocol showed the extended boiling could also cause loss of free acidity, hence extended boil NAG pH below 4.5 indicates the sample is PAF but above 4.5 might not signify the sample is NAF. To address the problem of loss of acidity during vigorous boiling, a calculated NAG on the split of the filtered NAG solution (without extended boil) was developed. The NAG capacity is calculated from cations and anions associated with acid-forming acid neutralising minerals as shown in the equations (30-32) below. If calculated NAG is less or equal to zero, it means the sample is likely to be NAF and otherwise means the sample is likely to be PAF (Miller et al., 2008; Stewart et al., 2009).

$$Acid\ component = \left[{}^{[S]}/_{32.06}\right] \times \left[{}^{Vol_{NAG}}/_{Wt_{samp}}\right] \times 98.07 \quad (30)$$

$$Neutralising\ Component = \left[\left({}^{[Ca]}/_{40.1}\right) + \left({}^{[Mg]}/_{24.3}\right) + 0.5 \times \left({}^{[Na]}/_{22.9}\right) + 0.5 \times \left({}^{[K]}/_{39.1}\right) - 0.5 \times \left({}^{[Cl]}/_{33.45}\right)\right] \times \left[{}^{Vol_{NAG}}/_{Wt_{samp}}\right] \times 98.07 \quad (31)$$

$$Calculated\ NAG\ Acidity = (Acid\ Component) - (Neutralising\ Component) \quad (32)$$

Where

- Concentration of S, Ca, Mg, Na, K, and Cl are in mg/L
- Vol_{NAG} is the volume of the original NAG solution in litres (normally 0.25L)
- Wt_{sample} is the weight of the sample used in the original NAG test in grams (normally 2.5 g)
- Calculated NAG Acidity units are kg H_2SO_4 per Ton

Classification of ARD Potential Based on Static Tests

The chemical static tests identify the likelihood of samples to pose an ARD risk based on the samples geochemical properties. The samples are classified as potentially acid-forming (PAF), non-acid-forming (NAF) or uncertain (UC). For a sample to be PAF its acid-producing potential should be significantly higher than its acid neutralizing potential. On the other hand, if potential acidity is lower than the acid neutralizing potential it is classified as NAF. The classification criteria used by static different static tests are shown in Table 10.

Table 10 ARD potential classification criteria of different methods adapted from Smart et al. (2002)

ARD prediction tests	Result	Units	Classification guideline
Acid-Base Accounting	NAPP > 20	kg H_2SO_4/Ton	Potentially acid-forming (PAF)
	-20< NAPP<20	kg H_2SO_4/Ton	Uncertain (UC)
	NAPP<-20	kg H_2SO_4/Ton	Non-acid-forming (NAF)
Net Acid Generation	NAG pH < 4.5 & NAG >5	kg H_2SO_4/Ton	Potentially acid-forming (PAF)
	NAG pH < 4.5 & NAG=5	kg H_2SO_4/Ton	Potentially acid-forming with low capacity (PAF-LC)
	NAG pH > 4	pH	Non-acid-forming (NAF)
Combined static tests	NAG pH < 4.5 and NAPP > 0		Potentially acid-forming (PAF)
	NAG pH > 4.5 and NAPP <0		Non-acid-forming (NAF)
	NAG pH>4.5 and NAPP>0 or NAG pH<4.5 and NAPP<0		Uncertain (UC)

2.5.2. ARD Kinetic Tests

Kinetic tests were developed to simulate field conditions and have been used to study the quality of products from ARD leaching and the respective rates of ARD formation of mine wastes (Morin and Hutt, 1998; Smart et al., 2002). The kinetic tests are applied as follow up tests after the static tests to get information of time-related behaviour of samples which cannot be generated by static tests. In

addition, they validate the ARD classification of samples as well as define the classification of the ARD potential of samples that would have been classified as uncertain by static tests (Smart et al., 2002).The commonly used kinetic tests are the humidity cells and the column leach tests. The major drawbacks of these tests are they are relatively expensive and may need to be run for long periods of time (months to years)due to lag time and longevity of ARD formation (Morin and Hutt, 1998).In order to address these shortcomings of the kinetic tests, a batch biokinetic shake flask test, which is more economical and faster than the humidity cells and leach columns was developed at UCT (Hesketh et al., 2010).

Column Leach Tests and Humidity Cells

Column and cells come in different sizes and shapes but they are all loaded with crushed sample which is subjected to cyclic oxidation/wetting, drying and flushing. The deionised water used for flushing collected and analysed for sulphide reactivity, oxidation kinetics, elements solubility and leaching behaviour (Morin and Hutt, 1998). The standard tests for humidity cells (ASTM D5744-96) recommend 20-25 times of the cycles to enable collection of meaningful data on pH, conductivity and dissolved elements. Operation of the humidity cell under the same standard has a 7-day cycle in which 1 kg of a sample of grain size 6 mm has 3 days of exposure to humid air, 3 days of dry air and the system is flushed on the last day. The commonly used free draining leach column described by Smart et al. (2002) has a 2-2.5 kg sample (nominal grain size 4mm) load weekly wet-dry cycle and a monthly flushing cycle. The material characteristics and the required results determine the test period of the leach column tests, but usually the results are reviewed on a 6 months' basis. According to Morin and Hutt (1998), the objective of the humidity cells is to provide primary-mineral reaction rates only. On the other hand, the column leach tests seek to provide primary- mineral reaction, secondary-mineral reaction and reaction by slow dissolution of less- reactive primary and secondary minerals.

Although column leach tests and humidity cells have been used as early as 1950, there are currently no standard methods that were tested and accepted for ARD characterisation for the coal mining industry (Banerjee, 2014). According to Dold (2017), there is very limited published research on the application of kinetic methods on coal. One of the published studies reported that no acidification or increase in elemental concentration was observed in humidity cell tests conducted over 15 weeks despite the samples being classified as PAF by ABA tests (Banerjee 2014). As a result, the humidity cell tests could not give conclusive results. Column leach tests conducted by Miller (2008) on 14 samples of coal and coal process waste for a period ranging from 20-112 weeks could not give conclusive results on five samples which had been classified by static tests as NAF. The lag periods before on-set of net acid generating behaviour in the absence of bacterial activity can be very long (up to decades), particularly where samples have a high content of acid neutralising minerals. Hence laboratory-scale tests over limited time periods may indicate that a sample is non-acid generating, whereas it may be acid generating over the longer term (Banerjee, 2014).

In addition to being generally expensive and longer operation time, the other common limitation of these kinetic test methods is their sensitivity to test conditions and methods of interpretation (Morin and Hutt, 1998). Human interpretation is often misled by precipitation of gypsum which is mistakenly taken as acid neutralization causing prediction of low ARD potential. As a result of the outlined limitation of the column leach and humidity cell tests scale-up to field data is generally associated with high uncertainty and interpretation of results is often controversial (Morin and Hutt, 1998; Dold, 2017).

Biokinetic Shake Flask Tests

The biokinetic tests shake flasks were developed by Hesketh et al. (2010) to study the ARD behaviour of samples incorporating the impact of micro-organisms on ARD formation. In the test, 150 ml of autotrophic basal salt (ABS) solution of pH 2 is added to 7.5 g of milled sample and the mixture is inoculated by a mixed bacterial culture comprising of iron and sulphur oxidisers such as *Leptosprillium ferriphilum* and *Acidothiobacillus caldus* respectively. The flasks are run on a 150-rpm shaking platform at 37 ^{O}C for 90 days. Sampling is done to obtain data on pH, redox, sulphate and dissolved elements concentration.

The tests have been applied on gold (Dyantyi, 2014; Opitz, 2013), copper (Hesketh et al., 2010) and coal tailings (Kazadi Mbamba et al., 2012; Kotelo, 2013; Opitz et al., 2015). Biokinetic tests provide an indication of the relative rates of biologically catalysed acid-forming and acid neutralising reactions, and the potential time-related behaviour of a sample following depletion of the acid neutralising minerals. In addition to the batch shake flask tests, Kotelo (2013) conducted the biokinetic tests on the Middelburg ultrafine coal waste in a semi-continuous mode by an interval replacement of 90 % of the supernatant with circum-neutral ABS solution. The results of the study show effect of microbial activity, with the acid neutralising capacity becoming rapidly depleted in the presence of bacteria, and the sample subsequently becoming net acid-forming under both batch and semi-continuous test conditions. Conducting the biokinetic tests in a semi-batch mode provided valuable data on the time-related behaviour of the coal waste under a microbial catalysed pseudo open system which can exist in a dump scenario.

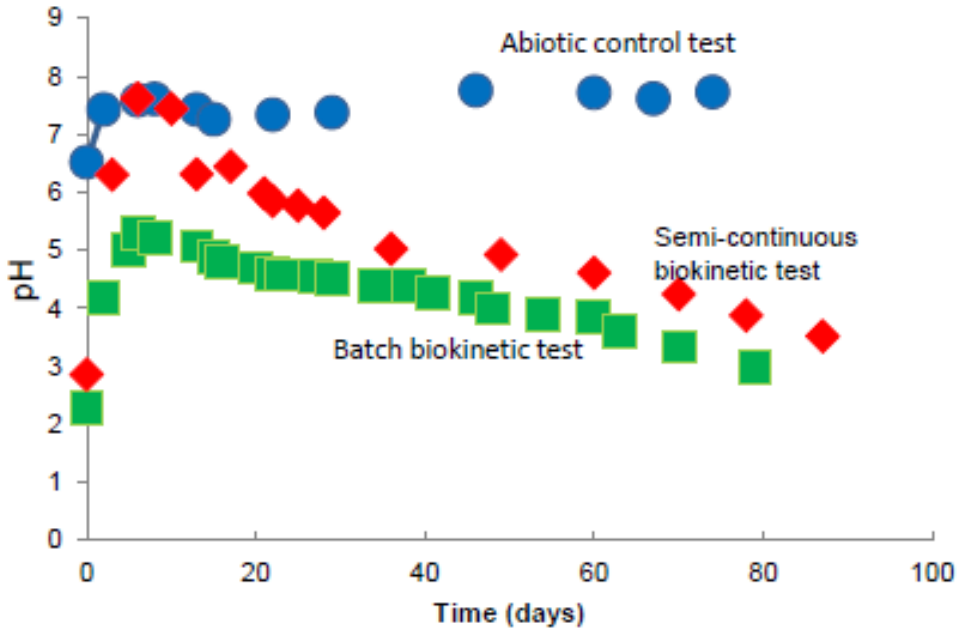

Figure 9 Biokinetic test results of a Middelburg ultrafine coal waste (Kotelo, 2013)

2.5.3. Theoretical ARD Based on Mineralogy

In Section 2.5.1 it was discussed that errors in measuring the neutralizing potential (NP) and the acid generating potential (AP) in static tests can result in the misclassification of the ARD potential of mine wastes. The static tests are prone to overestimate or underestimate the NP of waste samples since no distinction is made of the acid neutralising minerals and their neutralising capacities. Furthermore, the acid generation potential differs for different sulphur minerals and considering the AP of individual minerals will provide a better estimate than basing the acid generating capacity on the concentrations of sulphur forms, as in the case of the ABA tests (Paktunc, 1999). Several researchers have highlighted that ARD potential calculated based on a samples mineralogical composition can assist in interpreting static test results, providing complementary and validating information (Dold, 2017; Lawrence and Scheske, 1997; Paktunc, 1999; Parbhakar-fox and Lottermoser, 2015). Lawrence and Scheske (1997) developed a method for calculating NP from mineral abundances obtained through normative CIPW calculation of whole rock analysis and relative reactivity factors. The reactivities of typical coal minerals are shown in Table 11. This method was, however, questionable because it could predict NP from minerals that were not actually present in the sample since mineralogy of individual minerals was calculated and not directly determined (Paktunc, 1999).

Table 11 Relative reactivities of minerals at pH 5 (after Sverdrup (1990) and Kwong (1993) as cited by Lawrence and Scheske (1997))

Mineral group	Typical minerals	Relative reactivity at pH 5
Dissolving	Calcite, aragonite, dolomite, magnesite, brucite	1.00
Fast weathering	Anorthite, nepheline, forsterite, olivine, garnet, jadeite, leucite, spodumene, diopside, wollastonite	
Intermediate weathering	Sorosilicates, (epidote, zoisite), pyroxenes (enstatite, hypersthene, augite, hedenbergite), amphiboles (hornblende, glaucophane, tremolite, actinolite, anthophyllite), phyllosilicates (serpentine, chrysotile, talc, chlorite, biotite)	0.02
Slow weathering	Plagioclase feldspars (albite, oligoclase, labradorite), clays (vermiculite, montmorillonite)	0.01
Very slow weathering	K-feldspars, muscovite	0.01
Inert	Quartz, rutile, zircon	0.004

To overcome the shortcomings of this method, Paktunc (1999) proposed a new method of calculating NP using mineralogy abundance and stoichiometry of neutralization reactions. The bulk NP in kg H_2SO_4/Ton is calculated as:

$$NP = \sum_{i=1}^{k} \frac{98*10*X_i*c_i * n_s}{n_i*\omega_i} \quad (33)$$

Where: X_i is the amount of mineral i in wt. %; ci is the number of non-oxidizable cations in one formula unit; n_i is the moles of H_2SO_4 by oxidation of one mole of sulphide minerals; n_s is the moles of minerals required to consume n_s moles of H_2SO_4; ωi is the molecular weight of neutralizing mineral I (g/mol) and k is the number of neutralising mineral in the sample.

Since the total sulphur overestimates the AP in ABA by assuming all sulphur is pyritic, the calculated AP kg H_2SO_4/Ton) uses the formula (equation 34) which takes into consideration other sulphides other than pyrite.

$$AP = \sum_{i=1}^{m} \frac{98*10*X_s* n_s}{\omega_s} \quad (34)$$

Where; X_s is the amount of sulphide mineral s in wt. %; ω_s is the molecular weight of sulphide mineral s (g/mol) and n_s is the number of sulphide minerals in the sample.

The NAPP is calculated from the difference of AP and NP.

$$NAPP = AP - NP \quad (35)$$

Positive NAPP classifies the sample as PAF while negative NAPP classifies the sample as NAF. The correlation of calculated mineralogical NP and experimental NP by Paktunc (1999) and Lawrence and Scheske (1997) showed that the majority of the experimental ANC values obtained from the ABA tests were overestimated relative to the theoretical NP. The overestimation was attributed to the enhanced reactivity of slow weathering NP minerals and the assumption all neutralization was from calcite under static ABA tests. Use of mineralogy as a tool to evaluate ARD potential is still evolving and no published studies could be found on theoretical ARD of coal or coal wastes based on mineralogy. According to Paktunc (1999), the mineralogy based AP and NP gives an interpretation of static tests results and kinetic tests as the relative reactivity of each mineral can be determined from mineralogy analysis.

2.6. Assessment of Potential Environmental Risks

Environmental impacts associated with coal waste piles are significant in South Africa, particularly water pollution resulting from ARD and its associated elevated levels of elements and salts (Hall, 2013; Munnik, 2010). To address the need of first-order indication of potential risks posed by mineral waste researchers at UCT developed a protocol that allows systematic prediction of potential risk posed by solid mine waste on the environment (Broadhurst and Petrie, 2010). The protocol ranks and scores the potential risk based on the concentration, availability and properties of the constituents of the solid mine waste. The risk potential factor (RPF_i) is calculated from the equation:

$$RPFi = \frac{(ACi)^2}{ARCi \times BCi} \qquad (36)$$

Where AC_i is available concentration, ARCi environmentally accepted concentration and BC_i the natural background concentration. The ARCi values are obtained from guidelines for environmental indicators such as drinking water and soil. The BCi are the crustal abundances of the respective elements, while the ACi is the leached amount (Broadhurst and Petrie, 2010). Besides elemental and salinity data that can be obtained from kinetic ARD tests, sequential chemical extractions (SCE) are useful characterisation tools to provide the available concentration from leaching of waste piles (Parbhakar-fox and Lottermoser, 2015).The calculated RPFi is used to rank and score the environmental significance of the solid mine waste using the criteria in Table 12.

Table 12 Criteria for ranking and scoring the risk potential factor in terms of environmental significance (Broadhurst and Petrie, 2010)

Group Description	Maximum Risk Potential Factor/ 1000
Very high environmental significance	>10 000
High environmental significance	A:1 000 – 10 000 B: 100 – 1 000 C: 10 - 100
Moderate environmental significance	1 - 10
Low environmental significance	0.1 - 1
Non-strategic environmental significance	< 0.1

2.6.1. Sequential Chemical Extraction

Various techniques have been developed to separate and analyse the solid phase forms of elements in the matter. SCE is one such useful technique developed over the years for fractionating different forms of elemental phases particularly of sediments and soils using different reagents and conditions for extraction (Tessier et al., 1979). SCE is now also widely applied in characterising chemical and mineral wastes, for the identification and quantification of the mobilization behaviour and to assess the risk potential of elements in the waste (Dang et al., 2002; Hall et al., 1996; Sun et al., 2015). SCE has been applied to coal and coal wastes internationally including in South Africa (Dang et al., 2002; Hall et al., 1996; Opitz et al., 2015; Silva et al., 2011; Wagner and Hlatshwayo, 2005).

The quantification is done through successive extraction of sample constituent elements by chemical solutions (reagents) of varying but specific strengths and reactivities and the concentration of analytes (supernatant) mobilized is quantified by various analysing techniques e.g. ICP – MS, ICP –OES, AAS (Gleyzes et al., 2002). It is assumed each extraction stage is selective to the targeted fraction. The fractions examined are assigned according to the chemical surroundings and the defined species the element occurs (which is a function of mineralogy and chemistry). The extraction steps allow fraction mobilization (mobility decreases with progressive extraction) and importantly the bioavailability and the speciation of the elements, which allows the prediction of their environmental behaviour (Hall et al., 1996; Tessier et al., 1979). The commonly used SCE procedures are adopted or developed from the sequence proposed by Tessier et al. (1979) and the Commonly Bureau of Reference (BCR) method (Gleyzes et al., 2002; Huggins, 2002; Zimmerman and Weindorf, 2010). Other procedures used are Short, Galan and Geological Society of Canada (GCS) procedures (Zimmerman and Weindorf, 2010). The common leaching medium, partitioning fractions and mobilised phases are summarised in Table 13.

Exchangeable fraction is of elements adsorbed to the exposed surface that can change ionic compositions with water that can easily remove by salt solution while carbonate bound fraction is weakly absorbed to the matrix and is susceptible to pH changes and can be easily removed by an acid solution (Tessier et al., 1979). Fe and Mn Oxide Bound fraction is also called hydrous-oxide bound and

is susceptible to anoxic (reducing) conditions and can be extracted by a solution that dissolves insoluble sulphide salts (Gleyzes et al., 2002). The fraction was further divided into amorphous oxyhydroxides and crystalline oxides by the GSC. Some researchers further divided this fraction to EDTA extractable, moderately reducible and strongly reducible (Mittermüller et al, 2016; Zimmerman and Weindorf, 2010). Organic matter bound elements are organically bonded and the material must be oxidised to extract the elements. Residual fraction is also called lattice material as the materials are incorporated into the crystal structure of primary and secondary minerals. The elements are not easily removed and require strong acids to break the lattice structure, as a result, they are not expected to be released in the environment under natural conditions (Tessier et al., 1979).

Table 13 Fractions for element partitioning and their associated extracting reagents and mobilised phases in the Tessier sequential chemical extraction procedure adapted from Gleyzes et al. (2002)

Fraction	Extracting Reagents	Extracted phase
Fraction 1: Exchangeable	$MgCl_2$ / CH_3COONH_4 / $BaCl_2$, $Mg(NO_3)_2$ / $CaCl_2$ / KNO_3 / $Ca(NO_3)_2$ / NH_4Cl / NH_4NO_3	Adsorbed, ionic exchangeable
Fraction 2: Bound to carbonates	1 M CH_3COONa acidified with CH_3COOH / 0.1-1 M non-buffered CH_3COOH / EDTA	Carbonates, organic bound and Fe/Mn oxyhydroxides
Fraction 3: Bound to iron and manganese oxide	0.04-0.5 M $NH_2OH.HCl$ in 25 % v/v HOAc or 0.25 M HCl / 0.2 M $NH_4C_2O_4$ / $Na_2S_2O_4$+Na-citrate	Bound to oxides of Fe, Mn and Al
Fraction 4; Bound to Organic Matter	30 % H_2O_2 + 0.02 M HNO_3 / 0.7 M NaClO / 0.5 M NaOH / 0.1 M $Na_4P_2O_7$ / 0.1 M $K_4P_2O_7$	Bound to organic matter, some sulphides
Fraction 5: Residual	HF+ HCl+ HNO_3 or $HClO_4/H_2SO_4/H_2O_2$	Bound in crystalline lattice

Although widely used SCE are riddled with limitation as there is no single SCE procedure and no set of standards that can be applied across disciplines (Zimmerman and Weindorf, 2010). Several studies of SCE on trace elements have shown inconsistent results for certain elements like Cr, As, V and Se and for certain elements, it is recommended to develop standards should for reliable consistent data (Hall et al., 1996; Wagner and Hlatshwayo, 2005; Zimmerman and Weindorf, 2010). The major causes of inconsistency reported by several researchers are the lack of reagents that can only solubilise a target fraction and not the detrital fraction, non-uniformity in the leaching procedures and re-adsorption and redistribution of phases (Gleyzes et al., 2002; Hall et al., 1996; Huggins, 2002; Tessier et al., 1979; Wagner and Hlatshwayo, 2005; Zimmerman and Weindorf, 2010). Despite the limitations, SCE is widely used and regarded an essential tool to establish distribution, mobility and bioavailability in soils, sediments, and mine wastes (Gleyzes et al., 2002). To demonstrate the usefulness of SCE in identifying

elements of environmental concern UCT researchers adopted modified SCE test protocols from previous investigators and applied it on copper tailings (Broadhurst et al, 2009).

2.7. Summary of Literature Review

The processing of coal in South Africa to meet the local and international market specifications produces large volumes of coal preparation wastes pegged at 60 million tons per year in the report by Eberhard (2011). The compositions of coal and coal wastes are complex; with the constituents comprising of organic and mineral matter. The sulphur in both coal and coal wastes occurs in many forms and is associated with both the organic and mineral components. In addition, there are a number of elements in major, minor and trace levels in coal and coal wastes. The compositions of the coals vary quite significantly from region to region, as well as within the same coal deposits. Hence the coal cleaning process is quite complex, entailing many different technological options. This gives rise to a number of coal processing waste types (including fine to coarse discards, and ultrafine slurries), with varying physio-chemical characteristics. These wastes are largely disposed of in landfills and have been linked to environmental pollution, particularly acid rock drainage and its associated elevated levels of elements and salts. The environmental performance of the coal wastes is shown to be dependent on the mineralogy and physio-chemical properties. Adequate characterisation techniques and sufficient risk evaluation tools are fundamental to obtain reliable characterisation data necessary for assessing and mitigating the potential environmental risks of coal processing wastes.

Whilst many laboratory-scale methods exist for determining the mineralogical and chemical compositions and for characterising the potential environmental risks of mineral wastes. However, these methods have been largely developed for hard rock ores and application to coal wastes in particular, has been limited and characterised by high uncertainty. The complex compositions of coals and coal processing wastes make it difficult to interpret the results from standard tests for characterising the acid rock drainage potential of these wastes. Effects of organic acid have been reported to over-estimate the net acid generation capacity while the existence of various forms of sulphur and acid neutralizing minerals in coal wastes has been reported to cause uncertainty with acid-base accounting. A more detailed understanding of the mineralogical compositions of coal processing wastes as well as the deportment and behaviour of sulphur species is key in this regard. Of importance is the acid generating behaviour of coal wastes, and the associated pollution risks from the release of salts and elements. Further work is also needed to identify the potential water-related risks due to salinization.

Evaluation of accuracy, reproducibility and repeatability of commonly applied analytical techniques for total sulphur elemental analysis and sulphur forms ensures certainty with the physio-chemical characterisation data. The application of both QXRD and QEMSCAN allows identification and quantifying of both the organic and inorganic phases in the coal wastes as well as show how the phases

are associated. On the other hand, sequential chemical extractions (SCE) are an essential tool that can give details on leaching behaviour, mobility, and physiochemical availability of the elements. The SCE results can be modelled in the risk assessment protocol developed at UCT to evaluate potential risk posed by elements and salts in coal processing wastes based on their availability, concentration and toxicity. Development of the NAG extended boil protocol allows elimination of organic acids effect on net acid generation capacity of wastes with organic content. While the ACARP C15034 protocol was developed specifically for evaluating acid-forming species to assist in evaluating the maximum possible acid generating capacity of coal processing wastes. Mineralogy based theoretical ARD potential is an emerging tool that can validate static tests ARD potential by calculating theoretical acid generation and neutralisation capacity of individual minerals. However, the static tests and mineralogy calculated ARD neither considers the respective rates of ARD formation nor the effects of micro-organisms on ARD formation. On the other hand, the biokinetic tests show the time-related ARD behaviour taking into consideration microbial catalysis on ARD formation which is likely to occur in real disposal conditions.

2.8. Research Hypotheses and Questions

Review of literature shows various analytical techniques and risk assessment protocols of different merits have been developed some of them specifically for coal waste. The literature review also shows that reliable characterisation methods are necessary for the comprehensive and reliable characterisation of the relevant properties and behaviours of coal processing wastes. The following hypotheses were formulated from the literature review:

1. The ARD, toxic elements and salinity risks posed by coal processing wastes are insufficiently and inconsistently characterised. This is a result of the complex nature of coal wastes which causes uncertainty and limitation with elemental and mineralogical analysis using available techniques and risk assessment tools. The uncertainty in evaluation of ARD potential is because of occurrences and behaviour of sulphur species and effects of organic acids on the acid producing potential.
2. The coal processing waste generated from different coalfields and processing operations in South Africa have the potential to cause environmental impacts of varying magnitudes from ARD and elevated concentration of toxic elements and salts owing to their different geochemical properties.

To test these hypotheses and address the gaps and uncertainties in characterising coal wastes from the literature review findings, this research seeks to address the following research questions:

- How reliable and reproducible are the commonly used total sulphur and sulphur speciation tests and how much sulphur and what are the forms in coal processing wastes?
- How accurate are the commonly used elemental analysis techniques and what are the elemental compositions of the coal processing waste?

- What is the ARD potential of coal wastes using conventional static tests and biokinetic tests?
- How does extended boil NAG tests validate the ARD potential classification by the conventional static tests?
- How does the sulphur species behave under static tests and what is the implication on ARD potential
- What is the leaching behaviour of the coal waste elements under disposal conditions and the long-term environmental impact risk of salts and elements mobilized under disposal conditions?
- How does the mineralogy of the coal waste influence the environmental risk of the coal wastes?

CHAPTER 3

MATERIALS AND METHODS

The methodology to answer the research questions outlined in Chapter 2 is detailed in this chapter. In order to test the accuracy of analytical techniques, a South African coal standard was analysed and accuracy was calculated using certified values of the coal standard. Using the more accurate and precise techniques and evaluation protocols the potential environmental risks of coal processing waste were assessed. The case studies were done using coal processing waste samples from different S.A coal processing units. After the standard sample preparation, the research approach used mineralogical analysis, chemical analysis, physical analysis, ARD potential tests, and sulphur speciation, sequential chemical extraction, and ranking and scoring as expressed in Figure 10. Further details of the methodologies are given in Appendix A.

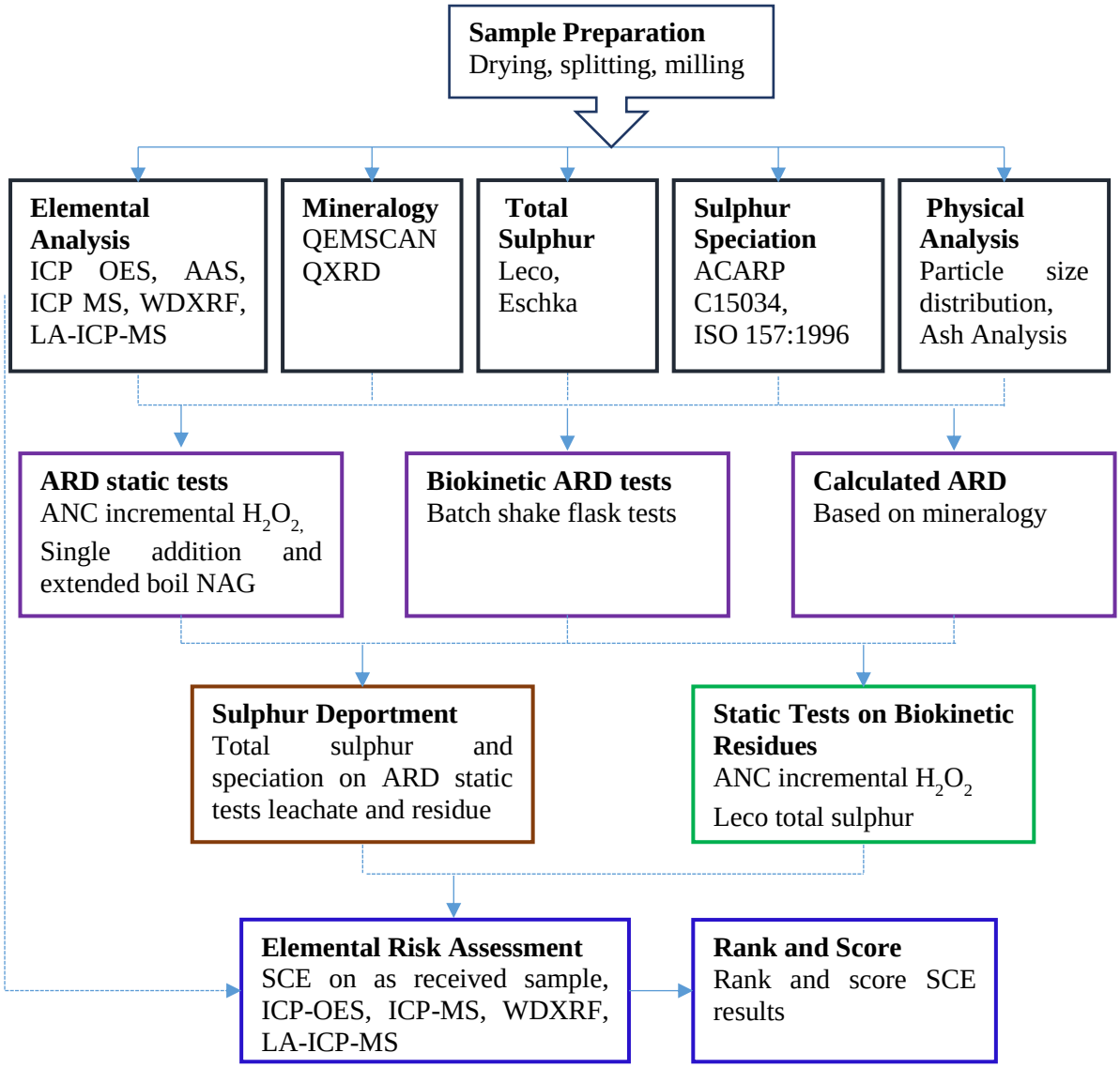

Figure 10 Schematic presentation of the experimental approach and methods used in this research

3.1. Sample Description and Preparation

Three coal processing waste samples, an ultra-fine slurry from a colliery in the Waterberg coalfield, an ultra-fine slurry and a coarse discard from the same colliery in the Witbank coalfield were used in this study. The samples were taken from different coal processing units and sample preparation was done using the standard preparation of samples for analysis (ASTM D-346; ASTM D-2013) to reduce particle size and splitting into representative samples according to the analysis to be done.

3.1.1. Waterberg Coal Slurry Sample (Sample A)

The sample is the same as the one previously used by Iroala (2014), and Opitz et al. (2015). According to Iroala (2014), "64 kg dried thickener feed (-180 µm) from a colliery in the Waterberg coalfield was blended and passed through a Dickie & Stockler rotary splitter, dividing it into ten equal portions. Two samples from adjacent positions were then combined and further divided into smaller samples. This

procedure was repeated until the samples were grouped into bags of approximately 0.5 kg which were sealed for airtight storage in sample bins."

3.1.2. Witbank Coal Slurry Sample (Sample B)

70 kg of as "arising "thickener underflow tailings were received as a slurry from a colliery in the Witbank coalfield. The slurry was poured into plastic dishes and placed in the 37 ^{O}C walk-in room for drying. The drying took two weeks, after which the samples were manually un-agglomerated. The samples were then split and divided into approximated 0.5 kg portions using 10-Dickie and Stockler splitter. The 0.5 kg sample bags were sealed and placed in storage bins.

3.1.3. Witbank Discard Sample (Sample C)

140 kg of discards from the dense medium separation and/or screening were also received from the colliery in the Witbank coalfield. The discards were placed in plastic dishes and placed in the 37 ^{O}C walk-in room for two weeks to dry. The samples were divided into approximately 5 kg portions by repeatedly cone and quartering. Two portions were used for particle size distribution and ash analysis, and another portion was crushed by a jaw crusher to 3mm. After the crushing, the sample was split using 10-Dickie and Stockler rotary splitter. The 0.5 kg sample bags were sealed and placed in storage bins.

3.1.4 Coal Standard (SARM 19)

For reference, a South African (Free State) coal standard reference material, SARM 19 was used to assess reproducibility and accuracy of methods for total sulphur determination and elemental analysing techniques.

The air-dried coal waste samples in the 0.5 kg zip-lock bags were pulverised to -75 µm and split to required amounts using a 10-Dickie and Stockler rotary splitter and 8-Rotary micro riffler (shown in Figure 11) depending on the amount required for the test.

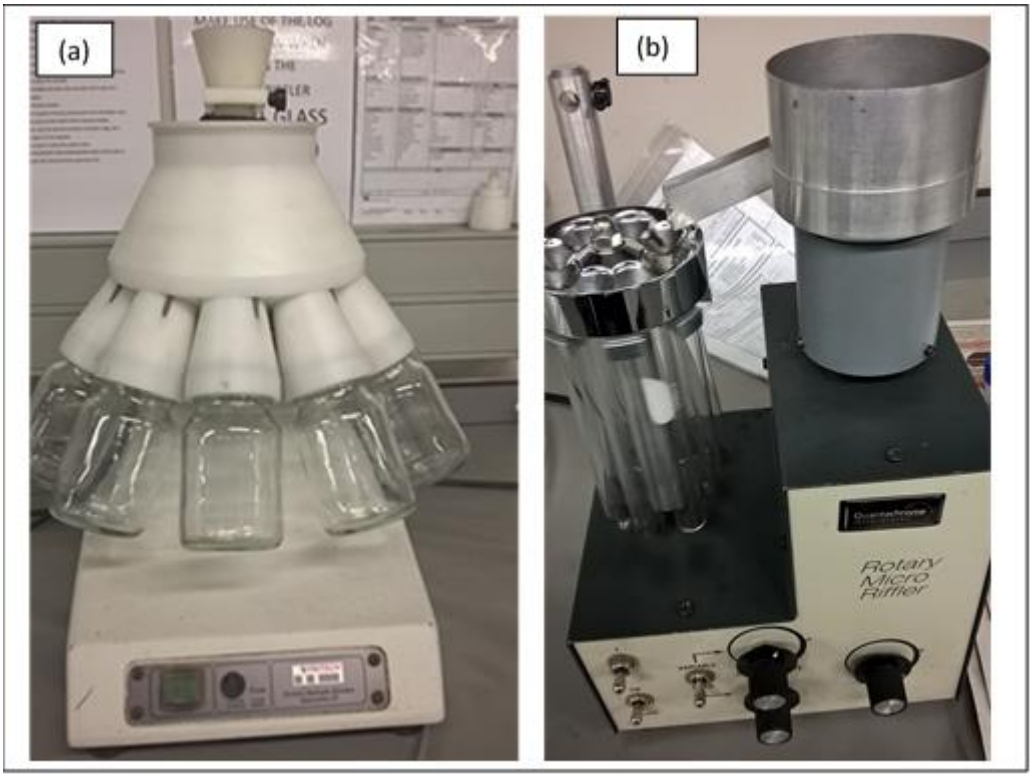

Figure 11 (a) a 10-Dick and Stocker Rotary Splitter and (b) an 8-Rotary Micro Riffler

3.1.5. Summary of All Conducted Tests

All the tests that were done on the three coal processing wastes samples and the coal standard SARM 19 are summarised in Table 14

Table 14 Summary of test work carried out on the coal standard (SARM 19) and the coal wastes sample A (Waterberg coal slurry), sample B (Witbank coal slurry) and sample C (Witbank coal discards)

Test Work	Sample A	Sample B	Sample C	SARM 19
Particle size distribution	✓	✓	✓	×
Ash analysis	✓	✓	✓	×
Leco Total S	✓	✓	✓	✓
Eschka total S	✓	✓	✓	✓
QEMSCAN	✓	✓	✓	×
XRD	✓	✓	✓	×
ISO 157:1996	✓	✓	✓	✓
ACARP C15034	✓	✓	✓	✓
ANC Test	✓	✓	✓	×
NAG Test	✓	✓	✓	×
Extended Boil NAG	×	✓	✓	×
Biokinetic shake flask test	✓	✓	✓	×
Sulphur deportment under ARD	✓	✓	✓	×
ICP-MS	×	×	×	✓
ICP-OES	✓	×	×	✓
WDXRF	✓	✓	✓	✓
LA-ICP-MS	✓	✓	✓	×
AAS	✓	×	×	✓
Sequential chemical extractions	✓	✓	✓	×
Risk ranking and scoring	✓	✓	✓	×

3.2. Particle Size Distribution

For experimental work, the un-pulverized Waterberg and Witbank coal slurry wastes were further split and divided into about 150 g using the same splitter, for the Witbank coal discards the two 5 kg portions were used as they were. The samples were then analysed for particle size distribution using dry sieving with the addition of rubber balls in the sieves to allow separation of the fine particles of the two coal slurry wastes which had a tendency to clump. The particle size distribution (PSD) was done in duplicate and the size fractions were determined from the average. Ash analysis was then done on each size fraction.

3.3. Ash Analysis (SANS 131:2011 / ISO 1171)

All sizes above 212 µm were first pulverised to below 212 µm. Followed by1g of each size fraction of the samples being weighed to the nearest 0.1mg into weighed silica crucibles in triplicates and placed in a cold furnace. Then the furnace temperature was raised to 815^{O}C ± 10 ^{O}C and maintained for 2 hours

before switching off the furnace. After combustion, the crucibles were transferred into desiccators for cooling before weighing. The ash content was calculated as a proportion of the original sample mass. The bulk ash content was calculated from the formula:

$$Ash = \frac{m_3 - m_1}{m_2 - m_1} \quad (37)$$

Where:

m_1 is the mass (g) of the empty crucible; m_2 is the mass (g) of the crucible and test portion and m_3 is the mass (g) of crucible and ash

The ash content was used to calculate mineral matter content using the Parr formula expressed as:

$$\% MM = 1.08\, A + 0.55 S \quad (38)$$

Where:

MM is mineral matter (%), A is ash (%) and S is total sulphur (%)

3.4. Mineralogical Analysis

The mineralogy of the sample is important to understand how the organic and inorganic constituents influence the potential environmental risks of the coal waste. Mineralogy analysis was carried out to show the quantities, association, deportment, species and structures of the constituencies. A theoretical ARD could then be calculated from AP and NP minerals in the samples. The samples were analysed by QEMSCAN and the results were validated using QXRD analysis and chemical assays.

3.4.1. QEMSCAN Analysis

The mineralogical composition of the coal wastes was analysed by a FEG (Field Emission Gun) QEMSCAN 650F machine (Figure 12) with twin Bruker XFlash 6130 detectors newly set up at UCT. The Bruker detectors use electron dispersion scatter (EDS) detection to measure elements. The minerals concentration values could be seen in the iDiscover programme for each Pixel measured. The QEMSCAN identified the minerals by matching the measured elemental composition to the mineral database referred to as species identification protocol (SIP). Each SIP entry is defined by the user based on physical properties such as density and chemical composition to match the X-ray spectra and back scatter electron (BSE) data. Then the measured spectrum is interpreted into elemental data which is matched to the SIP definitions and any pixels of elemental data with no SIP match are placed in the "other" group at the end of the list.

The settings of the QEMSCAN machine were at 25kV with a beam current optimized at 10nA on the Faraday Cup and a chamber vacuum set at <1x10-4. Gold, quartz and copper internal standards were used to calibrate the detectors at 232, 42 and 130 BSE, respectively using a common height of 13.0 mm. The carbon coated sample blocks were put in a Quorum Q150 € coater for electron charge dispersion. The blocks were made by mixing 0.2 g of sample and carnauba wax, setting in epoxy resin and polishing. See Appendix A.1.1. for a detailed method for the blocks preparation.

3.4.2. QXRD

In order to validate the QEMSCAN results for major phases, the QXRD analysis was done in duplicate for the three coal waste samples. The samples were spiked with 10 % corundum standard in order to identify the amorphous phase's percentage in the samples. The samples were first mixed with the corundum then the mixture was micronized to 10 µm allowing intimate mixing and liberation of particles. After micronizing, the samples were dried by placing under drying lamps. The samples were then analysed by a powder diffractometric QXRD, Bruker D8 equipped with Vantec detector. The detector has a fixed divergence and receiving slits with Co-K radiation. The Bruker Topas 4.1 software was used to identify the phases which were then calculated by Rietveld method to their respective percentages.

Figure 12 UCT FEG (Field Emission Gun) QEMSCAN 650F machine with two Bruker XFlash 6130 detectors

3.5. Total Sulphur Analysis

The total sulphur was determined using the standard gravimetric Eschka method and the standard combustion method using a Leco analyser SC 632 at UCT analytical lab and Leco SC 632 at ALS lab. The Leco analyses on the coal waste samples and SARM 19 were done in triplicate at UCT and in

duplicate at ALS over extended time periods to give an indication of reproducibility. On the other hand, the Eschka method was done on one sample a day for three consecutive days, in triplicate by the same person for repeatability indication. The standard error analysis gave the reproducibility of the method and a relative standard error (RSE) of the SARM 19 results relative to certified values gave the accuracy of the methods and machines used.

3.5.1. Standard Combustion Method (ASTM D-4239, Sub-method C /SANS 19579)

For Leco analysis 0.25 g of the sample was combusted at 1350 ºC and any moisture or particulates in the emitted gas captured by anhydrous magnesium perchlorate ($Mg(ClO_4)_2$) in the traps. As the gas flowed past an infrared absorption cell the radiation from the gas was absorbed at a frequency of radiation specific to SO_2. The absorbed radiation was proportional to the SO_2 in the combustion gases from which the sulphur in the sample was calculated. Standard reference materials with sulphur content in the range as the samples analysed were used to calibrate the instrument.

Figure 13 Leco S632 analyser at ALS laboratory

3.5.2. Standard Eschka Method (SANS 334:1992 / ISO 334/1992)

The Eschka method was done at UCT in triplicate. To test total sulphur,1.00 g of sample was mixed thoroughly with 2.5 g of Eschka mixture and placed in a crucible. The mixture was covered with 1 g of the Eschka mixture to avoid losses of sulphur as sulphur dioxide gas upon combustion at 800 ± 25 ^{O}C in a muffled furnace. The sulphur compounds evolved during combustion reacted with MgO and Na_2CO_3 producing $MgSO_4$ and Na_2SO_4. The sulphate was then extracted with hot water and determined gravimetrically as a $BaSO_4$ precipitate. The Eschka method is described in detail in Appendix A2.1.

3.6. Sulphur Speciation Protocols

The International Organisation for Standardization (ISO) 157:1996 and the Australian Coal Association Research Program (ACARP) C15034 protocols (Miller, 2008) were used to determine the sulphur forms in the three coal processing waste samples and SARM 19. The ISO 157:1996 assessment was done in triplicate at ALS laboratory over a 2-3 weeks' period for each sample to indicate repeatability. The ACARP protocol method was carried out in triplicate at UCT by the same person at the same time for each sample to indicate repeatability. The methods are described in more detail in Appendix A.3.

3.6.1. ISO 157:1996 Protocol

Two representative samples were used in the protocol; one was used for total sulphur by Leco analysis and the other for analysis of sulphate and pyritic sulphur.

Total Sulphur

Total sulphur results obtained from ALS using the Leco method were used in the ISO 157:1996 protocol.

Sulphate Sulphur Determination

5 g of sample was digested by adding 50 ml of 15 % HCl and boiling for 30 minutes then filtering and washing the residue with a total volume of 30 ml of 15 % HCl and hot water. The filtrate was used for sulphate sulphur determination. The washed residue and filter paper were soaked in 50 ml of 9 % HNO_3 and retained for pyritic sulphur analysis.

Firstly, all the soluble Fe was converted to Fe^{3+} by adding 30 % H_2O_2 to the extracted filtrate and boiling for 5 minutes. After making the solution alkaline by adding 2-3 drops of methyl red indicator and 25 % NH_3 solution, the solution was filtered and the residue (containing the precipitated iron) discarded. To the pale-yellow filtrate, 36 % HCl was added until the solution turned pink. Then 10 ml of 85g/L $BaCl_2$ solution was added to the agitated boiling solution forming a $BaSO_4$ precipitate which was filtered off. The S content was determined from the $BaSO_4$ weight after incinerating the filter paper/pad with the residue. The analysis was done in triplicate for all the samples except the Witbank discards for which analysis was done in duplicate.

Pyritic Sulphur Determination

The residue and filter paper soaked in HNO_3 from the HCl extraction step were macerated and the mixture boiled for 30 minutes. The mixture is filtered and the residue washed three times with 9 % HNO_3, and a further three times with hot water using a total volume of 30 ml. The washings are combined with the filtrate and the residues are discarded. In the filtrate, any colour arising from coal decomposition was destroyed by adding 5 ml of 30 % H_2O_2 and boiling for 5 minutes. After cooling Fe content was determined by atomic absorption spectroscopy (AAS), titration or colorimetric. The analysis was done in triplicate for all the samples except the Witbank discards for which analysis was done in duplicate. Pyritic S was determined by stoichiometry as follows:

$$Pyritic\ S = \frac{\rho_{Fe,1} - \rho_{Fe,2}}{m_1} \times 0.0287 \quad (39)$$

Where:

ρFe,1 is the concentration of Fe (µg/ml) in the diluted test solution, ρFe,2 is the concentration of Fe (µg/ml) in the blank test solution and m1 is the original test portion used in HCl extraction.

Organic Sulphur

Organic sulphur was then calculated as the difference between total sulphur and a combination of sulphate and pyritic sulphur:

$$Organic\ S\ (\%) = Total\ \ S\ (\%) - (Sulphate\ S\ (\%) + pyritic\ S\ (\%)) \quad (40)$$

3.6.2. ACARP C15034 Protocol

The ACARP C15034 protocol was conducted on three separate sub-samples, firstly a sub-sample was analysed for total sulphur by a Leco analyser. Secondly, another sub-sample was determined for sulphide sulphur using the CRS method according to Ahern et al. (2004) with spectrophotometry analysis of the sulphide concentration according to the method developed by Cline (1969). The last stage was KCl digestion on the third sub-sample, which was further split into two parts after digestion and filtration. One part was analysed for total soluble sulphates while the other part was titrated with NaOH to determine the proportion of soluble acidic sulphates such as melanterite (Miller, 2008; Stewart et al., 2009).

Total Sulphur

Total sulphur results obtained from ALS using the Leco method were used in the ACARP C15034 protocol.

Pyritic Sulphur Determination

In the CRS method (Ahern et al., 2004). 0.500 g of the sample was mixed with 2g of technical grade chromium powder in a 250 ml double –neck round bottom digestion flask. 10 ml of 95 % ethanol was added to the flask to wet the mixture. Then 60 ml of 6M HCl was slowly added to the mixture then the solution was heated to a gentle boil by a heating mantle. Digestion was for 20 minutes while the evolved H_2S gas was trapped in zinc acetate solution as ZnS. The sulphide content was determined using the method modified from the one developed by Cline (1969) in which 20 µL of the sample is added to 200 µL of zinc acetate solution in a test tube and topping to 5 ml with de-ionised water. Then 0.5 ml of N, N-dimethyl-p-phenylene diamine dihydrochloric and 0.5 ml of ferric chloride solution are added to the test tube giving a blue colour. After vortexing, the absorbance was determined by UV-VIS spectrophotometer at 670 nm. Then the sulphide concentration was determined from the standard curve gradient of 0.84 nm / (mg/ L) (Cline, 1969). The analysis was done in triplicate for all the samples.

Sulphate Sulphur Determination

The soluble sulphate sulphur was extracted by addition of 80 ml of 1 M inert KCl solution to 2 g of the sample before sealing the plastic bottle. The contents of the plastic bottle were vortexed for 1 hour then the mixture was filtered using 0.45 µm filter paper. After dividing the filtrate into two equal parts, one part was assayed for total soluble sulphates gravimetrically after precipitation with $BaCl_2$ (APHA, 2005). The second portion of the filtrate was titrated with 0.05 M NaOH to a pH of 7 to determine the soluble acid-forming sulphates (Stewart et al., 2009). The analysis was done in triplicate for all the samples. The proportion of the sulphur forms were calculated using the following equations:

$$KCl\ Acid\ Sulphate\ S\ (\%) = \frac{Vol_{NaOH} \times Mol_{NaOH} \times Vol_{Extract} \times {}^{32.06}/_{2}}{Wt_{Samp} \times Vol_{Titrated} \times 10} \quad (41)$$

Where:

- Vol_{NaOH} is the titration volume of NaOH required to bring the extract solution to pH 7
- Mol_{NaOH} is molar concentration of NaOH in mol/L
- $Vol_{Extract}$ is the volume of the original extract solution in ml (80 ml)
- Wt_{Samp} is the weight of sample used for original extraction in g (approx. 2g)
- $Vol_{Titrated}$ is the volume of the solution aliquot actually titrated in ml (30-40 ml)

Low-risk Sulphur Determination

Low-risk sulphur, which is the sulphur regarded to be not available under natural environmental conditions comprise of organic sulphur and jarosite was then calculated as:

$$Low\ Risk\ S\ (\%) = Total\ S\ (\%) - (CRS\ S\ (\%) + KCl\ S(\%)) \quad (42)$$

3.7. Elemental Analysis

A number of methods are available to analyse elemental composition of solids. A coal standard SARM 19 was used to investigate the accuracy of selected method application at University of Cape Town (UCT) and Stellenbosch University (SUN). The analytical methods investigated were ICP-OES, FAAS, ICP-MS and WDXRF for major elements analysis as well as ICP-MS and LA-ICP-MS for minor and trace elements analysis. The ICP-OES and FAAS analysis were done at the analytical lab in the Chemical Engineering department at UCT. The ICP-MS was done in the Geological Sciences department at UCT while the WDXRF and LA-ICP-MS were done at the Central of Analytical Facilities (CAF) at SUN. For ICP-OES and FAAS the sample preparation was done by microwave acid digestion, meanwhile, acid digestion was done for ICP-MS. The LA-ICP-MS and WDXRF analysis were done on the same fused pellets. Then the accuracy of the analytical methods was evaluated from the certified values of the SARM 19. Based on the accuracy of the results, selected methods were applied to determine the concentration of major (>0.1 %), minor (0.01-0.1 %) and trace (<0.01 %) elements in the three coal waste samples (see Table 15).

Table 15 Summary of elemental analysis on the coal standard (SARM 19) and the coal wastes sample A (Waterberg coal slurry), sample B (Witbank coal slurry) and sample C (Witbank coal discards)

Analysis	Laboratory	Samples	Elements analysed
Microwave acid digestion followed by ICP-OES	Analytical Lab in Chemical Engineering Department at UCT	SARM 19 and sample A	Fe, K, Al, Ca, Mg, Mn, Ti, Zr, P and Si
Microwave acid digestion followed by FAAS	Analytical Lab in Chemical Engineering Department at UCT	SARM 19 and sample A	Fe, Na and K
Acid digestion followed by ICP-MS	Laboratory in Geology Sciences Department at UCT	SARM 19	Al, Fe, Ca, Mg, Na, Ba, Mn, Be, Co, Cr, Cu, Ni, Pb, Mo, Ag, Cd, Sb, Tl, As, V and Zn
Fusion followed by WDXRF analysis	CAF at SUN	SARM 19 and samples A, B and C	Si, Al, Fe, Ti, Ca, Mg, Na, Cr, Mn, P and K
LA-ICP-MS on same fused pellet analysed by WDXRF	CAF at SUN	SARM 19 and samples A, B and C	As, Ba, Mn, Sr, Zr, Ce, Co, Cr, Cs, Cu, Ga, Ge, Hf, La, Ni, Pb, Rb, Sm, Th, U, V, Zn, Eu, Mo, Nb, Sb, Se, Sn, Ta, Tb, Y, Yb, Sc, Pr, Nd, Gd, Dy, Ho, Er, Tm, Lu, Cd, In, Te, Tl and Bi

3.7.1. ICP-OES and FAAS Procedure

50 mg of the Waterberg slurry and SARM 19 were placed in clean dry Teflon tubes and 6 ml of 32% HCl, 2 ml of 40% HF and 2 ml of 55% HNO_3 of analytical grade added to the samples. After addition of the acids, the vessels were closed tightly and the reaction allowed to complete for 15 minutes. The reaction vessels were then placed into a carousel which was placed in the MARS-5 Microwave digester. Digestion conditions were set at a 1600W power and 180 ^{O}C temperature with ramp time and hold time of 15 minutes each. After digestion, the vessels were allowed to cool to below40°C. The cooled samples were transferred to 25 ml polystyrene test tubes and diluted with Millipore deionised water to the mark for FAAS and ICP-OES analysis. Digestion was done in duplicate with one set of samples analysed by a Varian 730 -ES ICP-OES and the other analysed by an acetylene and air FAAS model Varian Spectra AA110.

3.7.2. ICP-MS Procedure

A mixture of 8 ml HF and 2 ml HNO_3 was added to Savilex beakers containing 50 mg of sample, then the beakers were sealed and placed on a hotplate for 48 hours to allow complete dissolution of samples. After digestion, the solutions in the beakers were evaporated followed by adding 2 ml concentrated HNO_3 and subsequently evaporating the solution twice. The final dried product was then taken up in 10

ml of 5 % HNO_3 solution containing 10 ppb Re, Rh, In and Bi, used as internal standards. The solution was diluted 5,000 times for As and Sb, and 50,000 for Na. the remaining elements were run on a 10,000 dilution but for Ca analysis a 20,000 dilution factor was used. The solution was then analysed by the Xseries2 Thermo Fisher ICP-MS instrument using argon as the carrier gas. Elements were measured using a peak-hopping mode and calibration curves were obtained using artificial multi-element standards, from which standard solutions were made.

3.7.3. WDXRF Procedure

Glass disks were prepared by combining 0.7 g of pulverized (< 70 µm) sample with 7 g of high purity flux of composition: 32.83 % $LiBO_2$, 66.67 % $Li_2B_4O_7$ and 0.50 % LiI. The glass disks were analyzed for major element concentrations by a PANalytical Axios Wavelength Dispersive spectrometer which operated on SuperQ PANalytical software. The spectrometer was fitted with a 2.4 kW Rh tube, LIF200, LIF220, PE 002, Ge 111 and PX1 analyzing crystals, gas-flow proportional counter and a scintillation detector. The gas-flow proportional counter was operated on a 9:1 Argon/methane gas mixture. Theoretical alpha and measured line overlap factors were applied to measured intensities to correct the matrix effects. The machine was calibrated using control standards of concentration ranges similar to the coal/coal waste samples which included NIM-G (Granite from the Council for Mineral Technology, South Africa) and BE-N (Basalt from the International Working Group).

3.7.4. LA-ICP-MS Procedure

The same glass disks used for WDXRF were used for trace elements analysis. The fusion disks were coarsely crushed and a chip mounted in a 2.4 cm resin disk with a capacity for 13 samples followed by mapping and polishing the mount. The coal processing wastes samples and the coal standard SARM 19 mounts were then ablated at193 nm resolution by an ASI Excimer laser connected to an Agilent 7700 ICP-MS operated by the LA-ICP-MS data reduction software package Iolite v.3.2, combined with VizualAge. Two spots of 100 µm were ablated at a frequency of 10 Hz and 2mJ energy with the carrier gas of a mixture of 0.35 L/min helium, 0.9 L/min argon and 0.004 L/min nitrogen.

In the beginning of a sequence, quality control basaltic glass certified reference standards BCR-2 or BHVO 2G from USGS (Dr Steve Wilson, Denver, CO 80225) were run in replicate to ensure effective ablation and reliable analysis. The instrument was also calibrated at the beginning of the sequence and after every 12^{th} sampled using NIST 612 the % SiO_2 from WDXRF measurement as the internal standard, using standard – sample bracketing.

3.7.5. Calculations

The accuracy of the analysing techniques for each measured element was calculated as the relative standard error (RSE) between the measured value and the certified values or uncertified average values of the SARM 19. Major elements were converted to oxide values using relative molecular mass

proportions of oxides to elements to compare ICP-OES, AAS and ICP-MS values to certified values which are oxides. The reverse was done to convert oxides to elemental values for certified values given as ppm for minor elements.

3.8. Characterisation of ARD Potential

ARD characterisation was carried out using the chemical static methods Acid Base Accounting (ABA), conventional single addition Net Acid Generating (NAG) and extended boil NAG test. ABA tests determined the net acid-producing potential while the NAG determined the net acid generating potential. The extended boil NAG tests were conducted to compensate for the effects of organic acid dissolution in the conventional NAG. The biokinetic batch shake flask tests were conducted to investigate the time-related acid generating behaviour of the samples in the presence of sulphur oxidising and iron oxidising micro-organisms. The performance evaluated by monitoring pH, Ferric/ Ferrous content, redox potential. The acid-producing and neutralising potential of the samples was also estimated on the basis of the mineralogical composition, as determined using the method by Paktunc (1999).

3.8.1. ABA Tests

In ABA, ANC was determined using incremental H_2O_2 Modified Sobek method (Weber et al., 2004) and the MPA was calculated using total sulphur determined by Leco analysis and using sulphide sulphur from CRS method to compare and evaluate the ARD potential of the samples. All the tests were done in triplicate for repeatability indication.

ANC Test

In the incremental H_2O_2 Modified Sobek method, 2g of the sample was placed in a 250 ml Erlenmeyer flask and standardized HCl of appropriate volume and concentration from fizz rating, was added to the flask. The mixture was digested by boiling at 80-90 ^{O}C for 1-2 hours on a hot plate. After boiling, cooling and making up to 125 ml, the mixture was filtered and titrated with standardized NaOH of appropriate concentration from the fizz rating. 10 drops of 30% H_2O_2 were incrementally added to the flasks to correct the siderite effects until there was no significant change of titration endpoints at pH 4.5 and pH 7. See Appendix A.4.1. for the detailed procedure.

3.8.2. Conventional Single Addition NAG Tests

In the conventional NAG tests (Smart et al., 2002), 250 ml of H_2O_2 was added to 2.5 g of the sample in a 500 ml Erlenmeyer flask and the mixture allowed to react overnight in a fume hood. Pre-boil NAG pH was measured before boiling the mixture gently for at least 2 hours. After digestion, the samples were cooled and volume corrected to 250 ml using deionised water then NAG pH was measured. The solutions were then filtered and titrated first to pH 4.5 then pH 7 with standardized NaOH of appropriate

molarity. NAG capacities were determined from the amount of NaOH consumed. The tests were done in triplicate (see Appendix A.4.2. for detailed procedure)

3.8.3. Extended Boil NAG Tests

For extended boiling NAG, the conventional NAG digestion was done on Witbank coal slurry and discards, both of which had a conventional NAG pH below 4.5. After filtration 100 ml of the NAG solutions were vigorously boiled for 3-4 hours while topping with deionised water to maintain a constant volume. After cooling to room temperature, the extended boil NAG pH was measured. See Appendix A.4.3. for detailed procedures of the protocol (Miller, 2008; Stewart et al., 2009).

3.8.4. Batch Biokinetic Shake Flask Tests

The biokinetic tests were done according to the method developed at UCT (Hesketh et al., 2010) and the detailed methodology is presented in Appendix A.4.4. Tests were carried out under four different conditions on each of the three coal waste samples in triplicate. The inoculated tests were run first and the un-inoculated were started three weeks after to manage the sampling of the flasks. The tests were run for 100 days instead of 90 days stipulated in the method to ensure complete reactions of acid generation and acid neutralizing minerals.

Test Conditions

- inoculated with controlled pH
- inoculated with uncontrolled pH
- un-inoculated with controlled pH
- un-inoculated with uncontrolled pH

Procedure

7.5 g of the milled sample was put in each sterilized 250 ml Erlenmeyer flask. 150 ml of autoclaved ABS solution of pH 2 was added to each flask under sterile conditions then some of the flasks inoculated to give a total cell concentration of 10^9 cells per flask. The inoculum was prepared by mixing equal volumes of a mesophilic mixed culture dominated by *Lesptospirillum ferriphilum* (iron oxidiser) and the moderate thermophilic culture dominated by *Acidothiobacillus caldus* (sulphur oxidiser). The cultures were obtained from stock reactors in Centre for Bioprocess Engineering (CeBER)at UCT. The flasks were weighed then sampled before placing on a shaking incubator at 150 rpm at 37 ^{O}C.

Sampling

The mass of each flask was measured and any weight loss due to evaporation corrected by adding deionised water for the uncontrolled pH conditions. For the controlled pH, acidified water of pH 2 was used. The pH and redox potential of the uncontrolled pH flasks was recorded. For pH controlled tests, pH was measured and if it was above 2, the flask solution was titrated to pH 2 using 0.5 M H_2SO_4 and the volume of acid consumed recorded. After titration, the redox potential was recorded. 0.5 ml aliquots

were then removed from the flasks for spectrophotometric sulphate, Fe^{2+} and total iron determination. Fe^{2+} and total iron assay were conducted using the 1-10 Phenanthroline method (Komadel and Stucki, 1988) and sulphate analysis using turbidity from barium chloride addition (APHA, 2005) (the stepwise methods for sulphate and Fe^{2+} and total iron analyses are described in Appendix A.4.4). Fe^{3+} was calculated from the difference between the total iron and Fe^{2+}. The remainder of the aliquots were kept for other elemental analysis should they be required. Sampling was done daily until the pH and redox had stabilised and/or redox was above 650 mV, then on a 2-4 days' interval until day 100 from start.

3.8.5. Theoretical ARD from Mineralogy

Different minerals in coal waste samples have different acid generating potential (AP) and neutralization potential (NP). For a better estimate of net acid-producing potential (NAPP), the contribution of each mineral was considered according to the quantity and capacity of each individual mineral. From the mineralogy results by QEMSCAN and QXRD analysis, the AP and NP were calculated using the Paktunc equations (Paktunc, 1999) discussed in chapter two. The acid-producing minerals considered in the calculation were the acid-forming sulphides and acid-producing sulphates such as jarosite. While the acid neutralizing minerals were carbonates, amphiboles, silicates and feldspars. The AP and NP were calculated using the equations:

$$AP = \sum_{i=1}^{m} \frac{98*10*X_S* n_s}{\omega_s} \qquad (43)$$

Where; X_s is the amount of sulphide mineral s in wt. %; ω_s is the molecular weight of sulphide mineral s (g/mol) and n_s is the number of sulphide minerals in the sample

$$NP = \sum_{i=1}^{k} \frac{98*10*X_i*c_i * n_s}{n_i*\omega_i} \qquad (44)$$

Where: X_i is the amount of mineral i in wt. %; c_i is the number of non-oxidizable cations in one formula unit; n_i is the moles of H_2SO_4 by oxidation of one mole of sulphide minerals; n_s is the moles of minerals required to consume n_s moles of H_2SO_4; ωi is the molecular weight of neutralizing mineral I (g/mol) and k is the number of neutralising mineral in the sample.

3.9. Sulphur Species Deportment under ARD

In order to understand the behaviour of sulphur species under static chemical ARD tests and their implication on the classification of ARD potential, sulphur speciation was conducted on the residues and leachates from ANC and NAG digestion. Representative samples of the coal wastes were digested according to the ANC and NAG tests methods (described in Section 3.8) but omitting the titration stages. The residues were dried at 37 ^{O}C for a week and the weight loss recorded, before being analysed for total S and S forms using Leco analysis and the ACARP C15034 protocol respectively. Analyses were done in triplicate and weight loss factor was incorporated in calculating sulphur %.

3.10. Static Tests on Biokinetic Residues

Residues from the biokinetic static tests were dried at 37 ^{O}C for a week and the weight loss recorded. Subsequently, ARD static ABA tests were conducted to determine the net acid-producing capacity remaining in the residues after biokinetic tests. The total sulphur was determined by Leco analysis carried out at the analytical laboratory at UCT.

3.11. Elemental Risk Assessment

The elements of environmental concern were first chemically extracted sequentially and partitioned into fractions using the protocol B of the method by Broadhurst et al. (2009). The elements were then ranked and scored using the risk-based performance indicator model developed by (Broadhurst and Petrie, 2010).

3.11.1. Sequential Chemical Extraction

The SCE was done progressively on initially 1.00 g of the coal processing waste samples. The extractions were done in duplicate for the three coal waste samples and a blank for each stage (to assess contamination) according to the protocol summarised in Table 16 (see Appendix A.5.1. for detailed SCE method). However, stage 7 was not done by aqua regia, $HClO_4$ and HF leaching as in the protocol because the ICP instruments used to analyse the leachates are damaged by HF. Instead, the residues from stage 6 were dried then pelletized by fusion and analysed by LA-ICP-MS and WDXRF equipment same as described in Section 3.7.3. and 3.7.4. The leachates from stage 1-6 were analysed by an Agilent 79 Q ICP-MS and a Thermo ICap 2600 ICP-AES at Stellenbosch University's CAF. The elements analysed in the leachates and residues are shown in Table 17.

Table 16 Sequential chemical extraction protocol B adapted from Broadhurst et al. (2009)

Stage	Fraction	Leach Conditions	Preferentially dissolved minerals
1	Water-soluble	40 ml deionized water, shaking for 1 hr, 25 ^{O}C,	Soluble salts; gypsum and possibly jarosite
2	Exchangeable	20 ml 1M NH_4AC (ammonium acetate), pH 4.5 adjusted with 1 M acetic acid, shaking 2 hr	Ion exchangeable
3	Adsorbed Carbonates	20 ml 1 M NaOAc (sodium acetate), pH 5 adjusted with HOAc (Acetic acid), 25 ^{O}C, 2hr	Carbonates minerals e.g. calcite and dolomite
4	Amorphous and poorly crystalline Mn, Fe -Oxides	20 ml 0.25 M $NH_2OH.HCl$ in 0.25 M HCl, pH 2 at 50 ^{O}C, shaking 2 – 12 hr	MnO_2, secondary jarosite, ferrihydrite, schwertmannite
5	Crystalline Mn, Fe – Oxides	30 ml 2 M $NH_2OH.HCl$ in 25 % acetic acid, pH 2 at 90 ^{O}C, shaking 3 – 24 hr	Goethite, haematite, magnetite
6	Secondary sulphides and organics	750 mg $KClO_3$and 5ml 12M HCl, followed by 4M HNO_3 at 90 ^{O}C	Pyrite, chalcopyrite, galena, covellite
7	Residue	Analysed as solids	Silicate minerals

Table 17 Techniques for analysis and the elements analysed in the leachates and residues from sequential chemical extractions

Fraction	Method of Analysis	Elements
1-6 (leachates)	ICP-AES (for major and minor and ICP-MS for traces	Si, Al, Fe, Ti, Ca, Mg, P, K, S, Mn, Ba, Sr, Na, As, Be, Co, Cr, Cu, Ni, Pb, Th, U, V, Zn, B, Li, Hg, Mo, Sb, Se, Sn, Cd and Tl
7 (final residue)	WDXRF for major and minor	Si, Al, Fe, Ti, Ca, Mg, P, K, Mn, Ba, Sr, Na
	LA-ICP-MS for traces	As, Ce, Co, Cr, Cs, Cu, Ga, Ge, Hf, La, Ni, Pb, Rb, Sc, Sm, Th, U, V, Zn, Eu, Mo, Nb, Sb, Se, Sn, Ta, Tb, Y, Yb, Cd, Pr, Nd, Gd, Dy, Ho, Er, Tm, Lu, Te, Tl, In and Bi

3.11.2. Ranking and Scoring of Elemental Risk Potential

The environmental significance of the elements found in the coal processing wastes were ranked and scored using the risk assessment protocol developed by Broadhurst and Petrie (2010). The protocol was used to evaluate the hazard potential based on total element concentration and the risk potential based on the potentially available concentration of the elements that can be released into the environment. The sequential chemical extraction results were used to determine the potentially available concentration of elements in terms of leaching conditions i.e. neutral leach, acid leach and oxidising leach. The readily

available concentration was regarded as those mobilised under mild conditions i.e. the water-soluble and exchangeable fractions. The total available concentration was regarded as the concentration mobilised in acidic and oxidising conditions i.e. in all fractions except the residual fraction. The hazard potential and risk potential of elements and salts associated with coal processing wastes were assessed using soil and water as environmental indicators. The hazard potential factor HPFi was calculated from total element concentration (determined as described in section 3.7) while the risk potential factor was calculated from available concentration from SCE as shown in the equations below:

$$HPFi = \frac{(TCi)}{ARCi \times BCi}^{2} \quad (45)$$

$$HPFi = EF_i \times EnF_i \quad (46)$$

Where:

$$EF_i = \frac{TC_i}{ARC_i} \quad (47)$$

$$EnF_i = \frac{TC_i}{BC_i} \quad (48)$$

For risk potential factor RPFi the available concentration (ACi) substitutes total solid concentration (TCi) to give the equation:

$$RPFi = \frac{(ACi)}{ARCi \times BCi}^{2} \quad (49)$$

Where:

- ARCiis the environmentally acceptable concentration from soil and drinking water standard guidelines
- BCi is the background concentration given by the natural concentrations of elements on the Earth's crust
- ACi is the available concentration obtained from SCE
- TCi is the total concentration obtained from the total elemental composition.

The environmental hazard and risk potential factors were then used to group the elements into the environmental significance according to the criteria in Table 18.

Table 18 Criteria for ranking and scoring the hazard/ risk potential factor in terms of environmental significance (Broadhurst and Petrie, 2010)

Group Description	Maximum Risk Potential Factor/ 1000
Very high environmental significance	>10 000
High environmental significance	A:1 000 – 10 000
	B: 100 – 1 000
	C: 10 - 100
Moderate environmental significance	1 - 10
Low environmental significance	0.1 - 1
Non-strategic environmental significance	< 0.1

CHAPTER 4

RESULTS AND DISCUSSION: CHARACTERISATION OF PHYSIO-CHEMICAL PROPERTIES

One of the objectives of this study is to address the uncertainties and deficiencies arising from the characterisation of coal processing wastes. This is done through evaluating hypothesis 1 set in Chapter 2 which seeks to compare and evaluate some of the analytical tools in terms of precision and/or accuracy. The applicability of the selected analysing techniques are tested on a coal standard, then applied on the coal waste samples. The characterisation results presented in this chapter include physical size distribution, ash content, mineralogical composition, sulphur and sulphur forms, elemental (metals, metalloids and non-metals) composition and deportment. The detailed methodology for the characterisation is described in Chapter 3 while the detailed characterisation data is presented in Appendix B.

4.1. Particle Size Distribution (PSD)

Dry sieving results shown in Figure 14, indicate that the majority of the particles in the Waterberg (85 %) and Witbank (80%) coal slurry wastes can be classified as “ultrafine” (<150 μm). The Witbank coal slurry sample had a wider particle size distribution than the Waterberg coal slurry waste, with a higher proportion of both the finer (25 and 50 μm ranges) and the coarser particle ranges (>150 μm). The majority (93 %) of the Witbank coal discards occurs in the “middling” (1-25 mm) and “coarse” (> 25 mm) particle size ranges, accounting for 58 % and 35 % of the sample respectively. Approximately 5.6 % and 1.4 % of the discards occurs in the fine (0.15-1 mm) and ultra-fine (<150 μm) ranges respectively. Detailed PSD data is presented in Appendix B.1.1

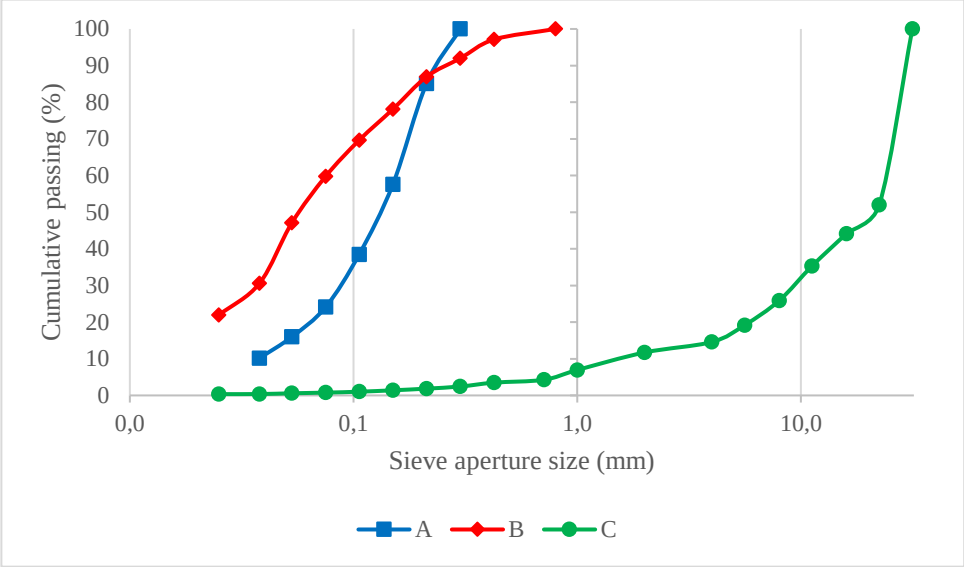

Figure 14 Particle size distribution of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards).

4.2. Ash Content (SANS 131:2011 / ISO 1171)

The ash contents of the three coal wastes were calculated according to weight loss after ashing and the total ash results are shown in Table 19 (see Appendix B.1.2. for ash analysis per size fraction). The slurry coal wastes from Waterberg and Witbank have ash contents of 49.1 % and 41.7 % respectively. These ash contents are within the 10-50 % range typical of SA coal processing wastes reported in the DME (2001) inventory results presented in Chapter 1 (Table 1 in Section 1.1.2.). The Witbank coal discards' ash content of 63.2 % is slightly higher than the typical 30-60 % range for discards reported in the DME (2001) inventory. These results agree with previous characterisation showing Waterberg coal slurry wastes to have higher ash contents compared to Witbank coal slurry wastes (Chapter 2 Section 2.2.3.). High ash contents signify high mineral matter contents in the coal processing wastes and the possibility of high elemental contents since most of the elements tend to exist in the mineral matter (Bergh, 2013; Vassilev and Vassileva, 1997).

Table 19 Total ash content of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

	Sample A	Sample B	Sample C
Total Ash Content (%)	49.1 ± 0.002	41.7 ± 0.002	63.2 ± 0.001

4.3. Total Sulphur

Total sulphur analyses were carried out to assess the reliability of the commonly used combustion and gravimetric methods, as well as to assess the total sulphur contents of the coal wastes. The total sulphur

contents in the coal wastes and the coal standard were analysed using the standard gravimetric Eschka method and the standard combustion method using a Leco analyser SC 632 at UCT analytical laboratory and Leco SC 632 at ALS laboratory. The results and discussion on the total sulphur content results and discussion are presented in Section 4.3.1 while the reliability of the sulphur determining methods is presented in Section 4.3.2. Detailed results are further presented in Appendix B.2.

4.3.1. Total Sulphur Concentrations

The results for total sulphur contents determined by the Eschka method and Leco analysis in the coal processing wastes and the coal standard are presented in Table 20 and Figure 15 The results show the highest sulphur content to be in the Witbank coal discards at 1.94 %, followed by the Waterberg coal slurry waste at 1.89 % and the lowest content in the Witbank coal slurry waste at 1.11 %. With the exception of the Witbank coal slurry waste, the coal processing wastes have higher total sulphur content compared to the coal standard's 1.54 %. The sulphur ranges for the samples compare well with the values in the DME (2001) report of 1-5% range for the discard wastes and below 2% for the slurry wastes. However, the measured sulphur contents are lower than the 2.04 -4.18 % obtained in previous Waterberg and Witbank coal wastes (Section 2.2.2 of Chapter 2). The total sulphur contents in the coal processing wastes are an indication of the low sulphur contents typical of South African coals (Hancox and Goetz, 2014).

Table 20 Total sulphur contents in coal standard SARM 19 and coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Sample	**Leco- UCT** Total S (%)	**Leco- ALS** Total S (%)	**Eschka*** Total S (%)
SARM 19	1.34 ± 0.01	1.54 ± 0.03	1.30 ± 0.02
A	1.54 ± 0.02	1.84 ± 0.01	1.89 ± 0.01
B	1.02 ± 0.02	1.06 ± 0.06	1.11 ± 0.05
C	-	1.94± 0.08	-

** In house analysis*

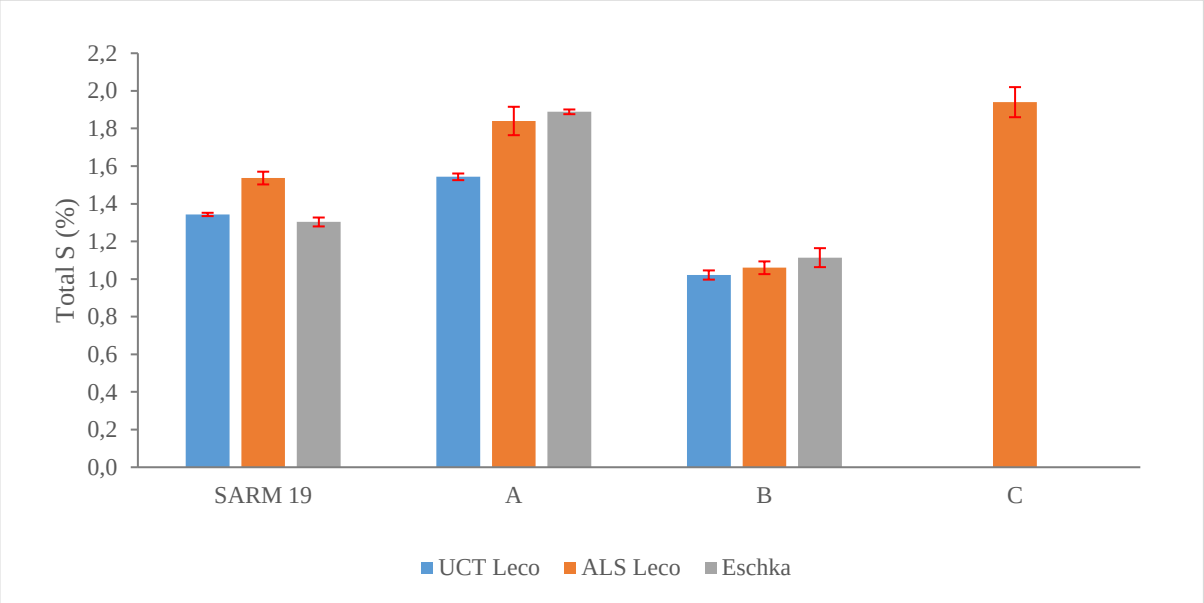

Figure 15 Total sulphur contents in coal standard SARM 19 and coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

4.3.2. Reliability of Analytical Methods

A comparison of total sulphur with the certified value for the coal standard SARM 19, (Table 21) indicates that all the methods gave comparable results with the low standard errors range of 0.01-0.03 % indicating high precision. However, only the Leco results from ALS are consistent with the 95 % confidence limit range reported for the certified coal standard with a relative standard error (RSE) of 3.13. The mean Leco value obtained by the UCT analytical laboratory was in the order of 10 % (RSE) lower than the "true" mean value, whilst the mean value reported for the Eschka test was over 12 % lower.

Table 21 Relative standard error of total sulphur analysing techniques based on coal standard SARM 19 certified values

Certified value		**Mean measured value**			**Relative error of mean values**		
Mean (%)	**95% confidence limit**	**Leco-UCT (%)**	**Leco-ALS (%)**	**Eschka (%)**	**Leco-UCT (%)**	**Leco-ALS (%)**	**Eschka (%)**
1.49	1.42-1.55	1.34±0.01	1.54±0.03	1.30±0.02	-9.84	3.13	-12.53

A comparison of mean values obtained for the two-coal slurry wastes in Table 20, indicates that despite being the most precise, the UCT Leco results are consistently in the order of 3.6-12.6 % lower than the Leco results obtained from the ALS laboratories. This coupled with the relatively high precision, indicates that the relative errors obtained for the UCT Leco results may be due to calibration errors. The

reason for the relatively large discrepancies between Leco and Eschka test results are not known but could indicate that the reliability of this method is dependent on the sample mineralogy.

4.4. Sulphur Forms

The sulphur species in the three coal wastes and the coal standard SARM 19, were determined using two chemical protocols, the ISO 157:1996 and the ACARP C15034 method. The objectives were to identify and quantify the sulphur species as well as to compare and evaluate the two protocols in terms of repeatability. The ISO 157:1996 protocol was conducted at ALS laboratory while the ACARP C15034 was conducted in-house at UCT. Sulphur speciation results are discussed in Section 4.4.1. and comparison results of the protocols are discussed in Section 4.4.2. The sulphur speciation results are further presented in Appendix B.3.

4.4.1. Concentration and Distribution of Sulphur Forms

The two chemical protocols used for sulphur speciation, ISO 157:1996 and ACARP C15034, gave comparable and slightly different results for the coal standard and the three coal wastes (Table 22 and Figure 16). The results show pyritic/sulphide sulphur contributes more than 50 % of the total sulphur with the coal standard SARM 19 having 47-52 %, while the Waterberg coal slurry waste, Witbank coal slurry waste and the Witbank coal discards have 56-61 %, 39-52 % and 53-56 % respectively. Sulphate sulphur accounted for 18-26 % of the total sulphur for the coal standard SARM 19, and both the coal slurry wastes, but only 12-15 % of total sulphur for the Witbank coal discards. The results show all the sulphate in Witbank coal discards to be acidic sulphates (e.g. melanterite and alunite) while negligible (1.2% and 0.5 %) acidic sulphates were evaluated in the coal standard SARM 19 and Witbank coal slurry waste. On the other hand, all the sulphates in the Waterberg coal slurry waste are non-acidic sulphates (e.g. gypsum and epsomite). The contribution of the remaining sulphur species, comprised mainly of organic sulphur, varied between 18 % and 43 %, with the proportion of organic sulphur being lowest in the Waterberg coal slurry waste (18-20 %) and highest in Witbank coal discards (23-43 %). These results are consistent with literature values (Table 4 in Section 2.2.2.) which showed pyrite as the major (48-80 %) sulphur species and substantial amounts (4-34 %) of sulphates and organic sulphur in coal processing wastes (Iroala, 2014; Kazadi Mbamba et al., 2012; Kotelo, 2013).

Table 22 Sulphur species concentration and distribution in coal standard (SARM 19) and coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) determined by ISO 157:1996 and ACARP C15034 protocols

Sulphur form	Mass (%) of sulphur form in sample							
	Sample A		Sample B		Sample C		SARM 19	
	ACARP	ISO	ACARP	ISO	ACARP	ISO	ACARP	ISO
CRS/ Pyritic	1.13±0.01	1.04±0.02	0.55±0.00	0.42±0.01	1.02±0.03	1.10±0.01	0.80±0.00	0.73±0.01
Acid sulphate	0.00±0.00		0.01±0.00		0.23±0.01	-	0.01±0.00	-
Non-acid sulphate	0.32±0.00		0.19±0.00		-	-	0.28±0.02	0.39±0.01
****Total Sulphate**	0.32±0.00	0.37±0.06	0.20±0.00	0.19±0.01	0.23±0.01	0.31±0.02	0.29±0.02	0.39±0.01
***Low-risk/organic**	0.39	0.43±0.04	0.32	0.45±0.04	0.69	0.54±0.06	0.44	0.42±0.03
Total	**1.84**	**1.84**	**1.06**	**1.06**	**1.94**	**1.94**	**1.54**	**1.54**

** calculated from total (S), sulphate (S) and pyritic (S) and in the ACARP C15034 protocol the low-risk (S) comprises of any jarosite in addition to the organic sulphur*

*** Total sulphate includes acid and non-acid-forming species*

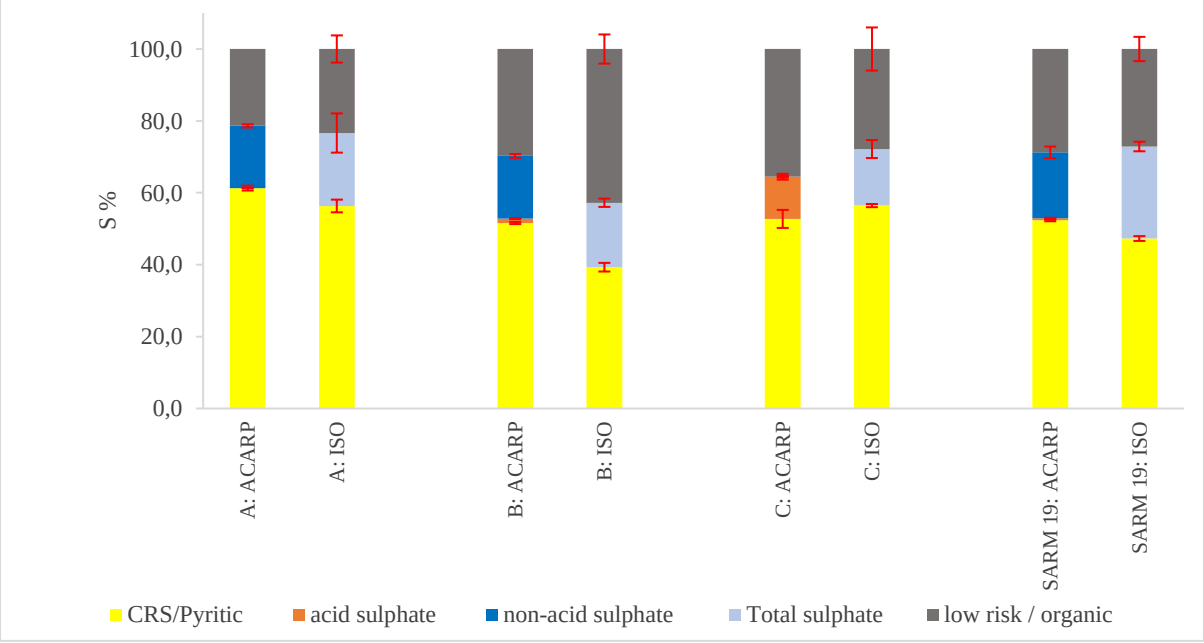

Figure 16 Distribution of sulphur forms in coal standard SARM 19 and coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) by ISO 157:1996 and ACARP C15034 protocols

4.4.2. Comparison of ISO 157:1996 and ACARP C15037 Protocols

The analyses were highly precise as indicated by the small standard errors in both protocols (as shown in Figure 16), but a further comparison of the protocols is shown in Figure 17 and Figure 18. The results show ACARP C15034 protocol was more precise in sulphate analysis for all samples. The pyritic/sulphide sulphur values were consistently higher in the ACARP C15034 analysis compared to the ISO 157:1996 protocol in all samples, except for Witbank coal discards. On the other hand, ISO method had consistently higher sulphate results for the three coal waste samples and the coal standard.

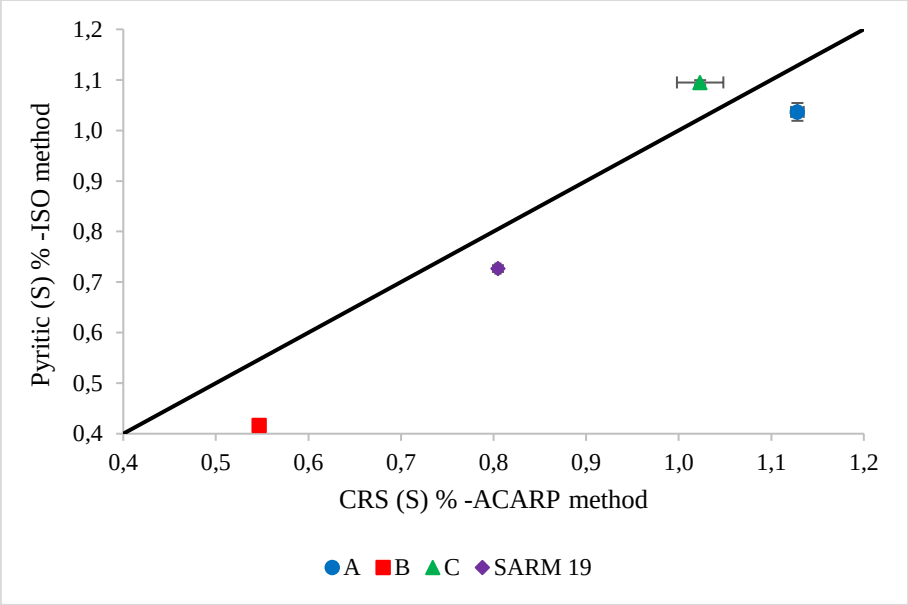

Figure 17 Comparison of ISO157:1996 and ACARP C15034 protocols in determining pyritic/sulphide sulphur on coal standard SARM 19 and coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

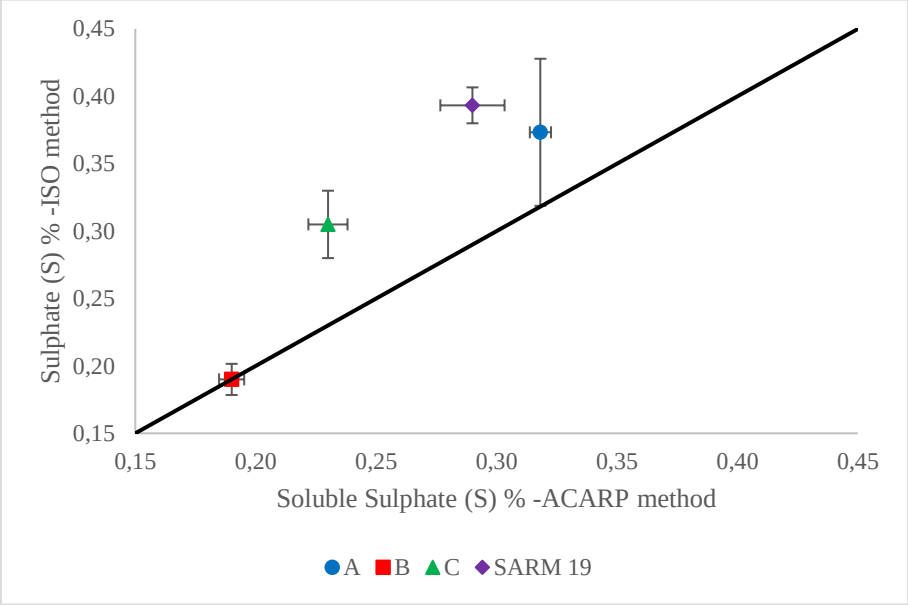

Figure 18 Comparison of ISO157:1996 and ACARP C15034 methods in determining sulphate sulphur on coal standard SARM 19 and coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

As discussed in Chapter 2, the ISO 157:1996 protocol makes a number of simplifying assumptions which could be the reason for the discrepancies in results compared to ACARP C15034 protocol. The ISO 157:1996 protocol assumes that HCl leaching only dissolves sulphate sulphur and that all the sulphide sulphur remains in the residue in the form of pyrite. The higher sulphate concentrations and the lower sulphide or pyritic sulphur values obtained for the ISO 157:1996 protocol in comparison to the ACARP C15034 protocol indicates that the relatively aggressive HCl leach, may have resulted in some dissolution of sulphide or pyritic sulphur, thus overestimating the sulphate sulphur and underestimating the sulphide or pyritic sulphur. The other assumption in the ISO 157:1996 protocol is that all the Fe that dissolves during the HNO_3 leach arises from pyrite. If the sample contains significant quantities of Fe from other mineral phases that dissolves in the HNO_3 leach step, then the ISO 157:1996 protocol will overestimate sulphide sulphur content. The cumulative errors of total sulphur, sulphide sulphur and sulphate sulphur determination will then manifest in the organic/low-risk sulphur errors since organic/low-risk sulphur is not directly evaluated but calculated from the difference. However, the discrepancies between the two methods are relatively minor (mostly <10 %), especially for sulphide sulphur.

4.5. Mineralogical Composition

The mineralogical analysis of components in the coal wastes was carried out to understand the occurrences of their constituents and how they relate to the environmental risk potential of the coal wastes. The mineralogy was determined by QEMSCAN and QXRD analysis and the results are presented in Section 4.5.1. and Section 4.5.2. respectively. Comparison of results from the two

analytical methods is presented in Section 4.5.3. The comparison also includes a comparison of coal and mineral matter compared to calculated mineral matter. Images showing association and distribution of the coal wastes' constituents are presented in Appendix B 4.

4.5.1. QEMSCAN Analysis

The mineral distributions in the coal wastes determined by QEMSCAN analysis are shown in Table 23 and Figure 19. Generally, the coal processing wastes were found to be made up of coal, carbominerite (coal made of 20-60 % mineral matter content and 40-80% organic content), kaolinite, quartz and K-feldspar with quantities differing from sample to sample. In Waterberg coal slurry waste, the results show the main constituents to be carbominerite, kaolinite, quartz and coal at 30.09 %, 21.38 %, 20.81 % and 19.13 % respectively. However, in the Witbank coal slurry waste, coal is the major constituent at 44.49 %, with kaolinite and carbominerite making up 34.94 % and 13.39 % of the total mass respectively. On the other hand, kaolinite at 51.76 %, coal at 19.64 % and quartz at 15.38 % were found to be the major constituents of Witbank coal discards. The measured kaolinite and quartz values for Waterberg coal slurry are consistent with literature values of 20.17 % and 18.69 % respectively reported by Iroala (2014) on the Waterberg ultrafine sample (Section 2.2.1). The measured kaolinite in all three coal wastes is consistent with the 20-70 % range but the quartz in the Witbank samples are lower than the 20-30 % range reported in SA coals by Pinetown et al. (2007).

The results also showed pyrite (of framboid and Euhedral structure as shown in images in Appendix B.4.) as the major sulphides in all the samples with significant amounts of chalcopyrite in Waterberg coal slurry waste and Witbank coal discards. Traces of gypsum in all three coal wastes and jarosite (in Waterberg coal slurry only) indicated slight weathering of the samples. The Waterberg coal slurry waste also contained a higher concentration of carbonate minerals, predominantly calcite, compared to the other two coal wastes. Other silicates present in the waste samples included the silicate minerals k-feldspar, mica and amphiboles (predominantly wollastonite, tremolite, chlorite and serpentine), as well as complex oxide minerals, including iron oxyhydroxides, rutile and apatite. The small quantities of undetermined mineral phases were classified as other.

Table 23 Mineralogical composition from QEMSCAN analysis of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Mineral	Mass (%) of sample			Mass (%) in mineral matter		
	Sample A	Sample B	Sample C	Sample A	Sample B	Sample C
Coal	19.13	44.49	19.64	n/a	n/a	n/a
Carbominerite	30.09	13.39	6.18	n/a	n/a	n/a
Pyrite (FeS_2)	2.54	1.83	2.72	4.70	4.01	3.93
Chalcopyrite ($CuFeS_2$)	0.15	0.00	0.53	0.28	0.00	0.76
Other Sulphides	0.01	0.00	0.01	0.02	0.01	0.01
Jarosite ($KFe_3(SO_4)_2(OH)_6$)	0.01	0.00	0.00	0.01	0.00	0.00
Gypsum ($CaSO_4.2H_2O$)	0.21	0.08	0.00	0.39	0.17	0.00
Epsomite ($MgSO_4.7(H_2O)$)	0.00	0.00	0.00	0.00	0.00	0.00
Dolomite ($CaMg(CO_3)_2$)	0.00	0.00	0.00	0.00	0.00	0.00
Calcite ($CaCO_3$)	1.39	0.01	0.00	2.57	0.01	0.00
Siderite ($FeCO_3$)	0.06	0.02	0.00	0.10	0.04	0.00
Amphibole	0.73	0.03	0.01	1.35	0.06	0.01
Kaolinite ($Al_2Si_2(OH)_4$)	21.38	34.94	51.76	39.56	76.60	74.67
Muscovite ($K_2Al_4[Si_6Al_2O_{20}](OH)_4$))	0.51	0.28	0.41	0.95	0.61	0.60
K-feldspar ($KAlSi_3O_8$)	1.34	0.58	1.69	2.49	1.27	2.43
Quartz (SiO_2)	20.81	3.13	15.38	38.50	6.87	22.18
Apatite ($Ca_5(PO_4)_3(OH,F,Cl)$)	0.02	0.21	0.03	0.04	0.47	0.05
Fe-oxyhydroxide	1.40	0.37	0.20	2.59	0.81	0.28
Rutile (TiO_2)	0.18	0.61	1.35	0.32	1.34	1.95
Other	0.05	0.04	0.06	0.10	0.08	0.08

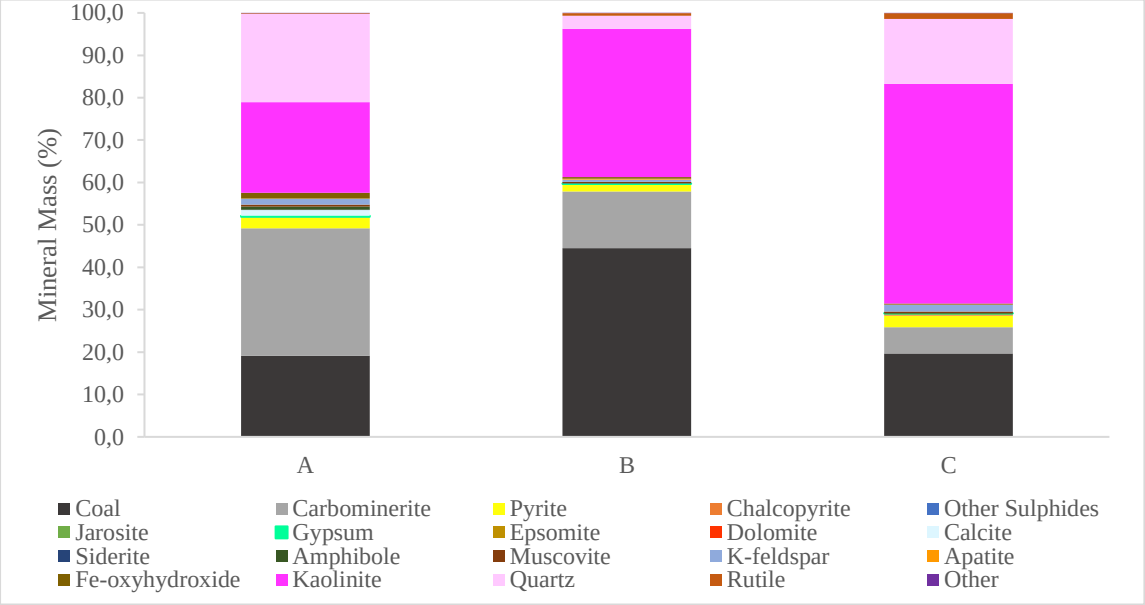

Figure 19 Graphic presentation of mineralogy results from QEMSCAN analysis of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

4.5.2. QXRD Analysis

Results from QXRD analysis shown in Table 24 and Figure 20 confirmed coal, kaolinite and quartz to be the major constituents but with different quantities from the QEMSCAN results. The Waterberg coal slurry waste results show 57.4 %, 16.4 % and 17.5 % of these major constituents respectively while the Witbank coal slurry waste has 60.5 %, 27.4 % and 7.3 % respectively. The results showed the Witbank coal discards to have 51.76 %, 33.06 % and 27.29 % of kaolinite, coal and quartz respectively. Unlike QEMSCAN, QXRD does not differentiate between the “high grade” coal and the “low grade” coal i.e. carbominerite. The results again showed the Waterberg coal slurry to have higher amounts of carbonates than the other two coal waste samples, however, QXRD results show that the carbonates are in the form of dolomite, calcite and siderite. The QXRD results have significant amounts of the sulphates jarosite, epsomite and gypsum in all the samples indicating the samples were weathered. Pyrite is again shown as the major sulphide in the samples. The QXRD classification of the mineral phases had no amphiboles.

Table 24 Mineralogy results from QXRD analysis of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Mineral	Mass (%) of sample			Mass (%) in mineral matter		
	Sample A	Sample B	Sample C	Sample A	Sample B	Sample C
Coal	57.44	60.53	33.06			
Pyrite (FeS_2)	0.48	0.23	1.92	0.88	0.50	2.77
Jarosite ($KFe_3(SO_4)_2(OH)_6$)	0.61	2.16	0.00	1.13	4.73	0.00
Gypsum ($CaSO_4.2H_2O$)	0.72	0.84	0.00	1.34	1.84	0.00
Epsomite ($MgSO_4.7(H_2O)$)	0.00	0.85	0.00	0.00	1.86	0.00
Dolomite ($CaMg(CO_3)_2$)	3.80	0.03	0.00	7.04	0.06	0.00
Calcite ($CaCO_3$)	1.39	0.01	0.00	2.42	0.02	0.00
Siderite ($FeCO_3$)	0.11	0.00	0.00	0.20	0.00	0.00
Kaolinite ($Al_2Si_2(OH)_4$)	21.38	34.94	51.76	30.30	60.14	48.29
Mica ($K_2Al_4[Si_6Al_2O_{20}](OH)_4$))	0.00	0.00	0.76	0.00	0.00	1.09
K-feldspar ($KAlSi_3O_8$)	0.00	0.00	1.52	0.00	0.00	2.19
Quartz (SiO_2)	17.49	7.34	27.29	32.37	16.09	39.36
Fe-oxyhydroxide	1.67	0.58	0.89	3.08	1.27	1.28
Rutile	0.00	0.00	1.14	0.00	0.00	1.64

The QXRD results on the Waterberg coal slurry were based on the amorphous (organic) and crystalline (inorganic) contents unlike previous analysis by XRD (shown in section 2.2.1.) which analysed the crystalline constituencies only. The QXRD results for Waterberg coal slurry waste in this study have lower gypsum, quartz, dolomite, calcite and kaolinite compared to Iroala (2014) results (Table 4 of section 2.2.1 in Chapter 2). Different results on the sample by QXRD could have been influenced by the preferential orientation of minerals which occurs when the same polycrystalline specimen has varying peak intensities under the X-ray beam (French and Ward, 2009; Pinetown et al., 2007). The other reasons for different results on the different batches of the same sample are the powder preparation process and the slight difference in composition between batches (non-uniformity).

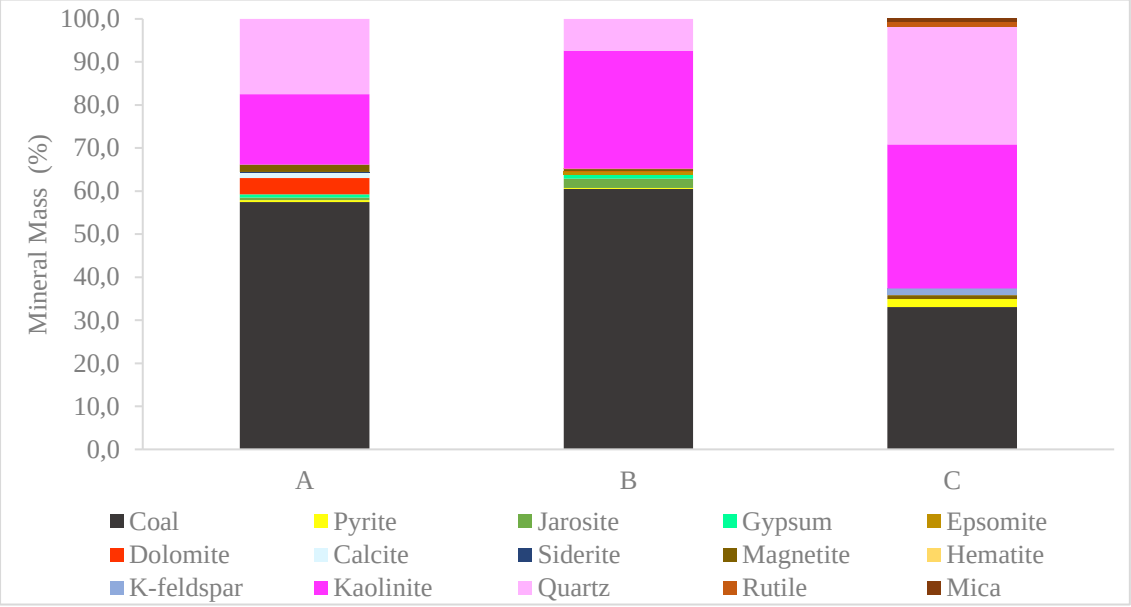

Figure 20 Graphic presentation of mineralogy from QXRD analysis of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

4.5.3. Comparison of Analytical Results for Mineral Composition

The coal and mineral matter contents evaluated by both QEMSCAN and QXRD are compared to calculated mineral matter and the results are presented in Table 25. The results indicate that the total mineral matter contents determined by mineralogical analysis are relatively consistent with those calculated from the ash and sulphur contents (from Leco analysis in Section 4.3.) according to the Parr formula. The higher mineral matter content in the Witbank coal discards reflects the relatively higher ash contents in the discards relative to the two coal slurry wastes. Furthermore, the results indicate that QXRD possibly overestimated the coal content in the Waterberg coal slurry waste hence underestimated the mineral matter content. Contrastingly with the Witbank coal slurry waste, the QEMSCAN and QXRD results for coal and mineral matter content are almost similar and matches well with the calculated mineral matter. However, with the Witbank coal discards, the QXRD results are closer to the calculated mineral matter results than the QEMSCAN results, showing QEMSCAN results to be possibly underestimating the coal content and overestimating mineral matter content. Several reports have reported amorphous macerals in coal produce an XRD pattern of high background continuum that can mask peaks of crystalline phases (van Alphen, 2007; French and Ward, 2009; Pinetown et al., 2007). This could be the reason for higher values of coal and lower values of some mineral phases determined in QXRD analysis compared to QEMSCAN results.

Table 25 Comparison of coal and mineral matter (M/M) content of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Mineral mass	Mass (%) in sample		
	Sample A	Sample B	Sample C
***Coal QEMSCAN**	49.22	57.88	25.86
Coal QXRD	57.44	60.53	33.04
M/M QEMSCAN	50.78	42.12	74.14
M/ M QXRD	42.56	39.47	66.96
****M/M Calculated**	54.04	45.62	69.32

**Includes coal and carbominerite*

**Calculated from Parr formula: MM (%) =1.08 Ash (%)+0.55 Total S (%)*

Comparison of the QEMSCAN and QXRD results in the Waterberg coal slurry, Witbank coal slurry and Witbank coal discards are presented in Figure 21, Figure 22 and Figure 23 respectively. The results show QEMSCAN results to be significantly higher in kaolinite, and pyrite, but lower in coal contents in all three coal waste samples. Quartz contents determined by QEMSCAN analysis are higher for the Waterberg coal slurry waste but lower for both Witbank coal slurry waste and Witbank coal discards in comparison to results from QXRD analysis. QXRD also evaluated significantly higher amounts of jarosite in the Witbank coal slurry and dolomite in Waterberg coal slurry compared to QEMSCAN. The results also show almost similar quantities evaluated by the two methods for the remainder of the mineral phases.

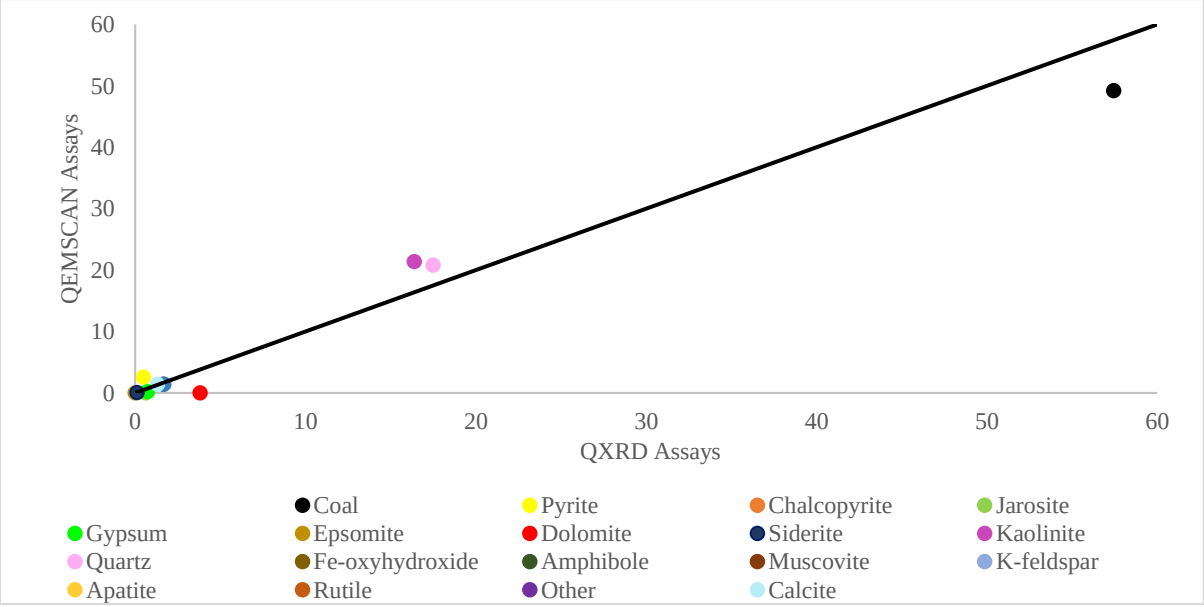

Figure 21 Comparison of QXRD and QEMSCAN on the mineral phases of Waterberg coal slurry

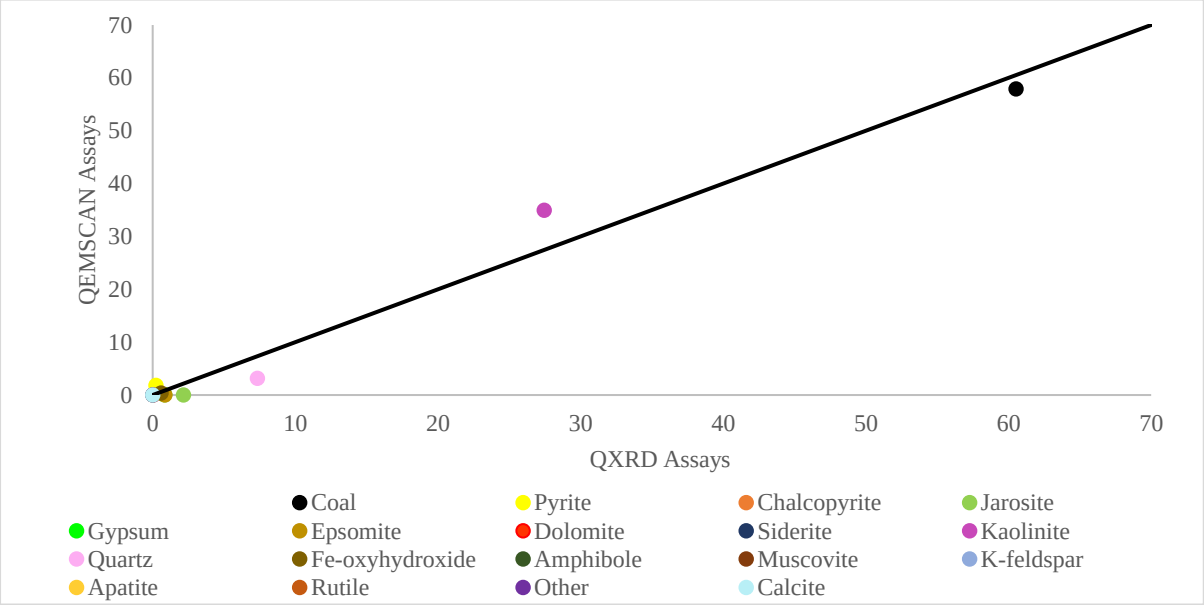

Figure 22 Comparison of QXRD and QEMSCAN on the mineral phases of Witbank coal slurry

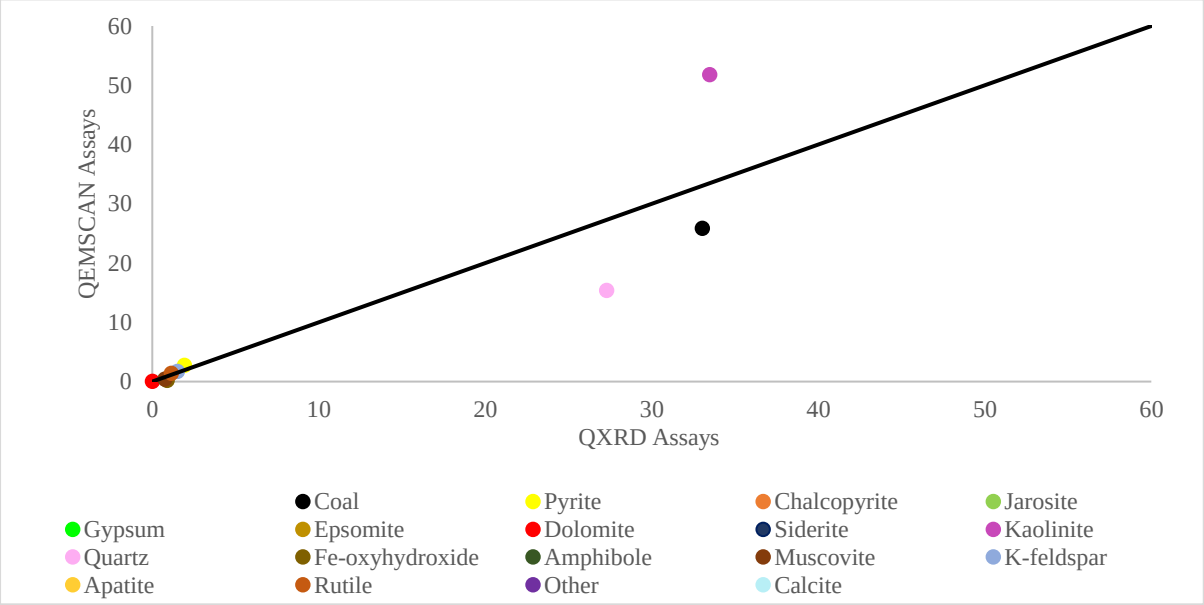

Figure 23 Comparison of QXRD and QEMSCAN on the mineral phases of Witbank coal discards

4.6. Element Composition and Deportment

Element composition analyses were conducted to determine the applicability of commonly used analytical techniques within the different laboratories at University of Cape Town (UCT) and Stellenbosch University (SUN) using a coal standard SARM 19 with certified composition. The other objective was to determine the elemental composition of coal processing wastes using analytical techniques of evaluated accuracy. The elemental composition (i.e. metals, metalloids and non-metals)

in SARM 19 were analysed by WDXRF and LA-ICP-MS at SUN, as well as FAAS, ICP-OES and ICP-MS at UCT as outlined in Section 3.7. of Chapter 3. The elements were analysed as ppm by the analytical techniques except for WDXRF and were converted to oxides using stoichiometric and vice versa to convert oxides to ppm. FAAS was used to analyse Fe and Na only due to high costs for analysis. The trace elements in SARM 19 and sample A were analysed by LA-ICP-MS, ICP-MS and ICP-OES but the ICP-OES laboratory reported the trace elements to be below the machines detection limits of 100 ppm. Due to element volatility, limitation on calibration strategies and machine sensitivity, Hg, B, Be, Cl, F, I and Ra although listed as elements of environmental concern by Swaine (2000), could not be analysed by all the methods used. Results on the applicability of analytical techniques are presented in Section 4.6.1. while the composition of coal wastes is presented in Section 4.6.2. The deportment of major elements is presented in Section 4.6.3.

4.6.1. Comparison and Evaluation of Laboratory Analytical Techniques

Elements have been categorised as major (>1000 ppm), minor (100-1000 ppm) or trace (< 100 ppm). Techniques used include WDXRF, FAAS, ICP-MS, ICP-OES and LA-ICP-MS (minor and trace elements only). Only the LA-ICP-MS and ICP-MS analyses were conducted in duplicate. Accuracy was evaluated in terms of the relative standard error (RSE) of measured value relative to certified values.

Major and Minor Elements in Coal Standard SARM 19

The measured major and minor elemental compositions and the certified ranges for SARM 19 are shown in Table 26, while the accuracy results are shown in Table 27 as RSE. The results show the XRF analysis conducted at SUN and LA-ICP-MS methods conducted at UCT were relatively accurate, resulting in RSE within ±10 % for most of the major and minor elements, except Mn, P and Mg. Apart from these three elements, all the values obtained by these methods fell within the 95 % confidence level ranges. In contrast the RSE for the ICP-OES analyses conducted at UCT were mostly above 10 %, with all but the Ti values falling outside of the 95 % confidence limit ranges. Results for Ca, Mg and Na were particularly inaccurate with RSE of -57 %, 33 % and 81 % respectively. On the other hand, FAAS analysis at UCT gave accurate results for Na within the 95 % confidence interval but less inaccuracy was observed for Fe analysis as indicated with the RSE value of 14 %. Similarly, ICP-MS analysis at UCT gave lower compositions than the 95 % confidence interval for the major and minor elements but the accuracy for Ba, Mn and Na was within the ±10% RSE range. The ICP-MS results were less accurate particularly for Ca and Al with RSE of -33 % and -55 % respectively.

Table 26 Major and minor elements in the coal standard SARM 19 analysed by different techniques in comparison to certified values

Element	Certified Value	95 % confidence limit	[+]WDXRF	[+]LA-ICP-MS	[++]ICP-OES	[++]FAAS	[+++]ICP-MS
Major elements in wt. % ash basis							
Al_2O_3	8.01	7.86 - 8.15	7.81	-	8.84	-	3.61 ± 0.00
CaO	1.39	1.37 - 1.41	1.36	-	0.60	-	0.93 ± 0.00
Fe_2O_3	1.75	1.73 - 1.76	1.70	-	2.17	1.99	1.53 ± 0.00
K_2O	0.24	0.24 - 0.25	0.23	-	0.28	-	-
MgO	0.20	0.20 - 0.22	0.17	-	0.27	-	0.16 ± 0.00
Na_2O	0.29	0.28 - 0.31	0.28	-	0.53	0.31	0.27 ± 0.00
SiO_2	15.00	14.88 - 15.14	14.71	-	-	-	-
TiO_2	0.34	0.32 - 0.34	0.32	-	0.32	-	-
Minor elements in ppm							
Ba	304.00	295.00 - 318.00	-	296.10 ± 5.25	-	-	276.80 ± 0.29
Mn	157.00	143.00 - 168.00	-	146.10 ± 2.10	*bdl	-	171.70 ± 0.32
P	130.00	108.00 - 135.00	106.59	-	-	-	-
Sr	126.00	125.00 - 141.00	-	120.25 ± 1.30	-	-	-
Zr	351.00	336.00 - 361.00	-	320.75 ± 2.30	300.00	-	-

** bdl = below detection limit [+] SUN Laboratory [++] UCT Chemical Engineering Analytical Laboratory [+++]UCT Geology Laboratory*

It is important to note that inter-laboratory reproducibility was not tested and reliability was based on accuracy (as % RSE) for a particular laboratory and these results do not necessarily show the accuracy of the analytical technique. The average accuracy of the WDXRF analysis at Stellenbosch University was evaluated to be better than ICP-OES, ICP-MS and FAAS at UCT in analysing major elements. On the other hand the LA-ICP-MS analysis carried out at SUN had better accuracy on analysis of minor elements. The WDXRF accuracy obtained in this study for all the elements except Mg and Mn is within the ± 5 % relative error reported by Huggins (2002). Similarly the precision measured by FAAS , ICP-MS and ICP-OES was higher than the respective 0.1-1 %, <5 % and <3 % RSD stipulated in literature (Tyler, no date). As discussed in Section 2.4.3. many factors such as sample preparation, machine sensitivity, calibration and spectral interferences could have affected accuracy of elemental analysis (Baedecker, 1987; Huggins, 2002).

Table 27 Relative standard errors (RSE) of analytical techniques used to determine major and minor elements in coal standard SARM 19

Element	[+]WDXRF	[+]LA-ICP-MS	[++]ICP-OES	[++]FAAS	[+++]ICP-MS
RSE for major elements (%)					
Al_2O_3	-2.53	-	10.39	-	-54.95
CaO	-1.99	-	-56.72	-	-33.30
Fe_2O_3	-3.08	-	24.18	13.56	-12.83
K_2O	-2.76	-	15.45	-	-
MgO	-17.23	-	32.66	-	-17.73
MnO	-23.54	-	-	-	9.36
Na_2O	-4.55	-	81.28	6.91	-6.39
SiO_2	-1.94	-	-	-	-
TiO_2	-5.30	-	-7.03	-	-
RSE for minor elements (%)					
Ba		-2.60	-	-	-8.95
Mn		-6.94	-	-	9.36
P	-18.01	-	-	-	-
Sr		-4.56	-	-	-
Zr		-8.62	-14.53	-	-

[+] *SUN laboratory* [++] *UCT Analytical Laboratory* [+++] *UCT Geology Laboratory*

Trace Elements in Coal Standard SARM 19

The measured elements compositions and the certified ranges are shown in Table 28 while the accuracy results are shown in Table 29 as % RSE. Most of the values measured by LA-ICP-MS at the University of Stellenbosch fall within the 95 % confidence limit ranges for the certified values, except for As, Cs, La and Sm. The RSE values were once again largely below 10 %, except for As, Zn, Tb, Se (RSE of-20 %, -27 %, -21 %, and 32 % respectively) and, in particular, Sb at RSE of 93 %. The laboratories have indicated that the LA-ICP-MS method is not suitable for the accurate analysis of As, Sb and Se due to their volatility. In contrast, the ICP-MS facilities at the University of Cape Town were only able to analyse relatively few trace elements, and, except for Be, Cu and Mo, the RSE generally exceeded 10 %. In contrast to literature (Section 2.4.3. in Chapter 2), the ICP-OES at UCT was not able to analyse trace elements due to higher detection limits than the 0.1-100 ppm reported in literature (Baedecker, 1987). The measured precision of LA-ICP-MS was higher for most minor and trace elements compared to the literature values of 2-5 % RSD (Becker and Dietze, 2003). These results also indicate that although LA-ICP-MS analysis at SUN had a better accuracy for most trace elements than ICP-MS, ICP-MS had better accuracy for some elements (i.e. Be and Mo). Thus, a combination of the analysing techniques can give more reliable results than individual techniques.

Table 28 Trace elements in coal standard SARM 19 analysed by different techniques compared to certified values

Element	Certified Value	95 % confidence limit	[+]LA-ICP-MS	[++]ICP-OES	[+++]ICP-MS
Trace element in ppm					
As	7.00	6.00 - 8.00	5.59 ± 0.42	*bdl	15.86 ± 1.15
Be	2.80	2.30 - 3.10	-	bdl	2.59 ± 0.05
Ce	56.00	51.00 - 59.00	51.47 ± 0.51	bdl	-
Co	5.60	5.00 - 6.60	5.57 ± 0.29	bdl	4.37 ± 0.36
Cr	50.00	47.00 - 58.00	53.49 ± 0.94	bdl	35.88 ± 0.49
Cs	1.40	1.30 - 2.00	1.18 ± 0.34	-	-
Cu	13.00	11.00 - 14.00	12.11 ± 0.60	bdl	11.78 ± 0.65
Ga	14.00	13.00 - 15.00	12.73 ± 0.84	-	-
Ge	13.00	10.00 - 14.00	10.51 ± 0.79	bdl	-
Hf	5.40	4.70 - 6.10	4.86 ± 0.23	-	-
La	27.00	26.00 - 29.00	24.75 ± 0.35	-	-
Ni	16.00	13.00 - 20.00	15.86 ± 0.88	bdl	12.22 ± 0.43
Pb	20.00	17.00 - 23.00	17.85 ± 0.52	bdl	24.20 ± 0.38
Rb	9.00	8.00 - 10.00	8.17 ± 0.34	bdl	-
Sc	7.60	7.00 - 8.30	8.38 ± 0.34	-	-
Sm	4.90	4.20 - 5.00	4.00 ± 0.32	-	-
Th	12.00	11.00 - 14.00	11.92 ± 0.22	dl	-
U	5.00	3.00 - 6.00	4.44 ± 0.12	bdl	-
V	35.00	33.00 - 37.00	35.09 ± 0.67	bdl	30.97 ± 0.78
Zn	12.00	12.00 - 16.00	15.30 ± 1.15	bdl	28.05 ± 0.83
Uncertified elements in ppm					
B	90.00	-	-	bdl	-
Br	2.00	-	-	-	-
Cl	32.00	-	-	-	-
Eu	0.70	-	0.66 ± 0.07	-	-
Hg	0.20	-	-	-	-
Li	37.00	-	-	bdl	-
Mo	2.00	-	2.34 ± 0.22	bdl	1.87 ± 0.71
Nb	10.00	-	9.98 ± 0.22	bdl	-
Sb	0.30	-	0.58 ± 0.09	bdl	0.16 ± 0.38
Se	1.00	-	0.68 ± 0.34	bdl	-
Sn	3.00	-	2.56 ± 0.23	bdl	
Ta	0.80	-	0.81 ± 0.05	bdl	-
Tb	0.70	-	0.55 ± 0.03	-	-
W	2.00	-	-	bdl	-
Y	20.00	-	19.03 ± 0.24	-	-
Yb	2.00	-	1.73 ± 0.17	-	-
Cd	-	-	0.16 ± 0.09	bdl	0.44 ± 1.77
Tl	-	-	0.16 ± 0.02	bdl	0.74 ± 0.55

** bdl = below detection limit* *[+] SUN laboratory* *[++] UCT Chemical Engineering Analytical Laboratory* *[+++]UCT Geology Laboratory*

Table 29 Relative standard errors (RSE) of the analytical techniques used to determine trace elements in coal standard SARM 19

Element	[+]LA-ICP-MS	[++]ICP-OES	[+++]ICP-MS
RSE of certified trace elements (%)			
As	-20.14	-	126.57
Be	-	-	-7.68
Ce	-8.10	-	-
Co	-0.54	-	-22.00
Cr	6.97	-	-28.24
Cs	-16.00	-	-
Cu	-6.85	-	-9.38
Ga	-9.07	-	-
Ge	-19.19	-	-
Hf	-10.09	-	-
La	-8.33	-	-
Ni	-0.88	-	-23.63
Pb	-10.78	-	21.00
Rb	-9.28	-	-
Sc	10.20	-	-
Sm	-18.37	-	-
Th	-0.67	-	-
U	-11.28	-	-
V	0.26	-	-11.51
Zn	27.50	-	133.75
RSE of uncertified trace elements (%)			
Eu	-6.36	-	-
Mo	16.75	-	-6.30
Nb	-0.25	-	-
Sb	93.33	-	-46.53
Se	-32.00	-	-
Sn	-14.83	-	-
Ta	0.81	-	-
Tb	-20.79	-	-
Y	-4.88	-	-
Yb	-13.75	-	

[+] SUN laboratory [++] UCT Chemical Engineering Analytical Laboratory [+++]UCT Geology Laboratory

4.6.2. Element Composition in Coal Processing Wastes

The combination of ICP-OES, FAAS (for Fe, Na analysis only) at UCT and WDXRF at SUN analysis were applied to determine major and minor elements in the Waterberg coal slurry. For the other two coal waste samples; only WDXRF was applied since it was evaluated to give the more accurate results

in the coal standard analysis. The same reason was used to select LA-ICP-MS at SUN for analysis of minor and trace elements in all the three coal wastes.

Major and Minor Elements in Coal Processing Wastes

The results in Table 30 show relatively high major element concentrations for Witbank coal discards, particularly in terms of Si, Al, and Ti content, which is indicative of the higher content of minerals, such as kaolinite, quartz and rutile. On the other hand, the results show the coal slurry wastes to be higher in Mn, Na and Ba compared to the coal discards. The results also indicate that the Witbank coal slurry waste has a slightly lower Si, but significantly higher Al content than the Waterberg coal slurry waste. This is consistent with the higher kaolinite/quartz ratio for the Witbank coal slurry waste, as per the mineralogy results. The Fe, Ca and Mg contents are also consistent with the higher Fe-oxyhydroxides, calcite and dolomite concentrations in the Waterberg coal slurry waste, relative to the coal wastes from Witbank. The Waterberg coal slurry waste also had the highest Mn content at 593 ppm. ICP-OES results for Mn, Al, K and Mg were lower than XRF results for the Waterberg coal slurry waste, but FAAS evaluated Fe composition lower than ICP-OES but higher than XRF.

Table 30 Composition of major and minor elements in coal waste samples A (Waterberg slurry), B (Witbank slurry) and C (Witbank discards) determined by different analysing techniques

	Sample A				Sample B		Sample C	
	[+]WDXRF	**[+]LA-ICP-MS**	**[++]ICP-OES**	**[++]FAAS**	**[+]WDXRF**	**[+]LA-ICP-MS**	**[+]WDXRF**	**[+]LA-ICP-MS**
Major elements in wt. % ash basis								
Al_2O_3	8.02	-	3.78	-	13.16	-	15.39	-
CaO	8.43	-	0.39	-	0.83	-	0.06	-
Fe_2O_3	5.22	-	6.41	5.92	2.34	-	2.50	-
K_2O	0.55	-	0.46	-	0.34	-	0.28	-
MgO	1.08	-	0.15	-	0.20	-	0.06	-
SiO_2	28.49	-	-	-	22.51	-	47.21	-
TiO_2	0.41	-	0.46	-	0.77	-	0.98	-
L.O.I.	49.34	-	-	-	59.27	-	32.84	-
Minor elements in ppm								
Ba	-	1040.00±14.5	-	-	-	942.50±14.00	-	279.81±15.56
Mn	-	593.15±5.25	400.00	-	102.95	-	42.44	-
Na	300.69	-	1800.00	bdl	241.72	-	bdl	-
P	**132.67**	-	-	-	1084.27	-	351.72	-
Sr	-	158.35±2.25	-	-	-	480.80±4.80	-	121.28±6.46
Zr	-	160.85±1.50	-	-	-	248.00±2.85	-	359.68±25.45

** bdl = below detection limit* *[+] SUN laboratory* *[++] UCT Chemical Engineering Analytical Laboratory*

Trace Elements in Coal Processing Wastes

The elemental composition of the three coal wastes are presented in Table 31. Generally, the results show that the concentration of the trace elements differ from sample to sample. Cr and Mo are outstandingly higher in the Witbank coal discards compared to the two coal slurry wastes. Whilst Ce, Ga, Th, Ta and Nb are higher in the coal wastes from Witbank compared to the coal waste from Waterberg. On the other hand, Zn and V are higher in the Waterberg coal slurry waste than in the coal wastes from Witbank. The concentration of Sb, Cr, Cu, Ni, and Zn in all the three coal wastes, as well as Th in the Witbank coal wastes, exceed the range in SA coals (Table 6 in Section 2.2.3) reported by Bergh (2013) and Wagner and Hlatshwayo (2005).

Table 31 Composition of trace elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) analysed by LA-ICP-MS at SUN

	Sample A	Sample B	Sample C		Sample A	Sample B	Sample C
Trace elements in ppm				***Trace elements in ppm***			
As	7.86 ± 0.42	4.49 ± 0.40	6.94 ± 0.34	**Nd**	25.70 ± 0.93	35.25 ± 1.10	26.84 ± 1.37
Bi	0.42 ± 0.06	0.24 ± 0.05	0.79 ± 0.05	**Ni**	34.15 ± 1.90	31.05 ± 1.90	29.05 ± 1.25
Cd	0.28 ± 0.14	0.06 ± 0.06	0.30 ± 0.06	**Pb**	26.06 ± 0.70	23.00 ± 0.65	33.24 ± 1.86
Ce	53.92 ± 0.76	90.35 ± 1.10	72.13 ± 3.85	**Pr**	6.27 ± 0.16	9.20 ± 0.26	7.44 ± 0.36
Co	15.92 ± 0.58	12.13 ± 0.48	6.12 ± 0.23	**Rb**	32.40 ± 1.15	20.03 ± 0.84	17.87 ± 0.72
Cr	82.10 ± 1.55	87.50 ± 1.90	199.87 ± 6.99	**Sb**	1.67 ± 0.19	1.15 ± 0.15	0.88 ± 0.08
Cs	3.75 ± 0.56	3.75 ± 0.57	3.57 ± 0.78	**Sc**	16.20 ± 0.56	14.48 ± 0.57	12.28 ± 0.78
Cu	32.75 ± 1.25	34.85 ± 1.30	42.72 ± 1.52	**Se**	1.34 ± 0.55	1.25 ± 0.55	1.55 ± 0.38
Dy	6.05 ± 0.33	5.96 ± 0.34	5.32 ± 0.40	**Sm**	6.47 ± 0.57	7.05 ± 0.46	5.23 ± 0.37
Eu	1.11 ± 0.10	1.27 ± 0.10	1.03 ± 0.06	**Sn**	4.55 ± 0.40	3.34 ± 0.32	5.73 ± 0.25
Er	3.22 ± 0.18	3.46 ± 0.27	3.26 ± 0.28	**Ta**	0.83 ± 0.06	1.50 ± 0.08	1.84 ± 0.13
Ga	13.04 ± 0.90	19.29 ± 1.28	19.89 ± 0.73	**Tb**	0.97 ± 0.06	0.94 ± 0.08	0.85 ± 0.06
Gd	6.11 ± 0.35	5.92 ± 0.49	4.87 ± 0.34	**Te**	< 0.5 ± 0.18	< 0.5 ± 0.21	< 0.5 ± 0.16
Ge	2.18 ± 0.39	3.24 ± 0.44	< 2.18 ± 0.24	**Th**	10.77 ± 0.30	20.12 ± 0.44	20.14 ± 1.44
Hf	4.32 ± 0.25	6.58 ± 0.34	10.42 ± 0.87	**Tl**	0.20 ± 0.03	0.08 ± 0.02	0.22 ± 0.04
Ho	1.17 ± 0.08	1.25 ± 0.09	1.14 ± 0.08	**Tm**	0.45 ± 0.05	0.50 ± 0.06	0.50 ± 0.04
In	0.09 ± 0.02	0.08 ± 0.02	0.28 ± 0.02	**U**	3.84 ± 0.16	5.43 ± 0.18	4.75 ± 0.23
La	25.57 ± 0.46	44.12 ± 0.74	34.08 ± 1.98	**V**	80.55 ± 1.55	69.20 ± 1.30	59.15 ± 2.01
Lu	0.44 ± 0.04	0.49 ± 0.05	0.49 ± 0.05	**Y**	31.74 ± 0.44	33.20 ± 0.64	29.33 ± 2.15
Mo	3.39 ± 0.43	2.88 ± 0.40	8.20 ± 0.40	**Yb**	2.87 ± 0.25	0.17 ± 0.30	3.47 ± 0.28
Nb	14.14 ± 0.30	20.96 ± 0.48	24.77 ± 1.24	**Zn**	80.25 ± 30.5	32.15 ± 2.25	50.50 ± 2.70

4.6.3. Deportment of Major Elements

QEMSCAN could directly evaluate the deportment of the major elements but for QXRD the elements were calculated using stoichiometry based on the chemical composition of the minerals. The deportment of the major elements hosted by the minerals in the coal wastes presented in Figure 24 and Figure 25

show the major elements to largely exist in the mineral matter of the coal wastes. Si and Al were found largely deported in kaolinite and quartz, while Mg is deported in, epsomite, amphiboles and "other" according to QEMSCAN but according to QXRD results the Mg is deported in dolomite in Waterberg coal slurry, epsomite in Witbank coal slurry and mica in Witbank coal discards. The Ca is largely hosted in calcite and amphiboles in Waterberg coal slurry and in apatite in the Witbank coal wastes according to QEMSCAN deportment. However, according to QXRD deportment, the Ca is hosted by dolomite and calcite in Waterberg coal slurry, epsomite in Witbank coal slurry and K-feldspar in Witbank coal discards. The results also show Fe to be largely deported in pyrite, jarosite and Fe-oxyhydroxides. K according to QXRD is deported in jarosite in coal slurries and mica for the discards but deported in K-feldspar and muscovite in all three samples according to QEMSCAN deportment. The deportment also showed Ti to be hosted solely in rutile. The sulphur deportment was evaluated to be mainly in pyrite with significant amounts in coal and carbominerite.

Although several studies such as Huggins (2002) and Ward (2002) have shown some elements including sulphur to exist in the organic matrix of coal, QXRD analysis results did not give details on elements deported in the coal, unlike QEMSCAN. Thus, the deportment from QXRD analysis is mineral matter based and might be incomplete for elements deported in coal. Both methods could not show the deportment of minor and trace elements due to detection limits.

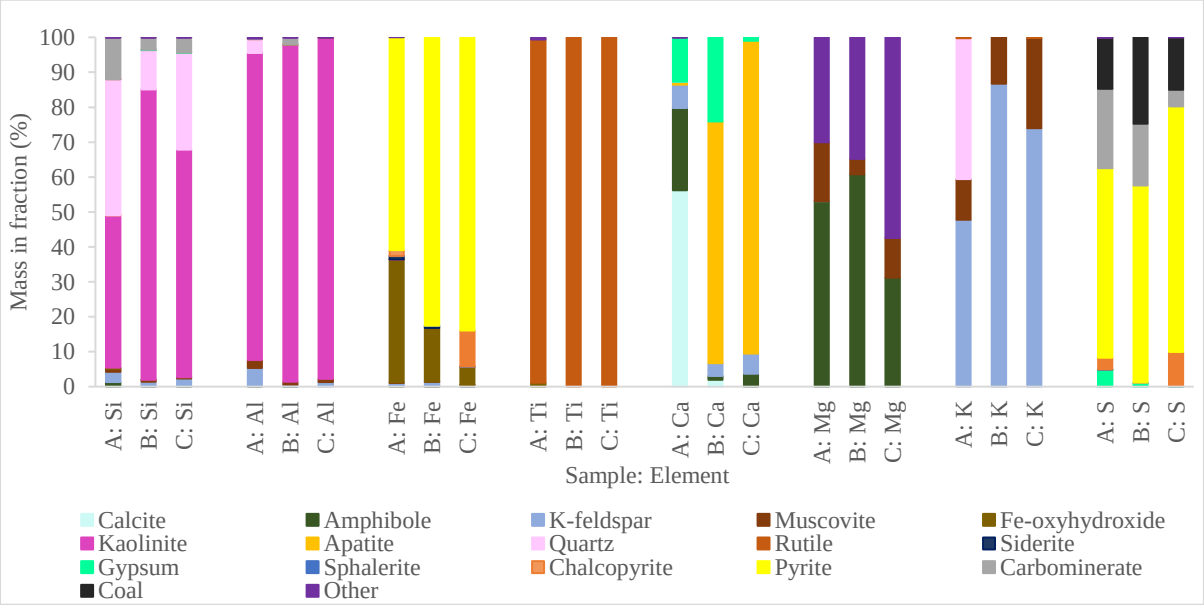

Figure 24 Deportment of major elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) based on QEMSCAN mineralogical analysis

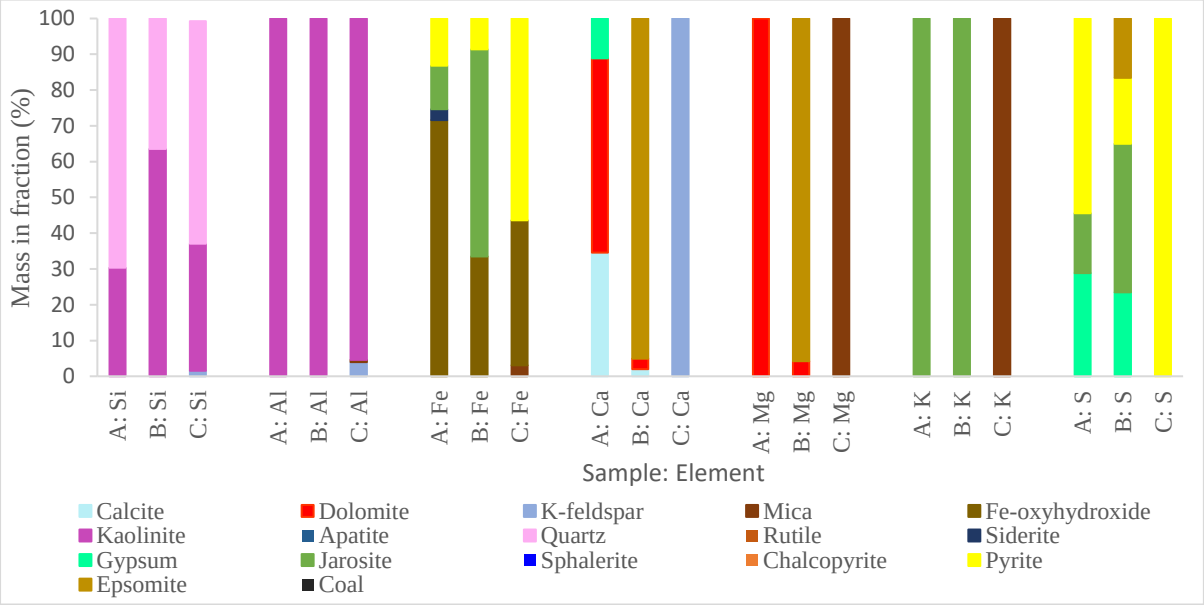

Figure 25 Deportment of major elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) based on QXRD mineralogical analysis

4.7. Comparison of Chemical and Mineralogical Results

Chemical assays by WDXRF were also used to validate mineralogy results on the major elements. Sulphur assays by Leco analysis were also compared to the mineralogy results. Furthermore, the sulphur forms evaluated by the chemical methods in the ACARP C15034 and ISO 157:1996 protocols were compared to the sulphur deportment evaluated by QEMSCAN analysis. QXRD deportment was not considered as the method does not evaluate the sulphur deported in the organic matrix. Results for assay reconciliation on major elements are presented in Section 4.7.1. while assay reconciliation for sulphur forms are presented in section 4.7.2. Quantitative data on assays reconciliation is presented in Appendix B.6.

4.7.1. Assays Reconciliation of Major Elements

Parity curves comparing QEMSCAN and WDXRF analysis on the major elements in Waterberg coal slurry, Witbank coal slurry and Witbank coal discards are shown in Figure 26, Figure 27 and Figure 28 respectively. While parity curves of WDXRF and QXRD assays on Waterberg coal slurry, Witbank coal slurry and Witbank coal discards are presented in Figure 29, Figure 30 and Figure 31 respectively.

Comparison of QEMSCAN and WDXRF

Comparison results of WDXRF against QEMSCAN assays, show QEMSCAN to slightly overestimate Al particularly for the Witbank coal discards likely as a result of kaolinite overestimation. The parity curves also show that QEMSCAN had lower Fe and Ca in the coal slurry wastes particularly for the Waterberg coal slurry waste when compared to WDXRF. Underestimation of Ca and Fe bearing minerals such as dolomite, calcite and siderite was possibly the cause of the lower values of Ca and Fe

in QEMSCAN assays when compared to WDXRF results. The results in Figure 26 also show QEMSCAN assays evaluated less Mg and S in Waterberg coal slurry compared to WDXRF, this is likely due to underestimation of Mg-bearing carbonates (such as dolomite) and soluble sulphates.

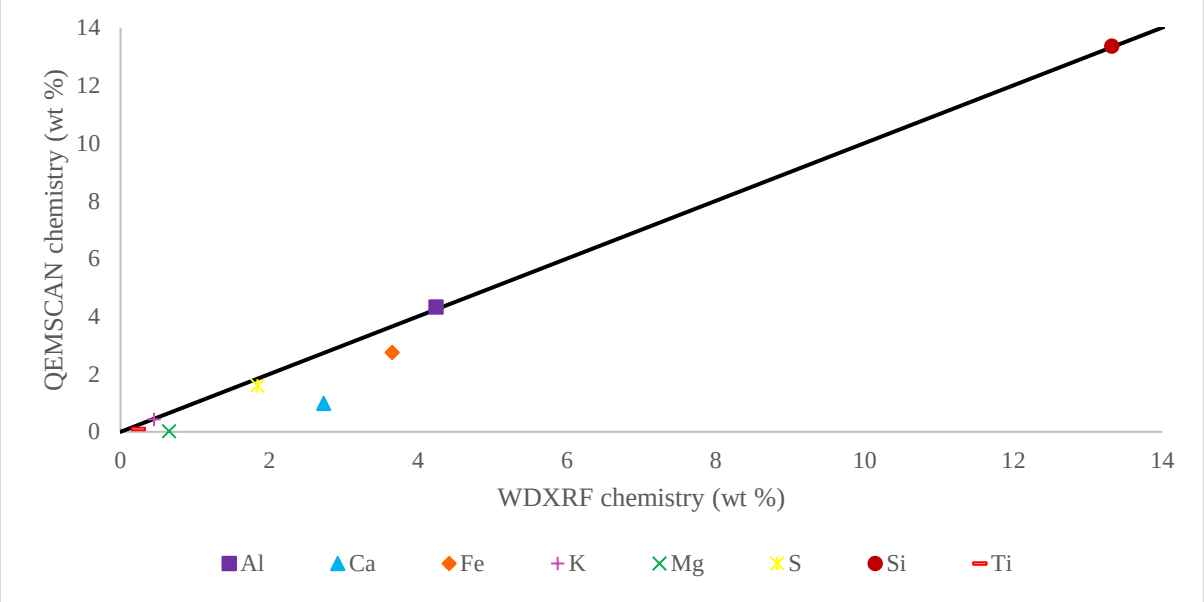

Figure 26 Assay reconciliation of WDXRF (NB total S by Leco analysis) and QEMSCAN on the major elements of Waterberg coal slurry

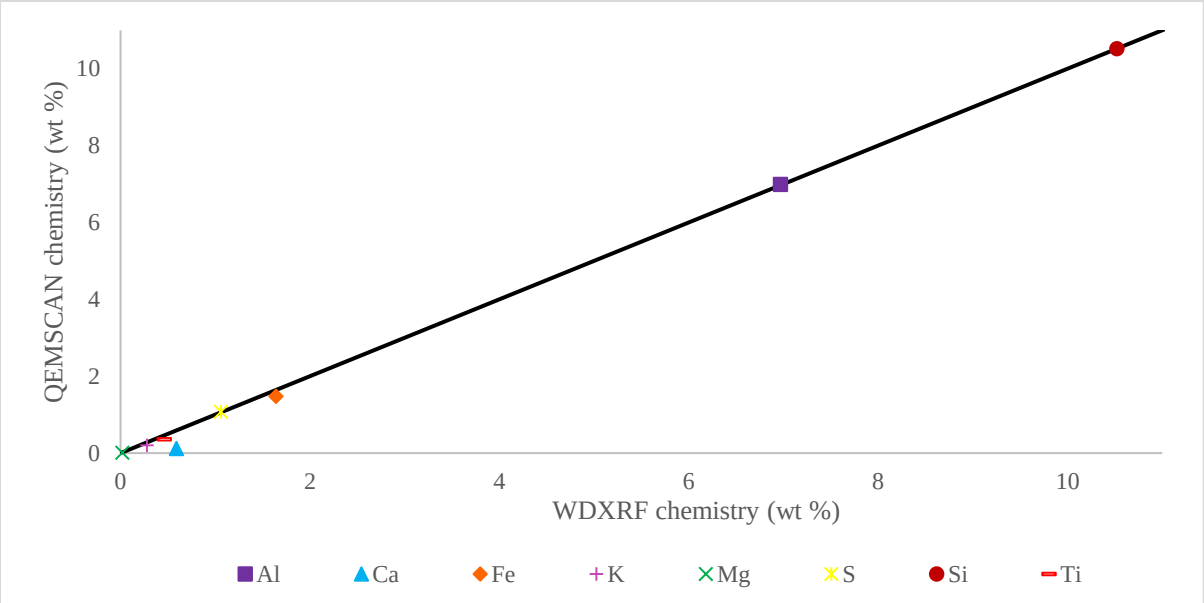

Figure 27 Assay reconciliation of WDXRF (NB total S by Leco analysis) and QEMSCAN on the major elements of Witbank coal slurry

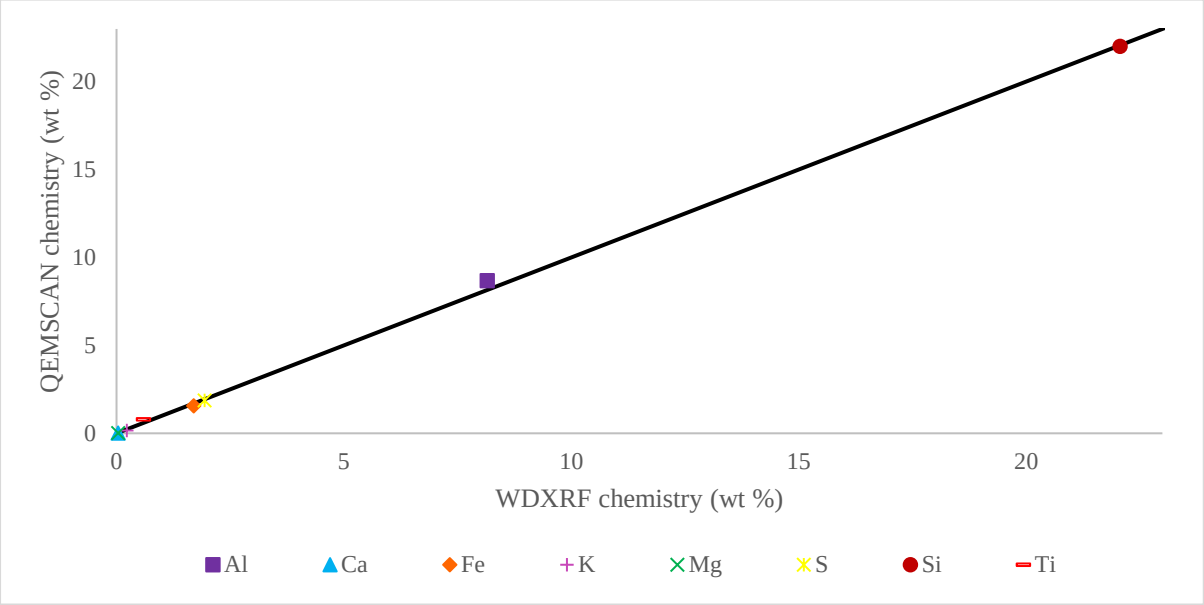

Figure 28 Assay reconciliation of WDXRF (NB total S by Leco analysis) and QEMSCAN on the major elements of Witbank coal discards

Comparison of QXRD and WDXRF

QXRD underestimated all the major elements with the exception of Fe, K and Ca in Witbank coal discards as well as Mg in all coal wastes compared to the WDXRF results. This indicates that QXRD could have analysed dolomite more accurately but overestimated coal and underestimated mineral matter including calcite compared to QEMSCAN analysis.

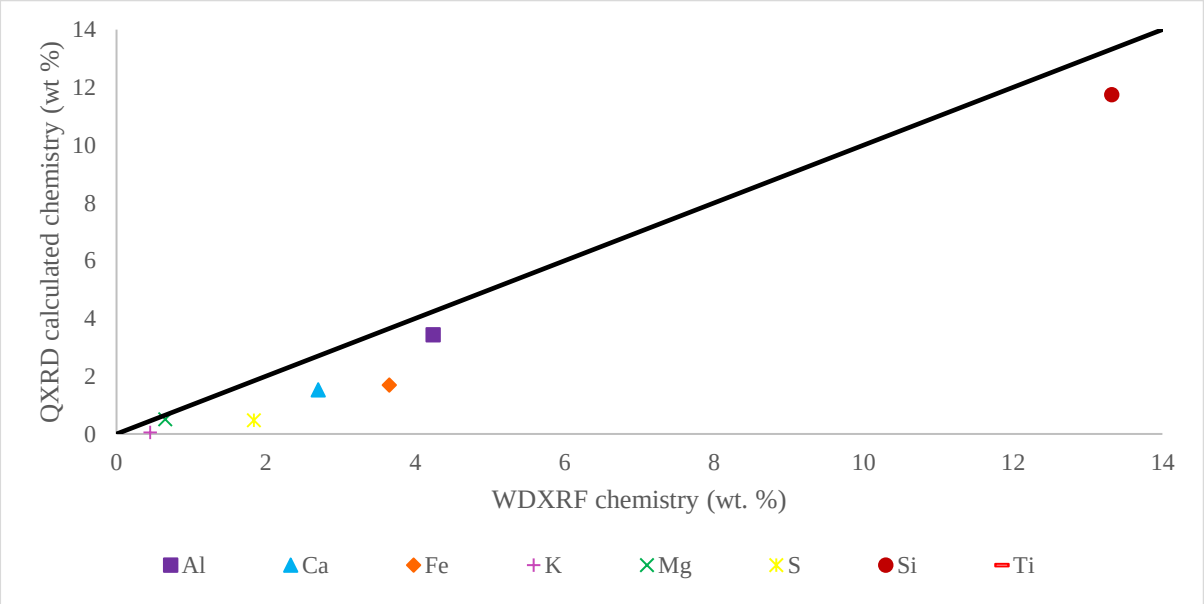

Figure 29 Assay reconciliation of WDXRF (NB total S by Leco analysis) and QXRD on the major elements of Waterberg coal slurry

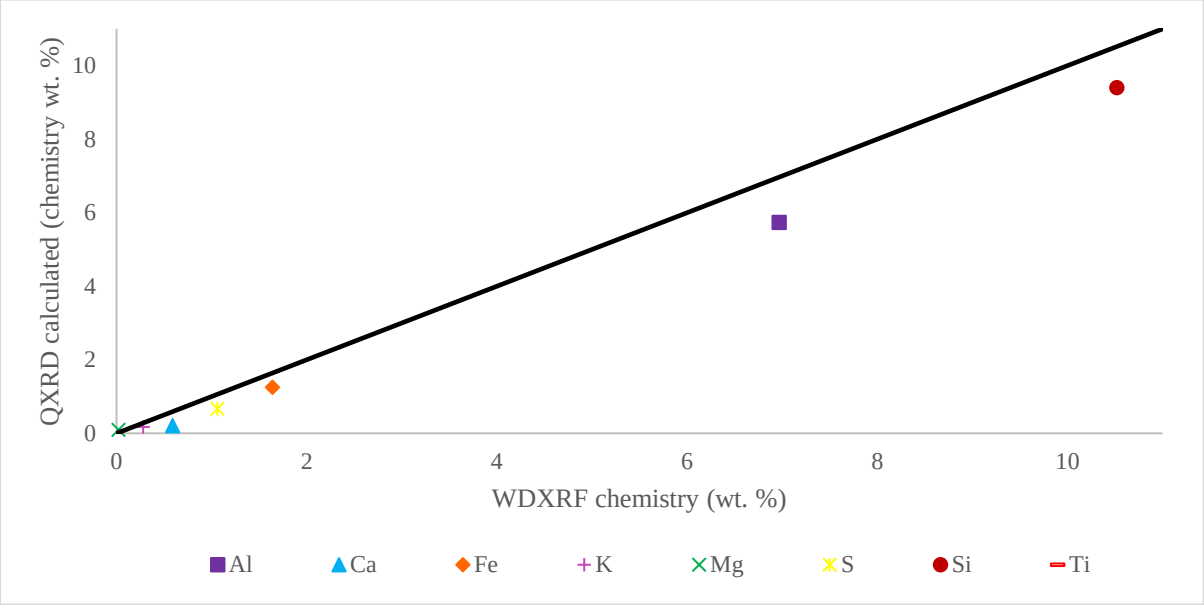

Figure 30 Assay reconciliation of WDXRF (NB total S by Leco analysis) and QXRD on the major elements of Witbank coal slurry

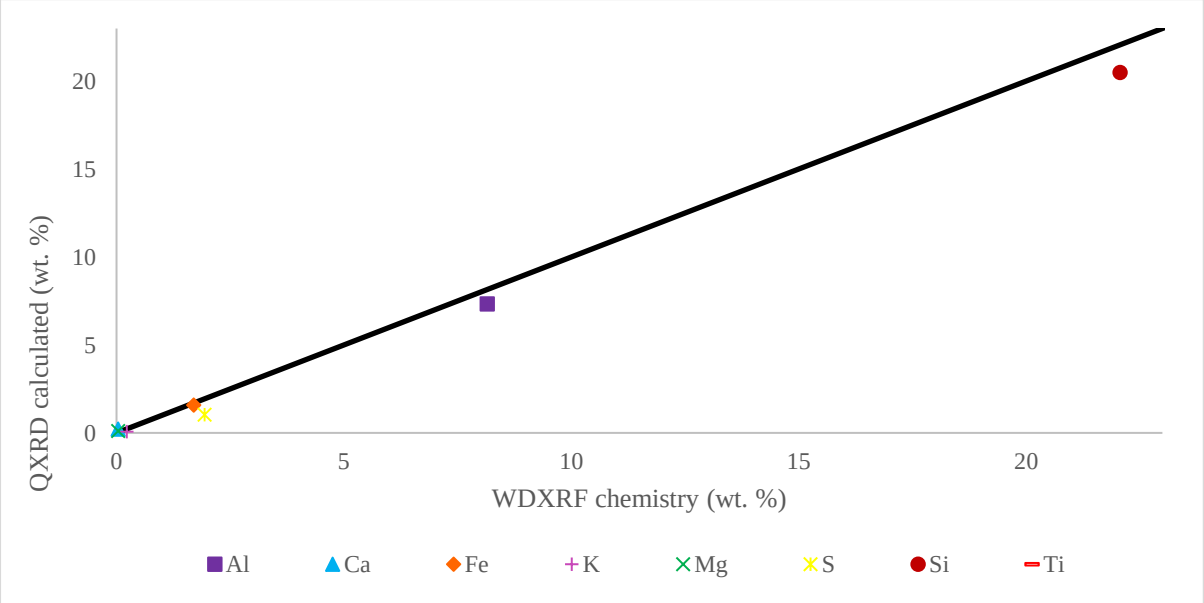

Figure 31 Assay reconciliation of WDXRF (NB total S by Leco analysis) and QXRD on the major elements of Witbank coal discards

4.7.2. Assays Reconciliation on Sulphur Forms

Results comparing the QEMSCAN and ACARP C15034 protocol in evaluating sulphur species in the three coal wastes are presented in Figure 32, while comparison of QEMSCAN and ISO 157:1996 protocol are presented in Figure 33.The results in Figure 32 show that QEMSCAN evaluated lower sulphate values for all the coal wastes compared to the ACARP C15034 method. QEMSCAN evaluated

slightly higher sulphide sulphur in Witbank coal slurry but significantly higher sulphide sulphur in Witbank coal discards and significantly lower values in Waterberg coal slurry compared to the ACARP C15034 protocol. On the other hand, QEMSCAN evaluated significantly lower organic/low-risk sulphur in the coal slurry wastes but higher values for Witbank coal discards in comparison to the ACARP C15034 protocol.

The results in Figure 33 show that QEMSCAN also evaluated lower sulphate values for all the coal wastes compared to the ISO 157:1996 protocol. The QEMSCAN evaluated slightly lower sulphide sulphur in Waterberg coal slurry but significantly higher sulphide sulphur in Witbank coal wastes compared to the ISO 157:1996 protocol. Although the QEMSCAN and ISO 157:1996 protocol evaluated equal amounts of organic sulphur in Witbank coal slurry, the QEMSCAN values were higher for Waterberg coal slurry and lower for Witbank coal discards.

These results perhaps indicate that QEMSCAN is underestimating sulphates in all coal wastes and sulphide sulphur in Waterberg coal slurry but overestimating sulphide sulphur in the Witbank coal wastes. The results also indicate the possibility of QEMSCAN underestimating organic sulphur in Witbank coal discards and overestimating organic sulphur in Waterberg coal slurry.

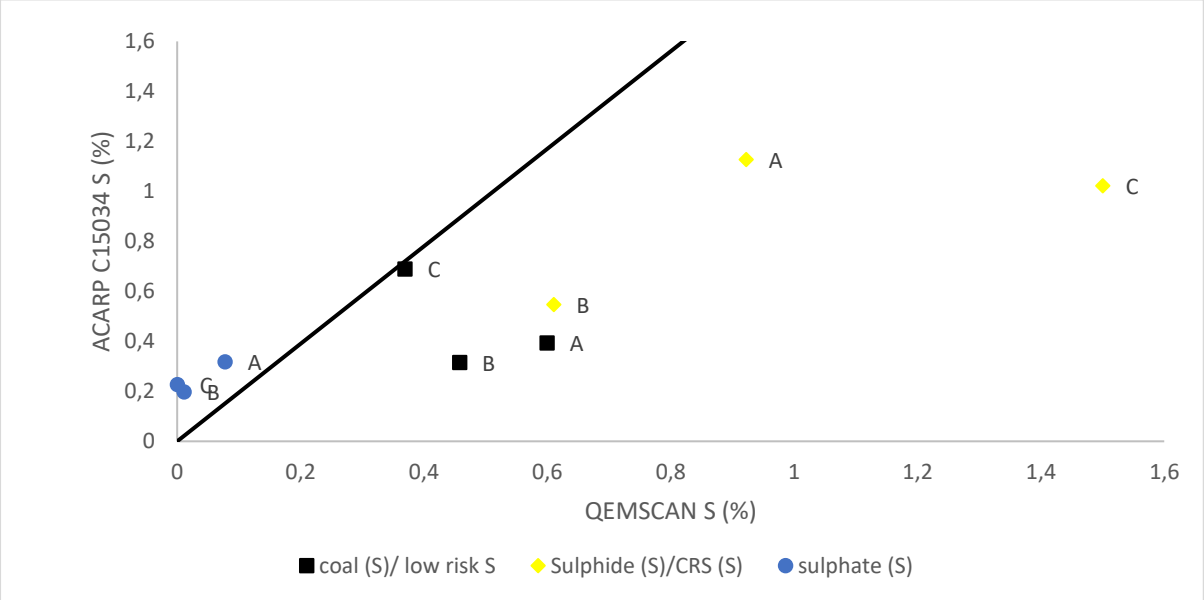

Figure 32 Assay reconciliation of QEMSCAN and ACARP C15034 on the sulphur forms in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

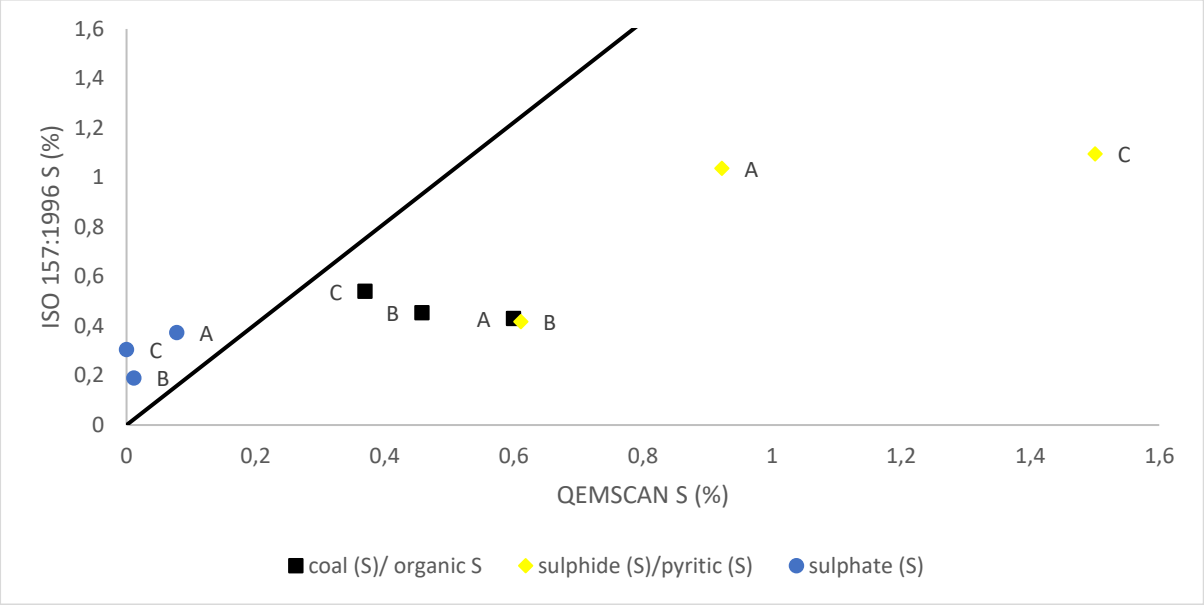

Figure 33 Assay reconciliation of QEMSCAN and ISO 157:1996 on the sulphur forms in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

The results from this chapter evaluates part of hypothesis 1 which states that:

- The ARD, toxic elements and salinity risks posed by coal processing wastes are insufficiently and inconsistently characterised. This is a result of the complex nature of coal wastes which causes uncertainty and limitation with elemental and mineralogical analysis using available techniques and risk assessment tools. The uncertainty in evaluation of ARD potential is because of occurrences and behaviour of sulphur species and effects of organic acids on the acid producing potential.

The results show the complex nature of coal wastes of having an organic and inorganic composition in addition to the limitation of each analysing technique can affect the consistency of the chemical and mineralogical analysis. However, the chemical and mineralogical compositions of coal wastes can be accurately and comprehensively analysed and validated by a combination of various tools of different merits, precision and accuracy. This was proven by the ability of different tools to evaluate slightly different but comparable quantities of total sulphur, sulphur forms, mineralogical and elemental composition of the coal standard and/or the three coal wastes.

CHAPTER 5

RESULTS AND DISCUSSION: POTENTIAL RISK ASSESSMENT

As discussed in Chapter 2, the major environmental concern of coal processing waste is reportedly water contamination because of ARD and its associated elevated levels of elements and salts. Evaluation of the risks in previous studies; from literature review, were compromised mainly by insufficient characterisation techniques and risk assessment tools. Hence the elemental and salinity risks of South African coal processing wastes are largely unknown. This chapter evaluates the hypotheses set in Chapter 2. The first hypothesis seeks to show that the uncertainty of ARD is a result of the limitation of the risk assessment tool as well as occurrences and behaviour of sulphur species and organic acids effect. The second hypothesis seeks to characterise the ARD potential as well as the elemental and salinity risk posed by the coal processing wastes of different geochemical properties.

5.1. Characterisation of ARD Generating Potential

As shown in the literature review, there are a number of uncertainties associated with the static ARD tests, NAG and ABA tests in the classification of ARD potential (Fey, 2003; Smart et al., 2002). It has been reported that total sulphur in ABA tests and organic acid effects in NAG tests could cause an overestimation of the net acid-producing capacity of coal wastes (Miller et al., 2008; Schumann et al., 2012; Stewart et al., 2009). These issues have been addressed in this research by studying the conversion behaviour of the sulphur species under static tests as well as validating the conventional NAG tests with the extended boil NAG test. Mineralogical data and biokinetic shake flask tests were also conducted to assist in the interpretations and validation the ARD characterisation results from static tests.

5.1.1. Static Chemical Tests

The ARD potential was classified by individual static chemical tests and by a combination of both ABA and NAG tests. The classification took into consideration net acid-producing potential (NAPP) calculated from maximum potential acidity (MPA) of both total sulphur and acid-producing sulphur. The classification also took into consideration the net acid generation (NAG) pH under conventional and extended boil conditions. The classification criteria are presented in Appendix C1.1 and the ARD characterisation results are discussed in the following sections.

Acid-Base Accounting (ABA)

Results for the ABA tests, using total sulphur, (S(T), and acid-forming sulphur, S(A), to calculate Maximum Potential Acidity (MPA) and Net Acid-Producing Potential (NAPP), are presented in Table 32 and Table 33 respectively. ABA results shown in Table 32 classified the Waterberg coal slurry as

non-acid-forming (NAF) due to the neutralising potential being higher than acid generating potential. Despite having similar ANC, the Witbank coal slurry was classified as uncertain (UC) as the results show no significant difference between ANC and MPA, while the Witbank coal discards were classified as potentially acid-forming (PAF) because of a higher MPA. The results in Table 33 show that, despite the Witbank coal discard sample being classified as PAF when total sulphur is used to estimate the MPA, the classification changes to UC when sulphides and acidic sulphates are used to estimate MPA. In all the three samples NAPP value decreased considerably when MPA was calculated from acid-forming sulphur only instead of total sulphur but did not change the classification of the two coal slurry wastes.

Table 32 ABA results and classification of ARD potential for coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) based on total sulphur

Sample	T (S) (%)	MPA (kg H_2SO_4 / Ton)	ANC (kg H_2SO_4 / Ton)	NAPP (kg H_2SO_4 / Ton)	ARD Class
A	1.84 ± 0.08	56.30 ± 2.30	102.30 ±1.10	**-46.79**	**NAF**
B	1.06 ± 0.06	32.44 ± 1.74	29.21 ±0.70	**3.22**	**UC**
C	1.94 ± 0.08	59.36 ± 2.44	29.10 ±1.11	**30.26**	**PAF**

Table 33 ABA results and classification of ARD potential for coal waste samples A Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)) based on acid-forming sulphur

Sample	A (S) %	MPA (kg H_2SO_4 / Ton)	ANC (kg H_2SO_4 / Ton)	NAPP (kg H_2SO_4 / Ton)	ARD Class.
A	1.13± 0.01	34.52 ± 0.21	102.30 ±1.10	**-68.57**	**NAF**
B	0.56 ± 0.00	17.14 ± 0.09	29.21 ±0.70	**-12.08**	**UC**
C	1.25± 0.03	38.27 ± 0.77	29.10 ±1.11	**9.17**	**UC**

Net Acid Generation (NAG) Tests

The NAG results for both conventional NAG and extended boil NAG are presented in Table 34. The NAG results further proved the Waterberg coal slurry as NAF and Witbank coal discards as PAF while conventional NAG tests classified the Witbank coal slurry as PAF but the extended boil NAG tests pH indicated uncertainty. According to Smart et al. (2002), the $NAG_{pH4.5}$ is derived from free acidity (i.e. H_2SO_4) and soluble Fe and Al while the dissolution of hydroxides of elements such as Al, Fe, K, Mg and Na also contribute to NAG_{pH7} acidity. The NAG pH of 5.2 for the Waterberg coal slurry thus indicates the absence of net acid generating potential from free acidity and a low NAG_{pH7} of 6.6 kg H_2SO_4 / Ton also indicates low acidity from the dissolution of metal hydroxides. On the other hand, a NAG pH of 3.9 and NAG capacity of 9.90 kg H_2SO_4 / Ton shows the Witbank coal slurry to be acid generating but with not very strong free acidity. However, the NAG_{pH7} of 33.80 kg H_2SO_4 / Ton capacity

indicate high acidity contribution of dissolution of metal hydroxides in the Witbank coal slurry. On the other hand, a NAG pH of 2.56 and NAG capacity of 25.86 kg H_2SO_4 / Ton validates the Witbank coal discards as PAF.

The increase of NAG pH from 3.9 to 5.2 after extended boiling showed the possibility of loss of organic acids which were contributing to the NAG capacity of Witbank coal slurry under conventional NAG tests. The colour change of the solution before and after the extended boil from a clear bright yellow to a cloudy yellow as shown in Figure 34 could be an indication of free acidity loss as explained by previous researchers (Miller, 2008; Stewart et al., 2009). However, the extended boil NAG pH of 5.2 does not necessarily classify the sample as NAF since there is also a possibility of loss of free acidity during rigorous boiling which could also have contributed to the NAG pH increase (Miller, 2008; Stewart et al., 2009). According to the protocol (See Section 2.5) further calculated NAG capacity is required to classify the ARD potential. On the other hand, only a slight increase in pH from 2.56 to 2.59 and a slight colour change under extended boil NAG tests indicated a slight effect of organic acids on the net acid generating capacity of Witbank coal discards.

Table 34 ARD potential of for coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) evaluated by conventional single addition NAG and extended boil NAG

Sample	Pre-boil NAG pH	NAG pH	*$NAG_{pH4.5}$ Capacity	*NAG_{pH7} Capacity	ARD Class.	Extended Boil pH	ARD Class.
A	4.57 ± 0.05	5.20 ± 0.03	-	6.60 ± 0.07	**NAF**	-	**NAF**
B	2.51 ± 0.01	3.90 ± 0.10	9.90 ± 1.80	33.80 ± 1.60	**PAF**	5.20 ± 0.01	**UC**
C	1.70 ± 0.01	2.56 ± 0.01	25.86 ± 0.11	11.99 ± 0.55	**PAF**	2.59 ± 0.01	**PAF**

* *Units in kg H_2SO_4 / Ton*

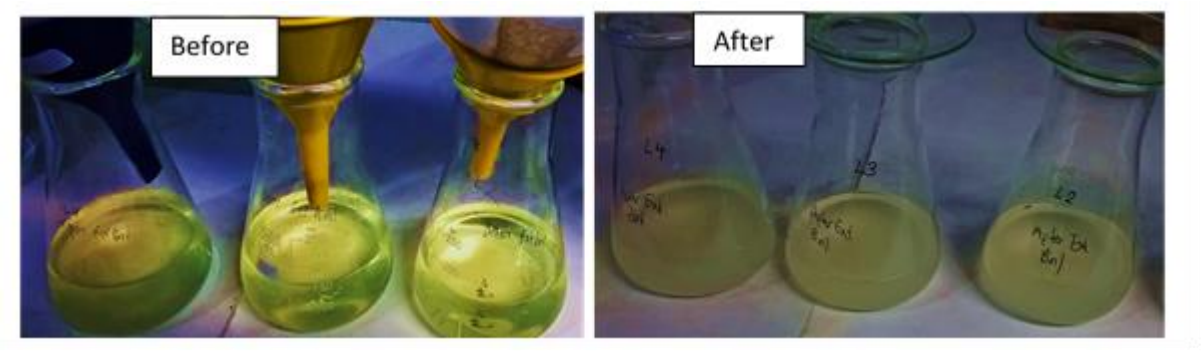

Figure 34 Colour change of Witbank coal slurry leachate before and after extended boil NAG tests from clear bright yellow to cloudy yellow

Combined Classification from ARD Static Tests

Results for NAG pH plots against NAPP values are shown in Figure 35. The combined classification criteria classified the ARD potential of Waterberg coal slurry as NAF regardless of whether NAPP values were determined using MPA calculated from total sulphur or acid-forming sulphur. Similarly, the Witbank coal discards are classified as PAF even after considering acid-forming sulphur for calculating MPA and the effects of organic acids on NAG. Contrastingly, the classification of the Witbank coal slurry varied depending on which sulphur species were considered to calculate MPA as well as considering the effects of organic acids on NAG pH. These ARD static tests results are inconclusive with the classification of the Witbank coal slurry's ARD potential.

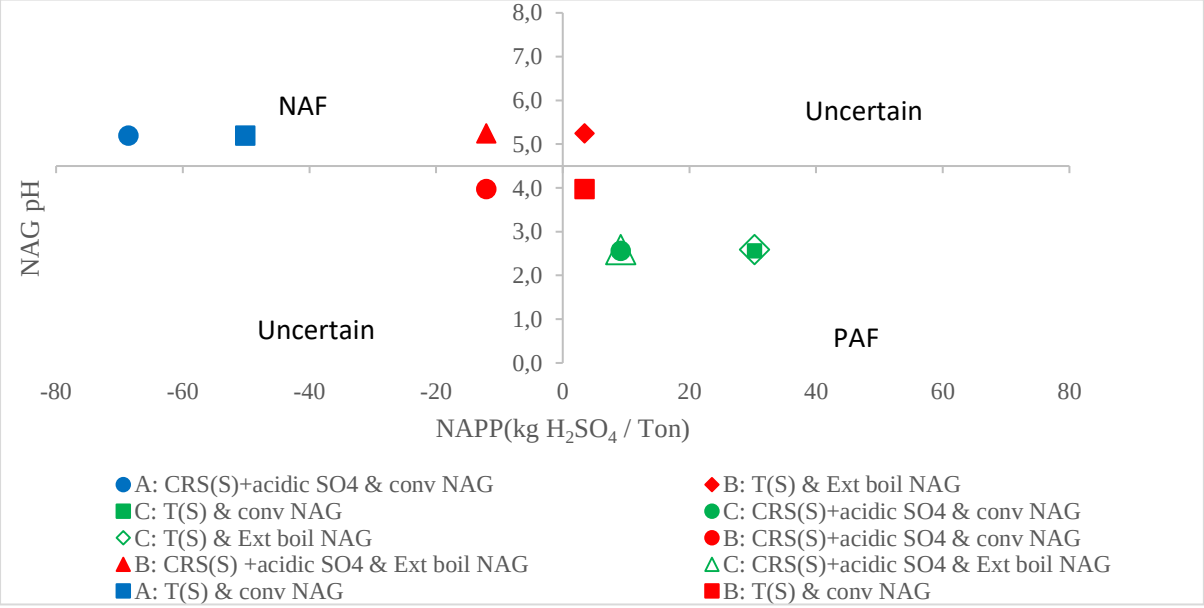

Figure 35 Classification of ARD potential of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) by a combination of ABA, conventional and extended boil NAG tests

Conversion and Deportment of Sulphur Species under ARD Static Test Conditions

To understand the behaviour of the sulphur species during NAG tests and ANC tests, the residues after NAG and ANC digestion were analysed for the sulphur species using the ACARP C15034 method. The comparison of sulphur species distribution before and after the ANC and NAG digestion are shown in Figure 36 and more results presented in Appendix C.1.2.

ANC Tests

The results in Figure 36 show that under ANC tests, the CRS sulphide content in the solids decreased by 21%, 50% and 17% in Waterberg coal slurry, Witbank coal slurry and Witbank coal discard samples respectively. The results also show that under ANC tests the low-risk sulphur increased by 35% and 14% in the Waterberg and Witbank coal slurry wastes, whilst there was a 12% decrease in the Witbank

discards. On the other hand, there was a 10-fold increase in the acid-forming sulphates in the two coal slurries but a 51% decrease in the Witbank coal discards under ANC tests. While 94 % and 82 % of non-acid-forming sulphates of Waterberg and Witbank coal slurry (respectively) solubilised into solution, the formation of non-acid-forming sulphates contributed 1.3 % of the total sulphur in Witbank discards. These results indicate that the relatively aggressive conditions of the ANC tests result in a partial conversion of the sulphides in the solid to soluble sulphate and acid-forming sulphates (such as melanterite, alunite and jarosite). The increase in acid-forming sulphates in the two-coal slurry wastes also indicates the possibility of dissolution of aluminium bearing silicates (like the amphibole wollastonite from mineralogy results) into acid-forming sulphates like melanterite $FeSO_4.7H_2O$ and alunite $(KAl_3(SO_4)_2(OH)_6$. The decrease in acid-forming sulphates and low-risk sulphur in Witbank coal discards suggests solubilisation of acid-forming sulphates and conversion of low-risk sulphur (mainly organic sulphur) in the solids to soluble sulphate. The oxidation of sulphide sulphur and conversion into sulphates and elemental sulphur generates acid, thus underestimating the ANC of the samples.

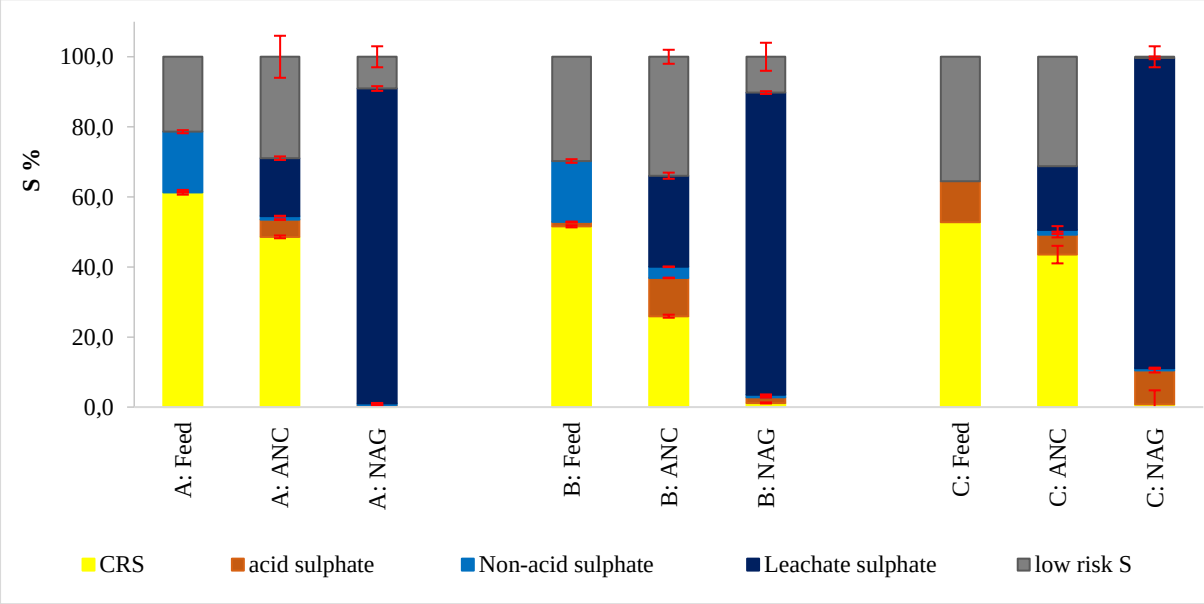

Figure 36 Conversion of sulphur species in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) under ARD static test conditions

NAG Tests

In the NAG tests nearly all (i.e. 99.9 %, 95.8 % and 98.5 % in Waterberg coal slurry, Witbank coal slurry and Witbank coal discards respectively) of the CRS sulphide converted to sulphate in the solution. On the other hand, 53 %, 38 % and 99 % of the low-risk sulphur (mainly organic) in Waterberg coal slurry, Witbank coal slurry and Witbank coal discards respectively also converted to leachate sulphate. These results indicate the aggressive NAG conditions could have caused the partial conversion of low-risk sulphur to acidity thus causing an overestimation of the NAG capacity. However small quantities

(1 % and 10 %) of the total sulphur remained as acid-forming sulphates on the residues of the Witbank coal slurry and discards respectively suggesting incomplete reaction of the sulphur species thus underestimating the net acid generating potential.

The results of the static tests and deportment of sulphur species under static test conditions proves hypothesis 1 which states that the uncertainty in evaluation of ARD potential is because of occurrences and behaviour of sulphur species and effects of organic acids on the acid producing potential. However, the effects of organic acids were observed in Witbank coal slurry (which was shown by the increase in NAG pH from 3.9 to 5.2 after extended boiling) but were negligible in the Witbank discards, meaning the hypothesis is true for some but not all coal wastes. On the other hand, the partial conversion of sulphides and acid forming sulphates under ANC tests and conversion of low risk sulphur under NAG tests in all coal wastes deviated from the assumptions made by the ABA and NAG tests, possibly causing an underestimation of ANC and overestimation of NAG tests. This proves the occurrences and behaviour of sulphur species in coal wastes causes uncertainty with ARD potential assessed by the static tests.

5.1.2. Theoretical ARD from Mineralogy

To evaluate the ARD potential on mineralogy basis, the ARD potential was determined as the net acid capacity from the acid generating potential (AP) and neutralization potential (NP) using the method developed by Paktunc (1999). The results for AP, NP and classification of theoretical ARD potential are presented in Table 35, Table 36 and Table 37 respectively. Detailed data on individual amphiboles, K-feldspars and Fe-oxyhydroxides is given in Appendix C.1.3.

The results in Table 35, show according to QEMSCAN analysis pyrite is the major acid-producing mineral, contributing 88.7 %, 99.9 % and 100 % of the AP Waterberg coal slurry, Witbank coal slurry and Witbank coal discards respectively. The results also show chalcopyrite to theoretically contribute 3.7 % and 11.2 % of the AP for Waterberg and Witbank coal slurry based on QEMSCAN results. However, based on QXRD results, pyrite contributions are 68 %, 23 % and 100 % of the AP for Waterberg coal slurry, Witbank coal slurry and Witbank coal discards respectively. Although the jarosite evaluated by QXRD contributes 31.5 % and 77.1 % of the AP for Waterberg and Witbank coal slurry respectively, the AP based on QXRD is lower compared to the QEMSCAN. As discussed in Section 4.5.3, the QXRD possibly underestimated the mineral matter including pyrite in the coal slurry samples while QEMSCAN overestimated the mineral matter including pyrite in Witbank coal discards. However, comparison of the Witbank coal slurry mineralogy showed QXRD evaluated lower pyrite and more jarosite than QEMSCAN. On the other hand, comparison of the ISO157:1996 and ACARP C15034 protocols to QEMSCAN (Section 4.7.2) showed QEMSCAN evaluated higher pyrite and lower sulphate values for the Witbank coal wastes. Perhaps the contribution of jarosite is significantly high

for Witbank coal slurry and should be analysed instead of including it as “low-risk” S in the ACARP protocol

Table 35 Acid generating potential (AP) of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) calculated on mineralogy basis

Mineral	**Sample A: AP** (kg H_2SO_4/Ton)		**Sample B: AP** (kg H_2SO_4/Ton)		**Sample C: AP** (kg H_2SO_4/Ton)	
	QXRD	QEMSCAN	QXRD	QEMSCAN	QXRD	QEMSCAN
Pyrite	7.79	43.21	3.76	29.91	31.38	44.48
Chalcopyrite	0.00	1.60	0.00	0.00	0.00	5.62
Sphalerite	0.00	0.11	0.00	0.04	0.00	0.07
Jarosite	3.59	0.03	12.68	0.00	0.00	0.00
Total	**11.38**	**43.21**	**16.44**	**29.95**	**31.38**	**50.17**

The theoretical NP results presented in Table 36, show the Waterberg coal slurry to have the highest NP at 88.3-106.8 kg H_2SO_4/ Ton followed by Witbank coal discards at 7.7-29.9 kg H_2SO_4/ Ton and the least in Witbank coal slurry at 0.7-27.0 kg H_2SO_4/ Ton. Although both QXRD and QEMSCAN evaluated the presence of calcite in Waterberg coal slurry, QXRD evaluated dolomite as the major carbonate while QEMSCAN evaluated the presence of intermediate-slow weathering silicates. The NP for Waterberg coal slurry calculated based on the QXRD results is higher than the QEMSCAN based NP. According to QEMSCAN results, dissolving, fast and intermediate weathering minerals in Waterberg coal slurry contributed 38.8 % of the total NP but QXRD results show all the NP was from dissolving calcite and dolomite. The results also show that according to QEMSCAN the majority of the acid neutralizing minerals in the Witbank coal wastes to be slow weathering K-feldspars, mica/muscovite and apatite. On the other hand, the QXRD results show traces of calcite and dolomite in Witbank coal slurry and muscovite in the Witbank coal discards as the only acid neutralizing minerals. As a result, NP for Witbank coal wastes calculated on QXRD mineralogy was found to be lower compared to QEMSCAN based NP. Furthermore, the QXRD results show all the NP in Witbank coal slurry to be from dissolving minerals but QEMSCAN results show only 3.4 % of the NP to be from fast-intermediate weathering minerals. While none of the NP in Witbank coal discards was found to be from fast or intermediate weathering minerals according to QXRD results, only 0.2 % was found to be fast-intermediate weathering according to QEMSCAN results.

Mineralogy comparison results in Section 4.5.3 showed that QXRD consistently gave lower results for minerals than QEMSCAN except for carbonates. Since the QXRD evaluated no acid neutralising silicates except mica in Witbank coal discards, the AP based on QXRD was found to be lower than the QEMSCAN based NP for Witbank coal wastes. Comparison of chemical and mineralogical analysis in Section 4.7.1 confirmed that QEMSCAN results were consistent with chemical analysis for most major

elements, except Ca and Mg which were low. This would indicate that QEMSCAN provided a more reliable estimate of NP minerals, except for the carbonates which are possibly underestimated.

Table 36 Neutralization potential for coal waste samples A (Waterberg slurry), B (Witbank slurry) and C (Witbank discards) calculated on mineralogy basis

Weathering NP Group	Mineral	Sample A: NP (kg H_2SO_4/Ton)		Sample B: NP (kg H_2SO_4/Ton)		Sample C: NP (kg H_2SO_4/Ton)	
		QXRD	QEMSCAN	QXRD	QEMSCAN	QXRD	QEMSCAN
Dissolving	Calcite	25.68	27.20	0.20	0.12	0.00	0.00
	Dolomite	80.82	-	0.60	-	0.00	-
Fast	Amphiboles	-	6.04	-		-	0.01
Intermediate	Amphiboles	-	1.02	-	0.59	-	0.05
Slow	Apatite	-	0.20	-	2.05	-	0.30
Very slow	K-feldspar	-	48.68	-	15.48	-	25.33
	Fe-oxyhydroxide	-	0.02	-		-	0.79
	Mica/ Muscovite	-	5.17	-	2.78	7.72	4.17
Total		**106.50**	**88.31**	**0.72**	**21.02**	**7.72**	**29.86**

Although the mineralogy determined by QEMSCAN analysis was different from the mineralogy determined by QXRD (as discussed in Section 4.5), the ARD potential classification was similar as shown in Table 37. The Waterberg coal slurry was classified as NAF and both the Witbank coal wastes classified as PAF. However, the calculated ARD method neither shows the time-related net acid generation nor take into consideration the microbial effect on the ARD formation.

Table 37 Classification of ARD potential calculated from mineralogy of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards

Sample	QEMSCAN mineralogy		QXRD mineralogy	
	NAPP (kg H_2SO_4/Ton)	ARD Class.	NAPP (kg H_2SO_4/Ton)	ARD Class.
A	-45.10	**NAF**	-96.64	**NAF**
B	8.93	**PAF**	15.72	**PAF**
C	20.34	**PAF**	23.66	**PAF**

5.1.3. Biokinetic Shake Flask Tests

The time-related ARD behaviour of the samples was assessed by monitoring pH and redox of the samples under four different batch biokinetic shake flask conditions detailed in chapter three. The uncontrolled pH conditions gave information on the behaviour likely to be exhibited under natural pH conditions in the dump disposal system. On the other hand, the pH controlled conditions portrayed the

behaviour of the samples under acidic conditions when the acid neutralizing capacity has been exhausted in the long-term dump disposal conditions. The microbial catalysis of the ARD reactions under the different pH conditions was also accounted for using naturally occurring microorganisms (non-inoculated conditions) and acidophiles likely to exist in an ARD-active dump (inoculated conditions). However, the batch shake flask tests do not represent a continuous flow system likely to be found in a dump scenario. The bio-kinetic test results for each sample are presented in the following sections and more results are presented in Appendix C.1.4.

Waterberg Coal Slurry

The pH profile and redox profile results are shown in Figure 37 and Figure 38. The results show that under the uncontrolled pH conditions for both inoculated and un-inoculated test conditions, the onset of acid neutralising reactions was indicated by a pH increase and redox decrease. The pH increased from the initial pH of 2 to above 7 and redox decreased to below 230 mV in 5-9 days rendering the acidophiles (whose optimum pH range is 1-3) inactive. A subsequent slight decrease in pH to values between 6 and 7 and the concomitant increase in redox potential is indicative of the onset of acid-forming oxidative dissolution of sulphide minerals. After day 17 for the inoculated and day 20 for the un-inoculated, there was a slight increase in pH to above 7 indicating moderate and slow weathering acid neutralisation. After day 30 the pH stabilised until the duration of the tests indicating no net acid generation.

Under controlled pH for both inoculated and un-inoculated conditions, the acid neutralization by fast weathering reactions increased the pH from the initial pH of 2 (to as high as 5.7) for the first 2 and 6 days respectively. The pH was controlled to 2 by addition of H_2SO_4 acid which removed the acid neutralizing capacity. Once the acid neutralizing capacity was removed, acid-forming reactions decreased pH to about 1.8 and redox increased to above 700 mV for the duration of the tests. This showed that the sample can form ARD under circumstances where the fast-moderate acid neutralizing capacity becomes exhausted. In all the test conditions the inoculated reactions were faster than the un-inoculated due to the inoculum culture which catalysed the ARD formation faster than the naturally occurring microorganisms.

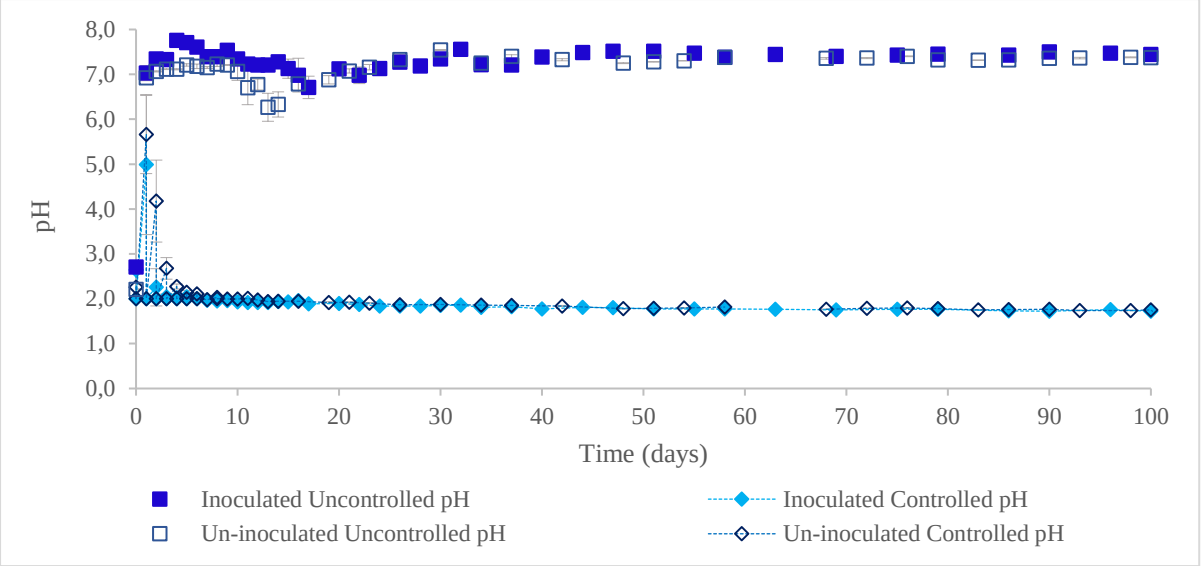

Figure 37 pH profile of Waterberg coal slurry under biokinetic batch shake flask test conditions

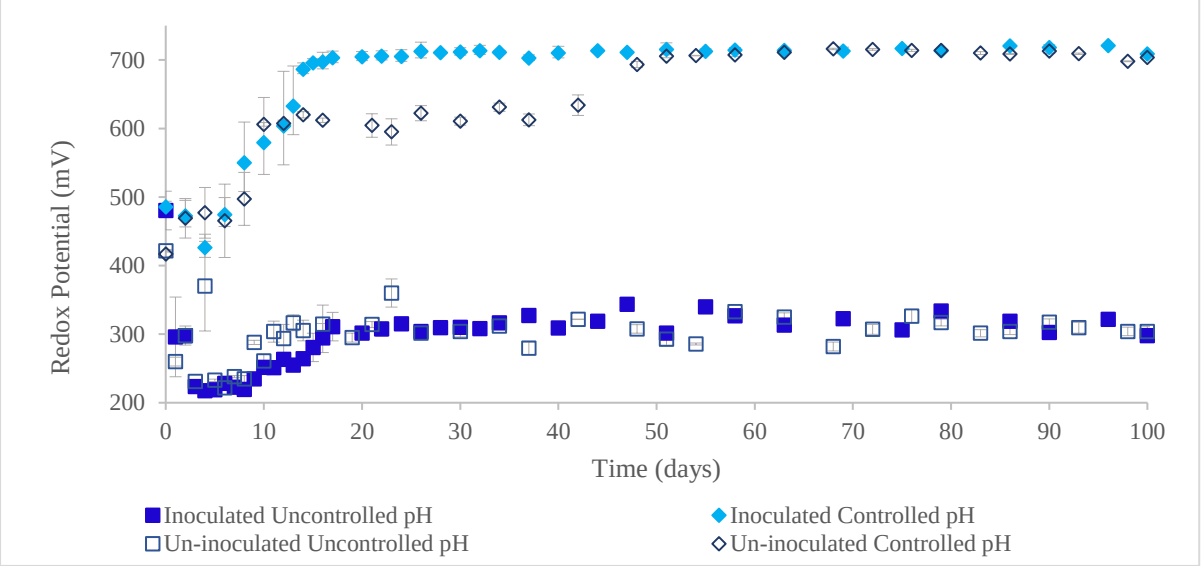

Figure 38 Redox profile of Waterberg coal slurry under biokinetic batch shake flask test conditions

Witbank Coal Slurry

The low pH and high redox profiled in Figure 39 and Figure 40, indicate that the sample is net acid generating under all biokinetic test conditions investigated. The effect of fast-moderate weathering acid neutralising reactions was observed in the first 2-6 days for the controlled pH conditions and 3-11 days for the un-controlled pH conditions. Under uncontrolled pH conditions, these acid neutralising reactions increased pH from the initial pH of 2.0 to 2.7 and 3.3 for the inoculated and un-inoculated conditions respectively. This implies the sample had no significant net acid neutralizing capacity. The subsequent onset of acid-forming reactions decreased the pH to 2.4 and 2.8, while redox increased to above 650 and 600 mV in inoculated and un-inoculated flasks respectively. However, the pH increased slightly

while redox potential decreased slightly at intervals from day 40 to day 100 because of the acid neutralization by moderate-slow weathering minerals. On the onset of acid-forming reactions when the fast-intermediate acid neutralising capacity was removed by addition of H_2SO_4 acid, the pH decreased to between 1.9 and 1.8 for the controlled pH conditions until the tests were stopped. Controlling the pH also caused a rapid increase in redox potential to above 650 mV also indicating a net acid generation.

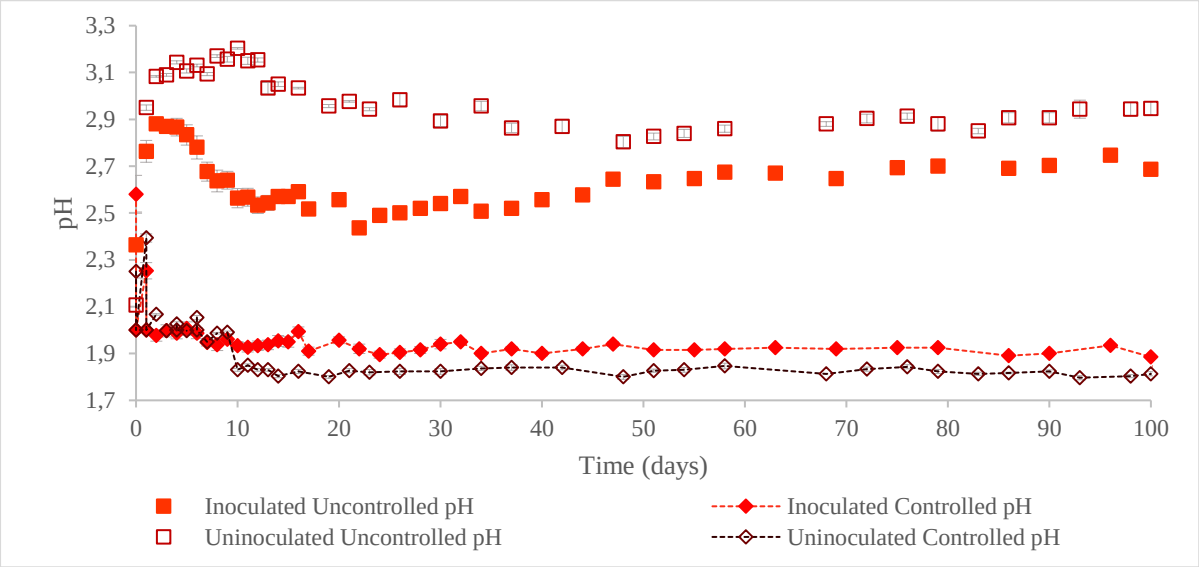

Figure 39 pH profile of Witbank coal slurry under biokinetic batch shake flask test conditions

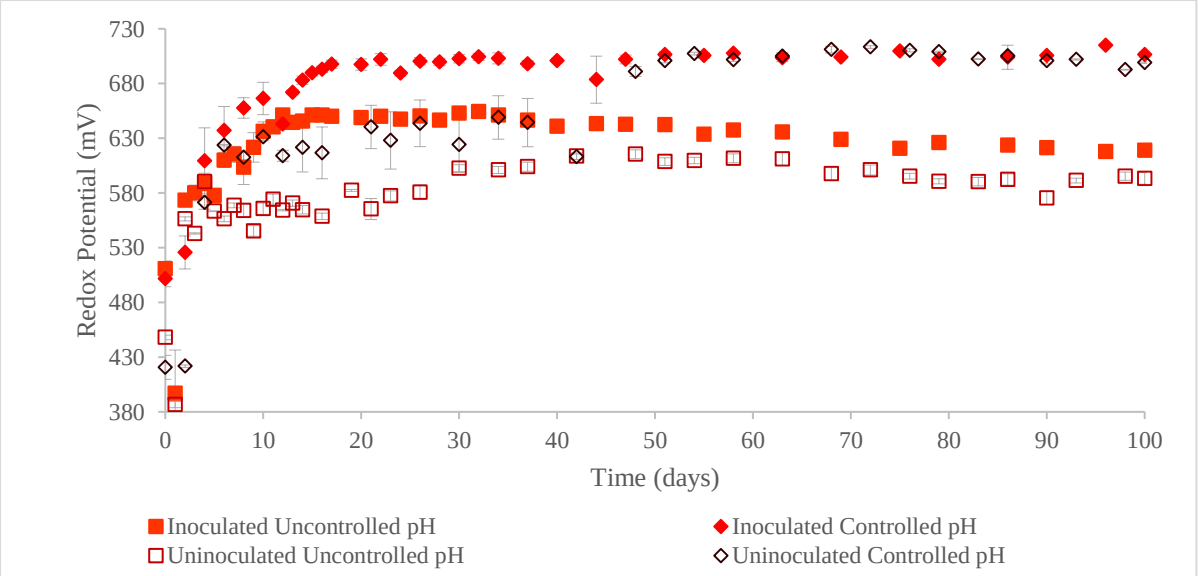

Figure 40 Redox profile of Witbank coal slurry under biokinetic batch shake flask test conditions

Witbank Coal Discards

Results show this sample to be strongly acid-forming under all the tests conditions as shown by pH values below 2 and high redox values above 680 mV in Figure 41 and Figure 42 respectively. Initially,

the pH increased slightly from the start of the experiments, signifying little acid neutralization capacity by fast weathering minerals. Then pH decreased to below 2 at the onset of acid-forming reactions; faster in the inoculated flasks than the un-inoculated flasks (after 4-6 days compared to 7-12 days). The pH decreased faster under controlled pH compared to un-controlled pH tests. This was possibly due to higher cell concentration in the inoculated flasks than in un-inoculated flasks. The slight pH increases at irregular intervals after day 20 in all the conditions indicate low acid neutralisation by moderate and slow weathering acid neutralizing minerals.

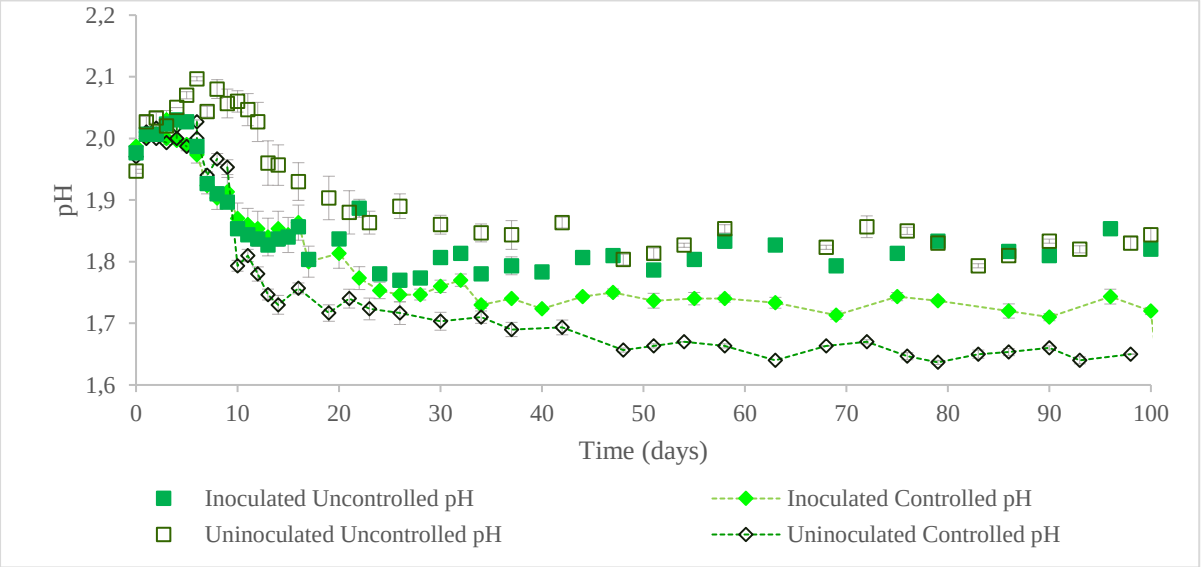

Figure 41 pH profile of Witbank coal discards under biokinetic batch shake flask test conditions

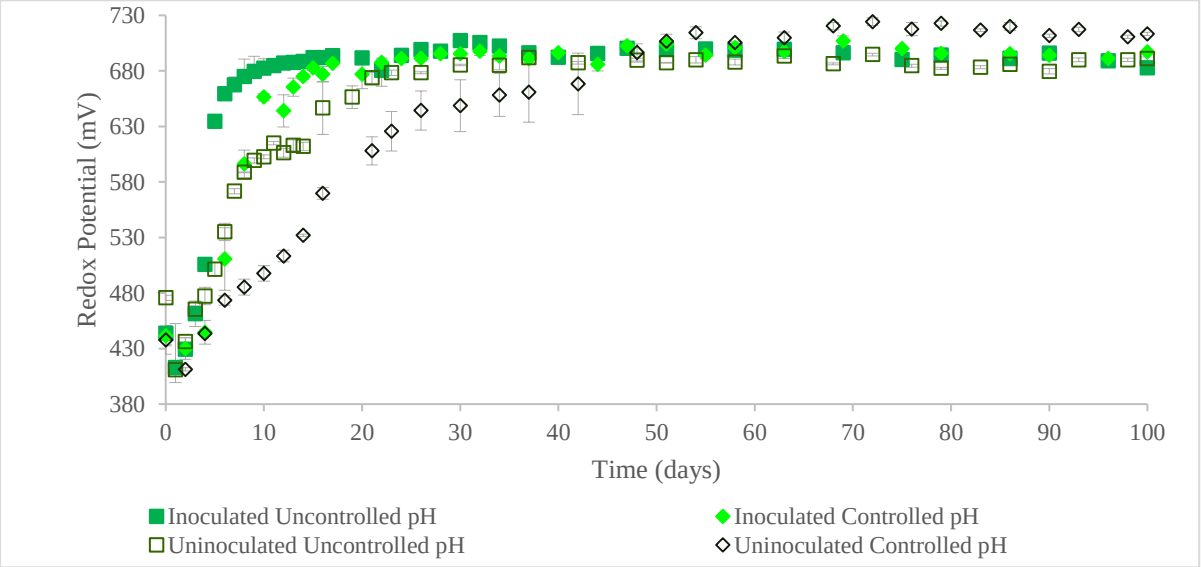

Figure 42 Redox profile of Witbank coal discards under biokinetic batch shake flask test conditions

5.1.4. ANC and Total Sulphur of Biokinetic Residues

After the biokinetic tests, the residues were washed with deionised water then dried before determining total sulphur by Leco analysis and conducting the static ANC tests. The comparison results of the total sulphur and ANC of the feed and the residues are presented in Table 38. The results show that between 67-98 %, 23-30 % and 12-15 % of the initial sulphur content of Waterberg coal slurry, Witbank coal slurry and Witbank coal discards respectively still remained after 100 days of running the tests. The results also show that most of the sulphur in the residues of Waterberg coal waste remained under controlled pH biokinetic test conditions. On the other hand, the sulphur in the residues of Witbank coal wastes was mainly found in residues from controlled pH conditions.

Table 38 The ANC and total sulphur results on the Biokinetic tests' residues of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Sample	Feed Total S (%)	Residue Total S (%)	Reduction in Total S (%)	Feed ANC (kg H_2SO_4/ Ton)	Residue ANC (kg H_2SO_4/ Ton)	Reduction in ANC (%)
Inoculated uncontrolled pH Biokinetic test						
A	1.84 ± 0.08	1.24±0.02	32.61	102.30 ±1.10	69.62±2.60	31.95
B	1.06 ± 0.06	0.32±0.00	69.81	29.21 ±0.70	27.84±0.86	4.69
C	1.94 ± 0.08	0.29±0.01	85.05	29.10 ±1.11	27.09±0.77	6.91
Inoculated controlled pH Biokinetic test						
A	1.84 ± 0.08	1.81±0.01	1.63	102.30 ±1.10	41.09±5.45	59.83
B	1.06 ± 0.06	0.27±0.01	74.53	29.21 ±0.70	25.31±0.32	13.35
C	1.94 ± 0.08	0.26±0.02	86.60	29.10 ±1.11	24.79±3.08	14.81
Un-inoculated uncontrolled pH Biokinetic test						
A	1.84 ± 0.08	1.29±0.02	29.89	102.30 ±1.10	72.18±0.43	29.44
B	1.06 ± 0.06	0.31±0.02	70.75	29.21 ±0.70	23.07±2.22	21.02
C	1.94 ± 0.08	0.29±0.01	85.05	29.10 ±1.11	14.96±3.00	48.59
Un-inoculated controlled pH Biokinetic test						
A	1.84 ± 0.08	1.77±0.03	3.80	102.30 ±1.10	31.60±2.78	69.11
B	1.06 ± 0.06	0.24±0.02	77.36	29.21 ±0.70	25.20±2.26	13.73
C	1.94 ± 0.08	0.24±0.02	87.63	29.10 ±1.11	19.22±1.96	33.95

The ANC comparisons show that the acid neutralising capacity of Waterberg coal slurry depleted by between 29.4 % and 69.1 % from the initial 102.3 kg H_2SO_4/Ton with more of depletion for the controlled pH tests than the uncontrolled pH tests. The constant pH of 2 under controlled pH conditions would have promoted dissolution of acid neutralising minerals. However, for Witbank coal slurry, the ANC decrease was only between 4.7 % and 21.0 % with the least depletion observed for the inoculated controlled pH test condition. For Witbank coal discards, the ANC decreased by between 34.0 % and 48.6 % for the un-inoculated tests but only slightly (6.9 -14.8 %) for the inoculated conditions.

5.1.5. Comparison of the ARD Potential Results Determined by Different Methods

Different methods as discussed in the earlier sections of this chapter showed different results for the characterisation of the ARD potential of the coal processing wasters. The acid generation potential results are compared in Figure 43, while the acid neutralizing potential and net acid generating potential comparisons are shown Figure 44 and Figure 45.

Acid-producing Potential

The acid-producing capacity values (shown in Figure 43) differed from method to method but all the methods evaluated the Witbank coal discards to have the highest value. ABA and QEMSCAN based AP evaluated the Witbank coal slurry to have lower AP than the Waterberg coal slurry in contrast to the QXRD based AP which was vice-versa. As discussed in Section 5.1.2, the AP evaluated on the coal wastes is dependent on the accuracy of the sulphur speciation method and the mineralogy analysis. Assay reconciliations (see Section 4.7.) have shown the QXRD values for sulphur differed more widely from the chemical assays compared to QEMSCAN. Thus, the AP results also show the QXRD based results differed more from either QEMSCAN or ABA values and QXRD likely underestimated the pyrite content of all three coal wastes.

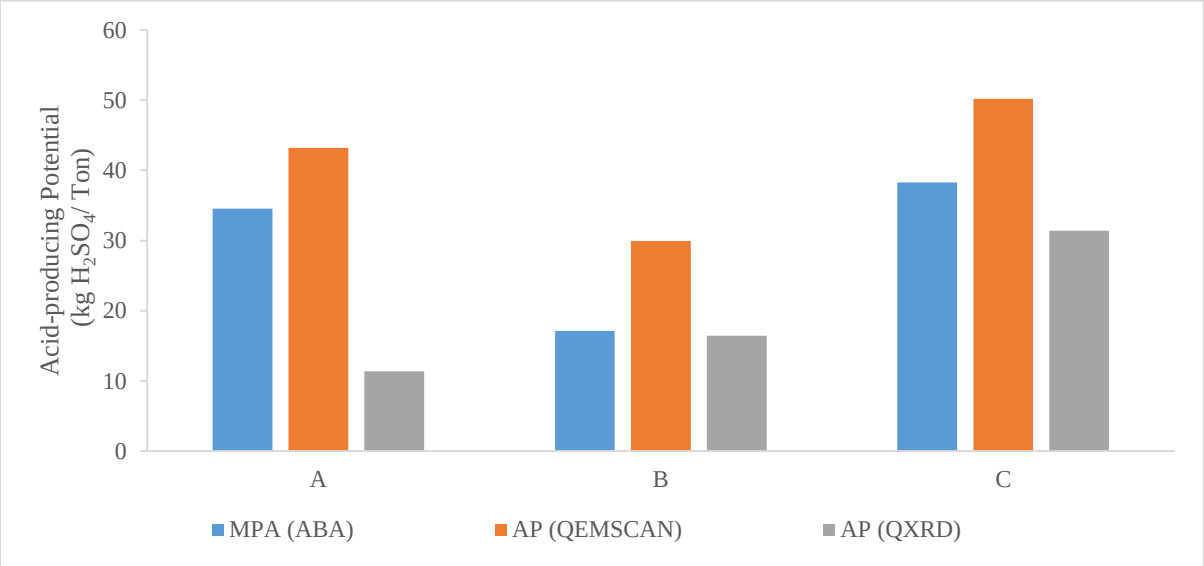

Figure 43 Comparison of acid generating capacity of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) determined by ABA and calculated ARD tests

Acid Neutralising Potential

The results in Figure 44 show the Waterberg coal slurry was evaluated by all the methods as having the highest acid neutralising potential but the results differ for the Witbank coal wastes depending on the test method. The biokinetic tests acid neutralizing potential, which was calculated as the difference between H_2SO_4 acid added to inoculated and non-inoculated samples under controlled pH test conditions (see Appendix C.1.4 for results), evaluated lower values compared to the other methods.

Since the biokinetic residues were found to have some ANC this indicates a possibility of slow weathering acid neutralising still remaining in the samples after the addition of H_2SO_4. As discussed in Section 5.1.2, the QEMSCAN possibly underestimated the NP minerals (possibly dolomite and/or calcite) in Waterberg and Witbank coal slurry wastes while QXRD possibly underestimated the acid neutralising silicates in the Witbank coal wastes (possibly slow weathering minerals such as feldspars). The accuracy of the mineralogy analysis hence affects the reliability of the theoretical acid neutralising potential.

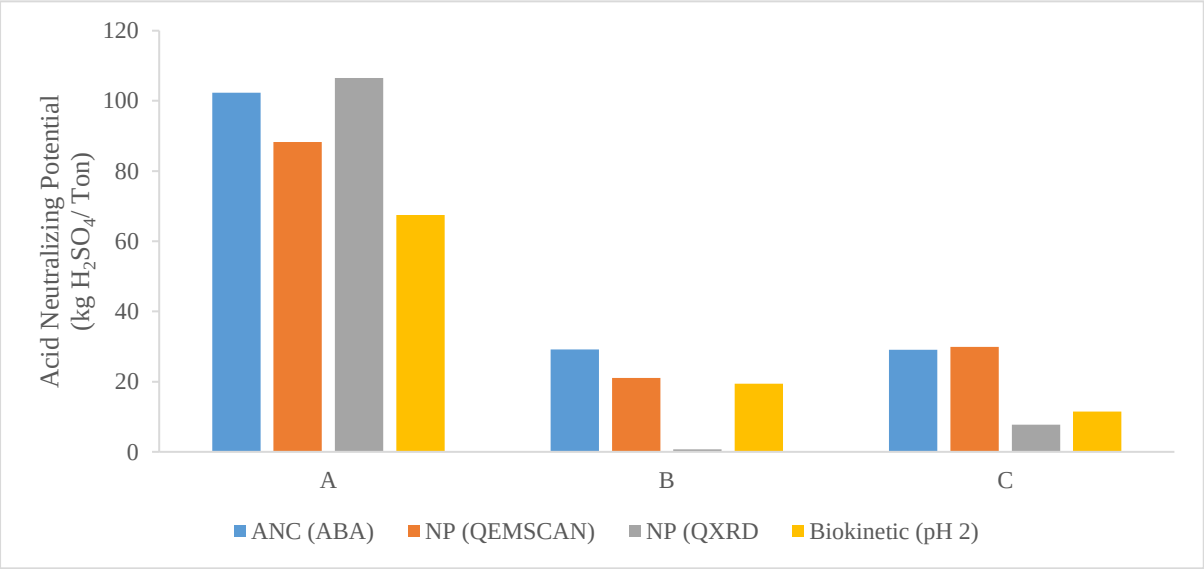

Figure 44 Comparison of acid neutralising potential of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) determined by biokinetic, ABA and calculated ARD tests

Net Acid-producing Potential

As presented in Figure 45, the methods consistently evaluated the NAPP of Waterberg coal slurry to be negative and Witbank coal discards to be positive. However, ABA differently evaluated the NAPP as negative for Witbank coal slurry but all the other methods classified it as positive. This could indicate the ABA is overestimating ANC for both Witbank coal slurry and discards. The aggressive ANC conditions may also have resulted in the dissolution of the slow reacting or even inert silicates resulting in an overestimation of the ANC. There is consistency with the evaluation of the NAPP of Witbank coal discards to be higher than the Witbank coal slurry which is also validated by the biokinetic tests pH profiles (Figure 39 and Figure 41). However, the static tests and the calculated mineralogy ARD tests neither take into consideration the relative rates of acid-forming and neutralization reactions when evaluating the net acid-producing potential.

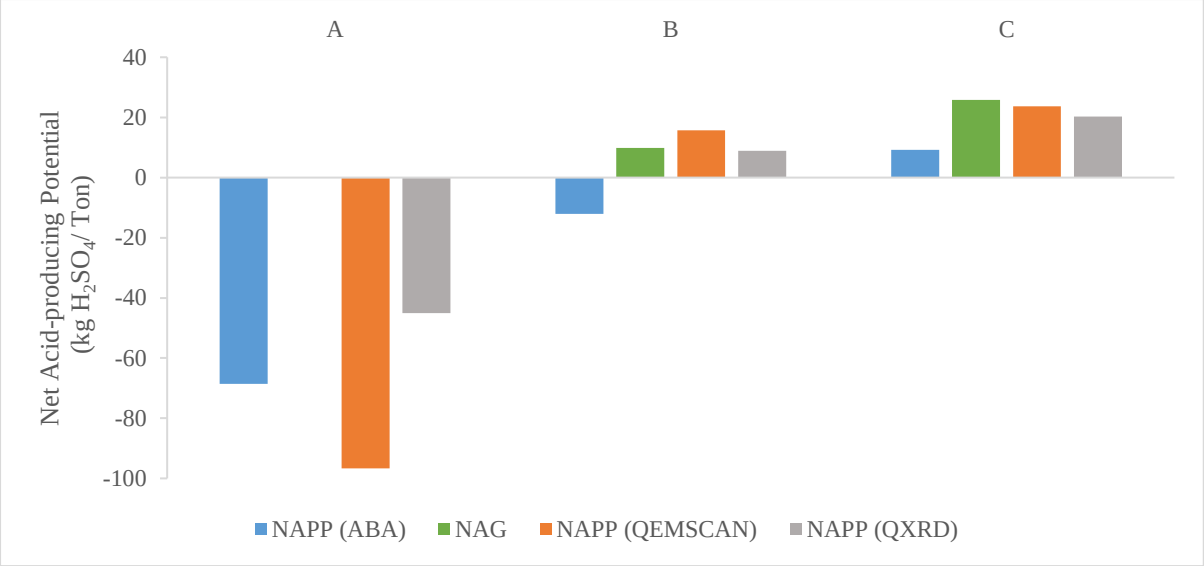

Figure 45 Comparison of net acid-producing potential of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) determined from ABA, NAG and calculated ARD tests

The ARD characterisation results by different methods on the same samples tested hypothesis 2 which states:

- The coal processing waste generated from different coalfields and processing operations in South Africa have the potential to cause environmental impacts of varying magnitudes from ARD and elevated concentration of toxic elements and salts owing to their different geochemical properties.

The results proved this hypothesis to be true as evidenced by the Waterberg sample being classified as NAF while the Witbank samples were PAF, but the evaluated acid generating capacity differed even for the two samples from the same geographical location. The ARD potential and time related behaviour was shown to be influenced by the mineralogy of the samples. However, the limitations of each ARD testing method caused uncertainty with classification of some samples and inconsistency with the magnitude of the ARD potential.

5.2. Elemental and Salinity Risk Assessment

The elemental and salinity risk potential of the coal processing wastes was characterised using the ranking and scoring methodology developed by Broadhurst and Petrie (2010). The first step in the ranking and scoring method was screening the hazard potential based on total concentration. This was followed by ranking and scoring the risk potential based on potentially available concentration (Broadhurst and Petrie, 2010). The potentially available concentration was determined from sequential chemical extractions (SCE), which were done according to the method developed at UCT (Broadhurst et al., 2009).

5.2.1. Hazard Potential

The hazard potential factors (HPFi) of the analysed elements were calculated on the basis of effect factors (EFi) and enrichment factors (EnFi). These factors were determined from total solid concentration (TCi), background concentration (BCi) and environmentally acceptable concentration (ARCi) in environmental indicators, water and soil (See Section 3.11.2 in Chapter 3 for equations). The hazard potential, effect and enrichment factors are shown in Table 39, Table 40 and Table 41 respectively, while the environmental significance of the elements in drinking water is shown in Table 42. The TCi, BCi and ARCi are presented in Appendix C.2.1.

Enrichment Factors (EnFi) for Total Concentrations

The results show the majority of the trace elements have EnFi above one indicating the elements are enriched in the coal waste samples relative to their average crustal abundance. The results show that the elements enriched in all three coal wastes to more than twice the relative crustal abundance are S, Se, Sb, Pb, Mo, As, U. In addition to these elements, Ba and Sn are also enriched to more than twice the crustal abundance in Waterberg coal slurry. In Witbank coal slurry, Ba and Th also exceed twice the crustal abundance. While in Witbank discards Cd, Th and Sn also enriched more than twice the crustal abundance.

Effect Factors (EFi) for Total Concentrations

The effect factors show that the majority of the analysed elements exceed the maximum required concentration in drinking water apart from Tm and Sn for Waterberg coal slurry. For Witbank coal slurry only Tb, Sn, Tm and Yb are below the maximum allowed concentration in drinking water. On the other hand, in Witbank coal discards only Tb and Tm are below the maximum allowed concentration in drinking water. However out of the 11 elements with a stipulated maximum allowed concentration in the soil guidelines (Department of Environmental Affairs, 2012), only S, Cr, Pb, Cu, and As in all the three coal wastes are in excess of the maximum allowed concentration.

Table 39 Hazard potential posed by major and minor elements of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) on drinking water determined from effect factor (EFi), enrichment factor (EnFi) and hazard potential factor (HPFi)

	Sample A			Sample B			Sample C		
	(EFi)	**(EnFi)**	**HPFi / 1000**	**(EFi)**	**(EnFi)**	**HPFi / 1000**	**(EFi)**	**(EnFi)**	**HPFi / 1000**
Major Elements									
Al	424207.61	0.52	219.45	696686.78	0.85	591.92	814692.20	0.99	809.42
Ca	854.32	0.55	0.47	185.57	0.12	0.02	13.50	0.01	0.00
Fe	121662.93	0.58	70.49	54503.85	0.26	14.15	58246.65	0.28	16.16
K	90.84	0.30	0.03	56.80	0.19	0.01	45.72	0.15	0.01
Mg	217.94	0.23	0.05	39.30	0.04	0.00	12.15	0.01	0.00
S	110.26	131.26	14.47	63.52	75.62	4.80	116.25	138.40	16.09
Si	26638.03	0.49	13.14	21040.79	0.39	8.20	44132.38	0.82	36.07
Ti	485.85	0.37	0.18	922.71	0.70	0.65	1175.36	0.89	1.05
Minor Elements									
Ba	1040.00	3.06	3.18	1084.27	1.08	1.18	351.72	0.35	0.12
Mn	11863.00	0.54	6.40	2059.01	0.09	0.19	848.81	0.04	32.75
Na	1.50	0.01	0.00	1.21	0.01	0.00	-	-	-
P	26.53	0.13	0.00	188.50	2.77	0.52	55.96	0.82	46.06
Sr	22.62	0.44	0.01	68.69	1.34	0.09	17.33	0.34	5.84
***Zr**	n/a	1.24	n/a	n/a	1.91	n/a	n/a	2.77	n/a

* *Maximum allowed concentration not found in drinking water guidelines* (Department of Water Affairs and Forestry, 1996; IRMA, 2016; Mamba et al, 2008)

Table 40 Hazard potential posed by trace elements of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) on drinking water determined from effect factor (EFi), enrichment factor (EnFi) and hazard potential factor (HPFi)

Element	Sample A			Sample B			Sample C		
	(EFi)	(EnFi)	HPFi /1000	(EFi)	(EnFi)	HPFi /1000	(EFi)	(EnFi)	HPFi /1000
As	786.00	3.74	2.94	449.00	2.14	0.96	693.50	3.30	2.29
***Bi**	n/a	16.74	n/a	n/a	9.70	n/a	n/a	31.44	n/a
Cd	56.60	1.89	0.11	12.60	0.42	0.01	59.90	2.00	0.12
Ce	53.92	0.90	0.05	90.35	1.51	0.14	72.13	1.20	0.09
Co	159.20	0.53	0.08	121.25	0.40	0.05	61.20	0.20	0.01
Cr	1642.00	0.59	0.96	1750.00	0.63	1.09	3997.30	1.43	5.71
***Cs**	n/a	1.97	n/a	n/a	1.97	n/a	n/a	1.88	n/a
Cu	32.75	0.48	0.02	34.85	0.51	0.02	42.72	0.63	0.03
Dy	6.05	0.98	0.01	5.96	0.96	0.01	5.32	0.86	0.00
Er	3.22	1.07	0.00	3.46	1.15	0.00	3.26	1.09	0.00
Eu	1.11	0.62	0.00	1.27	0.71	0.00	1.03	0.57	0.00
***Ga**	n/a	0.69	n/a	n/a	1.02	n/a	n/a	1.05	n/a
Gd	6.11	1.17	0.01	5.92	1.14	0.01	4.87	0.94	0.00
***Ge**	n/a	1.55	n/a	n/a	2.31	n/a	n/a	-	n/a
***Hf**	n/a	1.31	n/a	n/a	1.99	n/a	n/a	3.16	n/a
Ho	1.17	0.97	0.00	1.25	1.04	0.00	1.14	0.95	0.00
***In**	n/a	0.54	n/a	n/a	0.50	n/a	n/a	1.74	n/a
La	25.57	0.75	0.02	44.12	1.30	0.06	34.08	1.00	0.03
****Lu**	0.44	n/a	n/a	0.49	n/a	n/a	0.49	n/a	n/a
Mo	67.70	3.08	0.21	57.50	2.61	0.15	163.90	7.45	1.22
***Nb**	n/a	0.83	n/a	n/a	1.23	n/a	n/a	1.46	n/a
Nd	25.70	0.78	0.02	35.25	1.07	0.04	26.84	0.81	0.02
Ni	1707.50	0.38	0.65	1552.50	0.35	0.54	1452.50	0.32	0.47
Pb	2605.50	2.61	6.79	2299.50	2.30	5.29	3323.50	3.32	11.05
Pr	6.27	0.72	0.00	9.20	1.06	0.01	7.44	0.86	0.01
***Rb**	n/a	0.54	n/a	n/a	0.33	n/a	n/a	0.30	n/a
Sb	166.85	8.34	1.39	114.75	5.74	0.66	88.25	4.41	0.39
Sc	16.20	0.62	0.01	14.48	0.56	0.01	12.28	0.47	0.01
Se	33.38	26.70	0.89	31.13	24.90	0.78	38.75	31.00	1.20
Sm	6.47	1.08	0.01	7.05	1.17	0.01	5.23	0.87	0.00
Sn	0.91	2.07	0.00	0.67	1.52	0.00	1.15	2.60	0.00
***Ta**	n/a	0.49	n/a	n/a	0.88	n/a	n/a	1.08	n/a
Tb	0.97	1.03	0.00	0.94	1.00	0.00	0.85	0.91	0.00
Te	-	-	-	-	-	-	-	-	-
Th	47.21	1.79	0.08	88.25	3.35	0.30	88.31	3.36	0.30
Tl	101.75	0.38	0.04	40.00	0.15	0.01	111.50	0.42	0.05
Tm	0.45	1.01	0.00	0.50	1.11	0.00	0.50	1.12	0.00
U	191.75	2.13	0.41	271.25	3.01	0.82	237.25	2.64	0.63
V	805.50	0.42	0.34	692.00	0.36	0.25	591.45	0.31	0.18
Y	31.74	1.09	0.03	33.20	1.14	0.04	29.33	1.01	0.03
Yb	2.87	1.03	0.00	0.17	0.06	0.00	3.47	1.24	0.00
Zn	16.05	1.02	0.02	6.43	0.41	0.00	10.10	0.64	0.01

** Maximum allowed concentration not found in drinking water guidelines* (Department of Water Affairs and Forestry, 1996; Mamba et al., 2008; IRMA, 2016)

***Background concentration not found from crustal abundance ("Abundance in Earth's Crust". WebElements.com*

Table 41 Hazard potential posed by major, minor and trace elements of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) on soil determined from effect factor (EFi), enrichment factor (EnFi) and hazard potential factor

	Sample A			Sample B			Sample C		
	*(EFi)	(EnFi)	HPFi / 1000	(EFi)	(EnFi)	HPFi / 1000	(EFi)	(EnFi)	HPFi / 1000
Major Elements									
SO_4^{2-}	13.78	131.26	1.81	7.94	75.62	0.60	14.53	138.40	2.01
Minor Elements									
Mn	0.80	0.54	0.00	0.14	0.09	0.00	0.06	0.04	0.00
Trace Elements									
As	1.36	3.74	0.01	0.77	2.14	0.00	1.20	3.30	0.00
Cd	0.04	1.89	0.00	0.01	0.42	0.00	0.04	2.00	0.00
Co	0.05	0.53	0.00	0.04	0.40	0.00	0.02	0.20	0.00
Cr	12.63	0.59	0.01	13.46	0.63	0.01	30.75	1.43	0.04
Cu	2.05	0.48	0.00	2.18	0.51	0.00	2.67	0.63	0.00
Ni	0.38	0.38	0.00	0.34	0.35	0.00	0.32	0.32	0.00
Pb	1.30	2.61	0.00	1.15	2.30	0.00	1.66	3.32	0.01
V	0.54	0.42	0.00	0.46	0.36	0.00	0.39	0.31	0.00
Zn	0.33	1.02	0.00	0.13	0.41	0.00	0.21	0.64	0.00

* *Based on maximum allowed concentration in soil guidelines* (Department of Environmental Affairs, 2012)

Hazard Potential Factors and Environmental Significance for Total Concentrations

The elements in all three coal processing wastes which had HPFi exceeding 10 and ranked to pose high environmental significance in drinking water were evaluated to be Al and Fe. In addition, Si and S in both Waterberg coal slurry and Witbank discards also had HPFi of high environmental significance on drinking water basis. Ba and Pb also had HPFi of potential high environmental significance in Witbank discards. The results also show the trace elements; As, Sb, Cr, P, Mo, U, V, Cd, Ti, Se, Sb, Th, Ce, Ba, Pb and Cd in the three coal wastes to have HPFi between 0.1 and 10; high enough to pose low to moderate environment significance on drinking water bodies. The only major and minor elements with the potential to be of either moderate or low environmental threat to drinking water bodies were P, Si, Ca and Mn. The rest of the elements had low HPFi (below 0.1) and their potential environmental significance to drinking water bodies was ranked as non-strategic. On the other hand, only S in the three coal wastes had HPFi exceeding 0.1 and ranked as potentially posing a low-moderate environmental significance to soils. These hazard potentials are based on total concentration and do not account for bioavailability.

Table 42 Ranking of analysed elements of potential environmental significance in terms of water pollution on the basis of hazard potential A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) on drinking water based on maximum concentration

Environmental significance	(HPFi)/ 1000	Sample A	Sample B	Sample C
Very high	>10 000			
High	A:1 000 – 10 000 B: 100 – 1 000 C: 10 - 100	Al Fe, S, Si	Al Fe	Al Ba, Si, Fe, S, Pb
Moderate	1 - 10	Pb, Mn, Ba, As, Sb, Cr	Si, Pb, S P, Cr	Sr, Cr, As, Mo, Se, Ti
Low	0.1 - 1	Se, Ni, Ca, U, V, Mo, Ti, Cd,	As, U, Se, Sb, Ti, Ni, Pb, Ba, Th, V, Mn, Mo, Ce	U, Ni, Sb, Th, V, Cd
Non-strategic	< 0.1	Co, Th, Mg, Ce, Tl, K, Y, Nd, Zn, La, Cu, Sr, Sc, Sm, Gd, Dy, P, Sn, Pr, Yb, Er, Ta, Eu, Ho, Tm, Na, W, Te	Sr, La, Co, Y, Nd, Ca, Cu, K, Pr, Sc, Sm, Gd, Dy, Tl, Cd, Er, Zn, Mg, Tm, Ho, Tb, Eu, Yb, Na, Te	Ce, Tl, La, Y, Cu, Nd, Co, K, Sc, Zn, Pr, Sm, Gd, Dy, Er, Yb, Sn, Eu, Tb, Ho, Tm, Mg, Ca

5.2.2. Element Partitioning and Availability

As discussed in Chapter 2, sequential chemical extractions (SCE) can provide an indication of the availability of elements for release from solids under certain leaching conditions. They can also provide an indication of the potential forms and associations of elements, thus complimenting and validating the mineralogical analysis. The SCE partitioned the elements into seven fractions and the concentration of elements in each fraction was quantified by analytical techniques as detailed under Section 3.11.1 in Chapter 3. Mass balance calculations (presented in Appendix C.2.2.) showed element recoveries of between 90% and 110 % for the majority of the elements in all three coal wastes. The extracting environments were grouped into neutral (stage 1-2), acidic (1-5) and oxidising (1-6) conditions to represent the amount potentially extracted by water leach, acidic leach and oxidising leach conditions. These leach conditions can exist under various stages of the dump.

Partitioning of Elements

The SCE was done in 7 successive stages and the phase targeted in each fraction (F) are; F1-water-soluble fraction, F2-exchangeable fraction, F3-carbonate fraction, F4-amorphous Fe-oxide fraction, F5-crystalline Fe-oxide fraction, F6-organics and sulphides, F7-residual fraction. The results for major and minor elements partitioning are presented in Figure 46 and Figure 47 while the trace elements partitioning results are presented in Figure 48 and Figure 49. The results show each element had a unique partition pattern and that the same elements from different samples exhibited different leaching behaviour resulting in different partitioning patterns and/or different weight percent of the element extracted in each fraction.

Major Elements

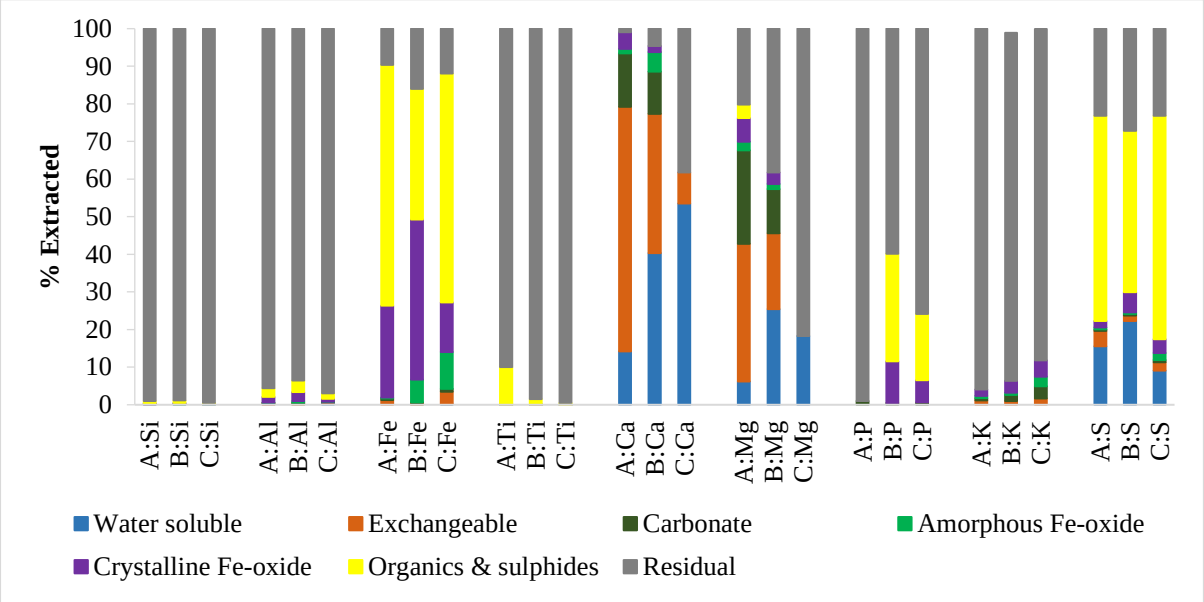

Figure 46 Partitioning of major elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) by sequential chemical extraction

Silicon, Aluminium, Titanium and Potassium

The majority (above 90 %) of Si, Al, Ti and K were partitioned as the residual phase in all three coal wastes. This indicates the elements are encapsulated within inert minerals thus are likely not released for a considerable long length of time under normal environmental conditions (Tessier et al., 1979). According to the mineralogy deportment of major elements (presented in Section 4.6.1 in Chapter 4), the major Si and Al hosting phases are kaolinite and quartz, while Ti is solely hosted in rutile. The mineralogy deportment also showed K-feldspar to be the source of K partitioned in the residual phase. The small quantities of Si, Al, Ti and K reporting in phases other than residual could be from elements bound to clays, carbonates, organic and oxides phases.

Calcium and Magnesium

The results show 14.2 %, 40.3 % and 53.6 % of the Ca in Waterberg coal slurry, Witbank coal slurry and Witbank coal slurry was found to be partitioned in the water-soluble while 65.0 % 37.0 %, and 8.2 % was partitioned in the exchangeable fraction. Similarly, 6.2 %, 25.4 % and 18.3 % of the Mg in Waterberg coal slurry, Witbank coal slurry and Witbank coal slurry was found to be partitioned in the water-soluble while 36.6 %, 20.1 % and 0.0% partitioned in the exchangeable fraction. The results also show the Waterberg and Witbank coal slurry wastes to have 14.2 % and 11.2 % of Ca respectively as well as 24.9 % and 11.8 % of Mg respectively in the carbonate fraction while none was partitioned in the carbonate fraction of Witbank coal discards. However, the results show Witbank coal discards to have higher proportions; 38.3 % and 81.7 % of the Ca and Mg in the residual phase compared to the Waterberg and Witbank coal slurry wastes which had 1 % and 2% Ca as well as 20.2 % and 38.2 % Mg

partitioned in the residual phase. Elements expected in the water-soluble fraction are those contained in water-soluble phases which according to the mineral characterisation in Section 4.6.1 in Chapter 4 are gypsum and epsomite. According to literature, elements in the water-soluble fraction can also be released from the dissolution of tertiary phases mobilised by drying and evaporation of pore water (Hall et al., 1996). The source of the Ca and Mg in the exchangeable fraction was possibly the simple oxides formed from partial weathering of carbonates. The partitioning of Mg and Ca in the carbonates fraction fits with the mineralogy deportment showing Mg and Ca deported in the carbonates; calcium and dolomite in the coal slurry wastes but none in the coal discards. According to QXRD deportment, the possible source of residual Mg in the discards is mica.

Iron and Sulphur

The results show a significant portion of the Fe (64.0 % 34.7 % and 61.3 %) and S (54.6 %, 43.0 % and 59.4 %) to be contained in the organic/ sulphide mineral fraction in the Waterberg coal slurry, Witbank coal slurry and Witbank coal discards respectively. However, for Witbank coal slurry the largest portion of Fe (42.6 %) and S (53.0 %) was partitioned in the crystalline Fe-Oxide fraction. The results also show 9.7 %, 16.1 % and 11.4 % of the Fe as well as 23.2 %, 27.1 % and 23.2 % of the S to be partitioned in the residual phase of the Waterberg coal slurry, Witbank coal slurry and Witbank coal discards respectively. Only small amounts (<10 %) of both elements were partitioned in the exchangeable, carbonates and amorphous oxides. While 15.5 %, 22.3 % and 9.1 % of the S and none of the Fe in the Waterberg coal slurry, Witbank coal slurry and Witbank coal discards was partitioned in the water-soluble fraction. From the mineralogy deportment and chemical sulphur speciation (see Section 4.4.1 and 4.6.1) the majority source of the Fe and S was determined to be pyrite and some of the sulphur was shown to exists in the sulphates, coal and carbominerite. Possible sources of the water-soluble S are likely soluble sulphates including gypsum, epsomite and melanterite which easily disintegrate by dissolution or oxidation upon interaction with water (Dang et al., 2002; Ward, 2002). From the mineralogy results in Section 4.6.1, the source of Fe-Oxides is likely Fe-oxyhydroxides and jarosite which is consistent with literature stating hydrous oxides of Fe as a possible source of Fe in the amorphous Fe-oxide fraction (Hall et al., 1996).

Phosphorus

The results show the majority (99%, 60% and 75.4 %) of the P in Waterberg coal slurry, Witbank coal slurry and Witbank coal discards respectively to be in the residual phase. The results also show significant amounts of the phosphorus to exist in the organic/ sulphide fraction as well as the crystalline oxide fraction in the Witbank coal wastes. According to Dang et al. (2002), the possible reason for elements existing in the crystalline oxide is the adsorption and complexing by Fe-oxyhydroxides colloids of elements from the decomposition of sulphides and oxidation of organic matter. The results imply that the majority of the P is bound in phases likely not released for a considerable long length of time under normal environmental conditions (Tessier et al., 1979)

Minor Elements

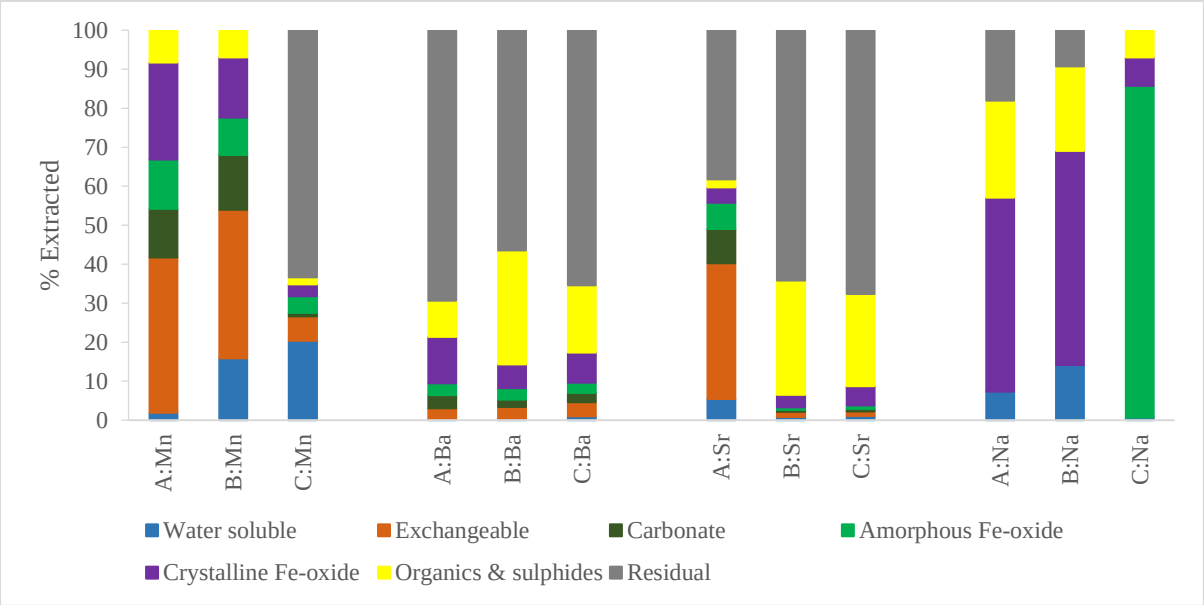

Figure 47 Partitioning of minor elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) by sequential chemical extraction

Manganese

The results show the highest proportion (39.7 % and 38.1 %) of the Mn in the Waterberg and Witbank coal slurry wastes to be in the exchangeable fraction but the majority in the Witbank coal discards; 63.4 % was in the residual. Amounts ranging from 0-24.9 % of the Mn was partitioned in the other phases of the coal wastes but none in the residual phase of the coal slurry wastes. The presence of Mn in the water and ion-exchangeable fractions of the three coal wastes indicate the presence of Mn as readily available salts such as sulphates and possibly chlorides. Mn was also found present in all three coal wastes as acid soluble organics, sulphides, carbonates (probably rhodochrosite) and oxides. On the other hand, the majority of the Mn in the Witbank discards found to occur in the residual phase is associated with inert silicates such as kaolinite, quartz that likely formed the residual phase.

Sodium

Just like Mn, the Na partitioning patterns in the two coal slurry wastes were similar but different from the discards. The majority (49.8 % and 54.9 %) of the Na in the Waterberg and Witbank coal slurry wastes respectively, was found to be in the crystalline Fe-Oxide phase. Another 24.9 % and 21.7 % of the Na in Waterberg and Witbank coal slurry wastes respectively reported to the organic and sulphides fraction, and the remainder in the residual and water-soluble fractions. On the other hand, 85.1 % of the Na in the Witbank discards was partitioned in the amorphous Fe-Oxide fraction, with 7.3 % and 7.0 % occurring in the crystalline Fe-Oxide and the organic and sulphides fractions respectively. According to the literature, Na extracted in the amorphous Fe-Oxide phase are associated with hydrous oxides of Al, Fe and Mn which are thermodynamically unstable oxides whose extraction is dependent on pH and

redox potential (Gleyzes et al., 2002; Hall et al., 1996; Tessier et al., 1979). The Na extracted in the crystalline Fe-Oxide phase was possibly associated with less reactive oxides extracted under stronger reducing conditions compared to the preceding stage. Goethite, hematite, limonite and chromite are the dominant Fe-oxyhydroxides in the coal processing wastes according to mineralogy results (Section 4.5 in Chapter 4). Sources of water-soluble Na could be water-soluble salts such as gypsum and epsomite.

Barium and Strontium

Ba and Sr had a similar partitioning pattern with the highest proportions of Ba (69.4 %, 64.2 % and 65.4 %) and Sr (38.3 % 64.2 % and 67.7%) hosted in the residual phase. In addition to the residual phase, a significant portion; 34.8 % of the Sr was found to exist in the exchangeable phase of Waterberg coal slurry. Significant amounts of Ba (29.3 % and 17.2 %) and Sr (29.3 % and 23.6%) in the Witbank coal slurry and discards respectively were partitioned in the organic and sulphide phase. All the three coal wastes had less than 12 % of water-soluble, carbonates, amorphous and crystalline Fe-Oxide phases. These results indicate most of the Ba and Sr in the three-coal waste except forzs Sr in Waterberg coal slurry exist in the residual phase which is considered to be unavailable under environment conditions (Tessier et al., 1979).

Trace Elements

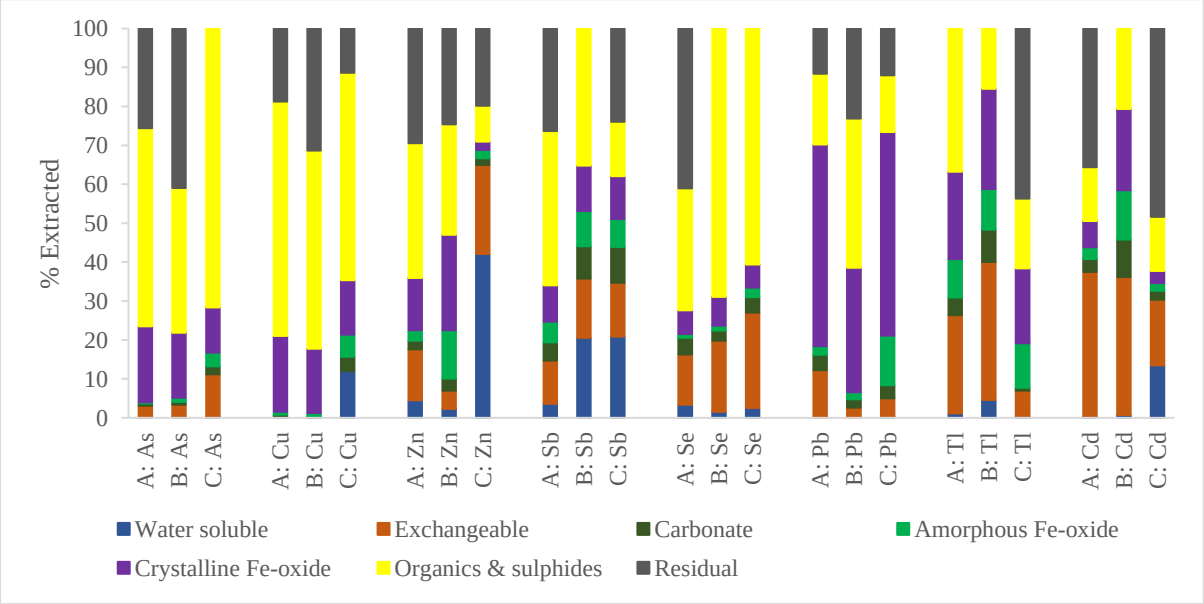

Figure 48 Partitioning of chalcophilic trace elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) by sequential chemical extraction

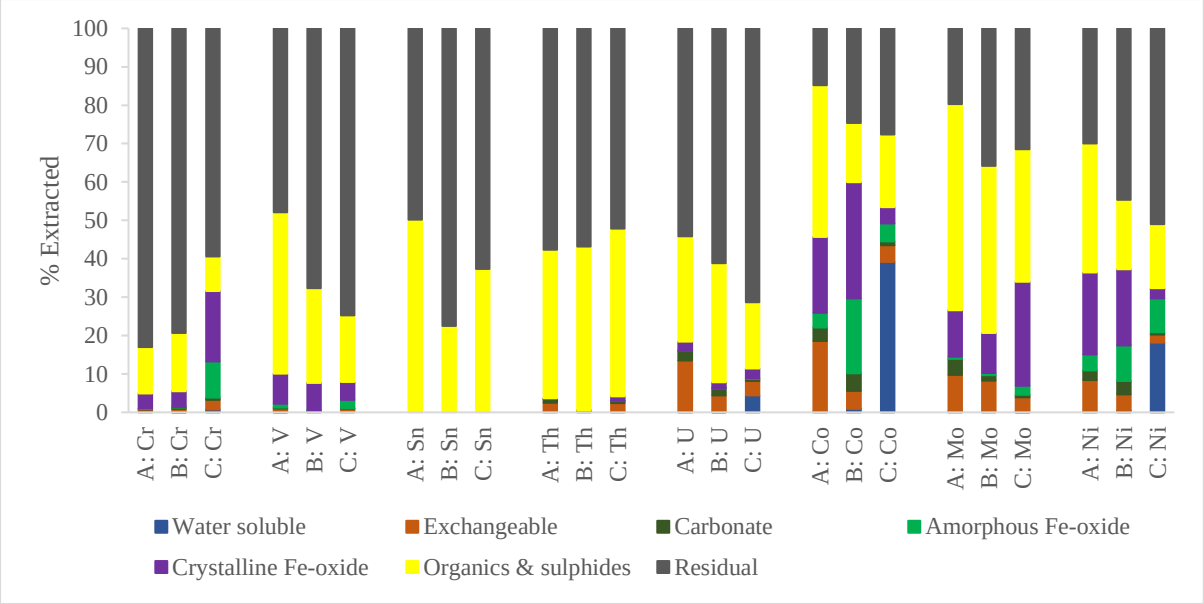

Figure 49 Partitioning of lithophilic and siderophile trace elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) by sequential chemical extraction

Chalcophilic Trace Elements

The chalcophiles As, Cu, Zn, Sb, Se, Pb Tl and Cd were found distributed in all fractions and in various proportions. Of this group elements such as As, Cu, Ni, Mo and Se had the highest proportion (31.3-71.6 %) deported to the organic/sulphide and to a lesser extent (11.4-41.1%) in the residual phases, with small amounts (5.9-19.5 %) reporting to the iron oxide fractions particularly the crystalline Fe-Oxide phase. The distribution of elements such as Zn and Sb tended to be more evenly distributed across the different fractions including the organic/sulphide, oxide, exchangeable and even water-soluble fractions. The Waterberg and Witbank coal slurry wastes had the highest proportion of Sb (39.6 % and 35.2 %) and Zn (34.6 % and 28.4%) in the organics and sulphide phase while 42.1 % and 23.9 % of the Zn and Sb were partitioned in the water-soluble phase for Witbank discards. In the case of Zn, this is consistent with the more amphoteric nature of the element which typically occurs as both more reactive oxides and stable sulphides. A notable exception is Pb, in which 51.8 %, 32.0 % and 52.3 % in Waterberg coal slurry, Witbank coal slurry and discards respectively, deported to the iron oxide fraction. On the other hand, the highest proportion of Cd in Waterberg coal slurry and Witbank coal discards (35.6 % and 48.4 %) was partitioned in the residual phase but in the Witbank coal slurry, it was deported in the crystalline Fe-Oxide phase (20.9 %) and organics/sulphide (20.7 %). Another exception is Tl which had the highest proportion reporting to the organic and sulphide phase (36.7 %) in Waterberg coal slurry, exchangeable (35.4 %) phase in Witbank coal slurry and residual phase (43.7 %) in the Witbank coal discards. These results indicate significant amounts of the chalcophiles are potentially available under mild, acidic and oxidising leach conditions

Lithophilic Trace Elements

The results in Figure 49 show the elements Cr, V, Sn, U and Th to be reporting mainly to the residual fraction and organics and sulphides fraction. Cr was found in all coal wastes partitioned mainly (59.4-83.0%) in the residual phase with less than 10 % existing in each of the remaining phases except 12.1 % and 15.1 % in the organics and sulphide phase of the coal slurry wastes and 18.3 % in the crystalline oxide of the Witbank discards. Although the highest proportion of V (47.9-74.8 %), Sn (49.8-77.5 %), U (54.1-74.8 %) and Th (52.1-57.7 %) was found partitioned in the residual phase significant amounts (17.3-42.0 %, 22.5-50.2 %, 17.3-30.9 % and 38.7-43.7 %) are associated with the organics and sulphide fraction in all the coal wastes. While small quantities (>10 %) of the elements are associated with the other fractions. These results indicate that these trace elements are mainly hosted by the relative inert silicates such as kaolinite and quartz, K-feldspars and possibly amphiboles.

Siderophile Trace Elements

The siderophile elements Co, Mo and Ni (shown in Figure 49) tended to partition more into the organics and sulphide fraction as well as the residual fraction. Significant amounts of the elements also reported in the Fe-oxides, exchangeable and water-soluble fractions. In Waterberg coal slurry, the larger proportion of Co, Mo and Ni reported to the organics and sulphide (39.6 %, 53.7 % and 33.6 %) fraction while 12.1- 21.3% reported in the crystalline Fe-Oxide fraction and 14.8-29.9 % reported in the residual fraction. The highest proportion of Co partitioned in the crystalline Fe-Oxide phase (30.3 %) in Witbank coal slurry and water-soluble phase (39.2 %) in the Witbank coal discards. Significant proportions of the Co amounting to 24.6-27.7 % and 15.4-18.9 % was found to exist in the residual and organics/sulphide fractions (respectively) of the Witbank coal wastes. On the other hand, the Mo in the Witbank coal slurry and discards was found to partition more (43.5 % and 34.5 %) in the organics and sulphide fraction and to a lesser extent (35.8 % and31.5 %) in the residual fraction. Only 10.1 % and 27.1 % of the Mo in the Witbank coal wastes reported in the crystalline Fe-Oxide phase. However, the highest proportion of Ni (44.7 % and 50.9 %) reported in the residual phase for the Witbank coal slurry and discards respectively, while less than 20 % reported in each of the remaining fractions. These results indicate most of the siderophile elements can be extracted under oxidising leach conditions although significant amounts in the residual fraction are regarded unavailable.

Element Availability under Leach Conditions

In Section 5.2.1 the hazard potentials were determined based on the total concentrations of elements in the solid samples. However, as demonstrated by the results of the SCE tests, many of these elements either occurred as or were associated with relatively inert phases and may thus not be available for release to the environment, depending on the environmental conditions. Concentration levels of potentially available elements have hence been calculated from the results of the SCE tests under neutral or mild leaching conditions (accumulated amount reporting to fractions 1 and 2), acid leach conditions (accumulative amount reporting to fractions 1-5) and oxidising leach conditions (accumulative amount

reporting to fractions 1-6). The total concentration for some trace elements for stages 1-6 calculated as a difference between total solid concentration and stage 7 concentration are presented in Appendix C.2.2. The concentration reporting to fraction 7 (residual) was considered inert and not available for release to the environment. The results for the potentially available concentration of analysed major and minor elements are presented in Table 43 while the trace elements are presented in Table 44. It is important to note that some trace elements analysed by ICP-MS and ICP-OES in stages 1-6 (i.e. Be, Li, Hg and B) could not be analysed by WDXRF and LA-ICP-MS in stage 7. Some elements were also analysed by LAICP-MS in stage 7 but not analysed in stages 1-6 by ICP-MS and the elements are Cs, Ce, Cs, Dy, Eu, Er, Ga, Ge, Gd, Hf, Ho, In, La, Lu, Nd, Pr, Rb, Sc, Sm, Tb, Ta, Tm, Y, and Yb.

Major and Minor Elements

The accumulated available concentrations in Table 43 show the total concentration of elements generally increasing from neutral, acidic and oxidising leach conditions with some elements increasing to a greater extent than others. The potentially available concentrations of S and Fe are shown to be relatively high under all conditions for all waste samples, but particularly under oxidising conditions. Ca was found to be also very high (18540-23187 mg/kg) while Mg was significantly high (2318-4327 mg/kg) under all conditions for Waterberg sample, which had a relatively high Ca and Mg content in comparison to the Witbank coal wastes (as shown in Section 4.6.2 in Chapter 4). Despite their high total concentration levels, the available concentrations of Al and Si, although still significant (24-4013 mg/kg), were relatively low for the three coal wastes as these elements were found to be mainly associated with inert phases (see Figure 46). Similarly, the elements P, K, Ti, Ba and Sr which were shown to be mainly in the residual phase (see Figure 46 and Figure 47) were found to be only available in relatively low concentrations under all leach conditions for all coal wastes.

Table 43 Potentially available concentration of major and minor elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C(Witbank coal discards) under neutral, acid and oxidising leaching conditions

	Sample A			Sample B			Sample C		
	Neutral leach	Acid leach	Oxidising leach	Neutral leach	Acid leach	Oxidising leach	Neutral leach	Acid leach	Oxidising leach
Major elements in mg/ kg									
Al	165.98	899.47	1878.47	216.97	2122.61	4013.61	556.77	1203.32	2311.07
Ca	18539.75	23186.65	23186.65	4236.20	5225.87	5225.87	252.33	252.33	252.33
Fe	437.25	8966.81	30744.31	75.84	7575.60	12918.10	598.32	4625.37	14985.37
K	85.13	283.66	283.66	80.50	282.12	282.12	45.04	303.83	303.83
Mg	2317.80	4132.76	4326.81	623.74	845.45	845.45	84.03	84.03	84.03
S	10818.88	12271.72	42346.65	7549.83	9499.09	23144.05	6557.01	10110.20	44642.06
Si	53.54	626.46	1350.96	27.10	462.36	1160.61	24.75	557.24	1136.49
Ti	0.75	2.21	269.40	0.43	1.87	70.76	0.39	1.16	25.67
Minor elements in mg/ kg									
Ba	34.48	240.24	344.69	29.72	126.53	385.69	14.80	55.60	110.68
Mn	253.37	557.56	607.81	57.30	98.81	106.18	16.74	21.88	23.04
Na	23.51	183.29	263.30	55.60	271.90	357.18	8.23	1191.35	1280.89
P	0.00	1.41	1.41	0.00	112.80	390.58	0.00	21.17	78.17
Sr	66.36	98.40	101.75	9.40	28.47	157.02	2.74	10.53	39.10

Trace Elements

The accumulated available concentrations shown in Table 44 under each leaching conditions differ from sample to sample and from element to element. The trace elements; Th, U, V, Cr and Sn largely partitioned in the residual phases were found to have a very low concentration that can be considered to be potentially available. Most of the trace elements had considerable amounts partitioned in the organics and sulphides phase thus resulting in a significantly higher concentration for oxidising leach available concentration (stages 1-6) compared to the acidic leach available concentration (stages 1-5). Most elements except for Zn, Co, B, Cd, Sb, Se had low proportions partitioned in the water-soluble and exchangeable phases thus were found to have negligible potential availability under the neutral leach conditions. These results indicate that acid and oxidising leach can mobilise most of the trace elements to higher concentrations than neutral leach.

Table 44 Potentially available concentration of trace elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C's (Witbank coal discards) under neutral, acid and oxidising leach conditions

	Sample A			Sample B			Sample C		
	Neutral leach	Acid leach	Oxidising leach	Neutral leach	Acid leach	Oxidising leach	Neutral leach	Acid leach	Oxidising leach
Trace elements in mg/ kg									
As	0.32	2.41	7.64	0.24	1.53	4.13	0.45	1.14	4.02
B	12.20	16.65	27.10	6.27	9.58	17.87	7.66	9.93	14.39
Be	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.19	0.19
Cd	0.16	0.21	0.27	0.07	0.15	0.19	0.10	0.13	0.18
Co	3.06	7.51	14.01	0.57	6.11	7.68	2.72	3.34	4.52
Cr	0.59	3.98	13.71	0.65	3.98	14.88	3.54	34.03	43.73
Cu	0.17	7.73	29.92	0.03	7.04	27.21	3.04	8.93	22.39
Hg	0.02	0.04	0.21	0.00	0.04	0.35	0.00	0.04	0.24
Li	0.09	0.67	2.36	0.10	4.05	4.05	1.26	4.81	8.32
Mo	0.44	1.20	3.62	0.29	0.74	2.28	0.35	3.08	6.19
Ni	2.94	12.73	24.45	1.40	11.26	16.70	6.14	9.82	14.90
Pb	3.48	20.00	25.17	0.88	12.79	25.51	1.40	20.61	24.70
Sb	0.40	0.91	1.98	0.59	1.07	1.64	0.58	1.04	1.28
Se	0.33	0.57	1.21	0.24	0.38	1.21	0.22	0.32	0.81
Sn	0.00	0.00	2.30	0.00	0.00	0.98	0.00	0.00	0.68
Th	0.27	0.39	4.59	0.06	0.09	7.75	0.44	0.74	8.52
Tl	0.07	0.18	0.28	0.06	0.14	0.16	0.02	0.13	0.19
U	0.54	0.74	1.83	0.23	0.41	2.03	0.37	0.52	1.30
V	0.88	8.74	45.13	0.10	5.37	22.53	0.58	4.70	14.95
Zn	17.92	36.57	71.85	3.00	20.21	32.39	48.97	53.50	60.45

5.2.3. Risk Potential

The risk potential of the analysed elements was calculated based on enrichment factors and effect factors using the potentially available concentration determined from sequential chemical extractions. The risk potential was assessed using soil and drinking water as environmental indicators. Detailed results on the risk potential, effect and enrichment factors are presented in Appendix C.2.3. The risk potentials factors were then ranked and scored in terms of environmental significance.

Effect Factors (EFi) for Leach Conditions

The Effect factor (EFi) ranges under neutral, acidic and oxidising leach conditions relative to drinking water limits are presented in Table 45. The results show that, even though the available concentrations were significantly lower than the total concentrations in most cases, a number of elements extracted under the three conditions still exceeded the maximum allowed concentrations in drinking water i.e. the EFi exceeded one. Exceptions are Sn, Yb, Eu, Tb, Ho, Tm and Te in the case of Waterberg slurry waste, which had effect factors below one even under oxidising conditions. The EFi based on soil guidelines presented in Table 46 shows only S to be leached under neutral conditions to concentrations exceeding the maximum allowed concentration in soils. In addition to S, Pb in all three coal wastes can also be

leached under acidic conditions to concentrations above maximum allowed concentration. Furthermore, Cu and Cr in Witbank coal slurry and discards also had EFi above one under acid leach. Oxidising leach conditions can extract S, Pb, Cr, and Cu in the three coal wastes as well as As in Waterberg coal slurry to concentrations above the maximum allowed concentrations.

Table 45 Effect factor ranges for elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C's (Witbank coal discards) under neutral, acidic and oxidising leaching conditions relative to allowed concentration in drinking water

EFi range	**Elements with effect factors in the range**		
	Sample A	**Sample B**	**Sample C**
Neutral Leach			
>10	Fe, S, Mn, Pb, Sb, As, Cd, Tl, Co, Cr, Mg, Hg, Al, Ba, Ca, Ni, B, U, Cd, Si	Fe, Pb, Ni, Ba, Cd, B, Tl, Ca, U, Cr, Mg, As, B, Mn, Sb, Al, S	Fe, Pb, Ni, Ba, Cd, Tl, U, Cr, As, B, Mn, Sb, Al Co, S
1-10	K, Sr, Th, V, Zn, Mo, Se	Si, K, Sr, Co, V, Mo, Se	Si, Ca, Mg, Be, V, Mo, Se, Cu, Th, Zn, Li
<1	Ti, P, Na, Be, Cu, Li, Sn	Ti, P, Na, Be, Cu, Th, Zn, Hg, Li, Sn	Sr, Ti, P, Na, Hg, Sn, K
Acid Leach			
>10	Fe, S, Mn, Pb, Sb, As, Cd, Tl, Co, Cr, Mg, Si, Hg, Al, Ba, Ca, Ni, B, U, V, Mo, Se, Sr	Fe, Pb, Ni, Ba, Cd, B, Tl, Ca, U, Cr, Mg, As, Mn, Sb, Al, S, Si, V, Hg, Mo, Co, P	Fe, Pb, Ni, Ba, Cd, B, Tl, U, Cr, As, Mn, Sb, Al Co, S, Si, V, Zn, Hg, Mo
1-10	K, Th, Zn, Cu,	K, Sr, Se, Na, Cu, Zn, Li,	Ca, Mg, K, Be, Se, Cu, Th, Li, P, Sr, Na
<1	Ti, P, Na, Be, Li, Sn	Ti, Be, Th, Sn	Ti, Sn
Oxidising Leach			
>10	Fe, S, Mn, Pb, Sb, As, Cd, Tl, Co, Cr, Mg, Hg, Si, Al, Ba, Ca, Ni, B, U, Mo, Se, Sr, Th, V, Zn, Cu, Ti, Sc, Y	Fe, Pb, Ni, Ba, Cd, B, Tl, Ca, U, Cr, Mg, As, Mn, Sb, Al, S, Si, V, Hg, Mo, Co, P, Sr, Se, Cu, Ti, Th, Ce, La, Nd, Y	Fe, Pb, Ni, Ba, Cd, B, Tl, U, Cr, As, Mn, Sb, Al Co, S, Si, V, Zn, Hg, Mo, P, Se, Cu, Th, Li, Ce, La, Nd
1-10	K, Na, Li, Ce, La, Sm, Yb, Pr, Nd, Gd, Dy, Er	K, Na, , Zn, Li, Sc, Sm, Pr, Gd, Dy, Er	Ca, Mg, K, Ti Be, Sr, Na, Sc, Sm, Pr, Gd, Dy, Y
<1	P, Be, Sn, Eu, Tb, Ho, Tm, Lu, Te	Be, Sn, Eu, Tb, Yb, Ho, Tm, Lu, Te	Sn, Eu, Tb, Yb, Ho, Er,Tm, Lu, Te

Table 46 Effect factor ranges for elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C's (Witbank coal discards) under neutral, acidic and oxidising leaching conditions relative to allowed concentration in soils

EFi range	Elements with effect factors in the range		
	Sample A	**Sample B**	**Sample C**
Neutral Leach			
1-10	S	S	S
<1	Mn, As, Co, Cr, Cu, Ni, Pb, V, Zn, Hg, Cd	Mn, As, Co, Cr, Cu, Ni, Pb, V, Zn, Hg, Cd	Mn, As, Co, Cr, Cu,Ni, Pb, V, Zn, Hg, Cd
Acid Leach			
1-10	S, Pb	S, Cr, Cu, Pb	S, Cr, Cu, Pb
<1	Mn, As, Co, Cr, Ni, V, Zn, Hg, Cd	Mn, As, Co, Ni, V, Zn, Hg, Cd	Mn, As, Co, Ni, V, Zn, Hg, Cd
Oxidising Leach			
>10	S		S
1-10	As, Cu, Cr, Pb	S, Cu, Cr, Pb	Cu, Cr, Pb
<1	Mn, Co, Ni, V, Zn, Hg, Cd	As, Mn, Co, Ni, V, Zn, Hg, Cd	As, Mn, Co, Ni, V, Zn, Hg, Cd

Enrichment Factors (EnFi) for Leach Conditions

The enrichment factors (EnFi) results presented in Appendix C.2.3 show an increase from neutral, acid and oxidising leach but most elements had EnFi below one under all conditions. This signifies that under the three leach conditions the available concentrations of the particular elements are below the average crustal abundance. Exceptions are S, Se and Sb in all three coal wastes as well as B and Cd in Waterberg coal slurry which had EnFi values above one under all leach conditions. Pb, As and Cd also had EnFi above one in all three coal wastes under acid leach conditions. Elements with EnFi exceeding one under oxidising leach conditions were found to be S, As, Pb, B, Hg Mo, Sb, Se and Cd in all three coal wastes, as well as Ba and U in the two coal slurry wastes and Th in the two Witbank coal wastes. These results indicate the acidic and oxidising leach conditions can extract higher proportions of the elements compared to relatively mild or neutral conditions.

Risk Potential for Drinking Water: Neutral Leach Conditions

The ranking and scoring results in terms of potential water-related risks, presented in Table 47, show no elements to be of high or very high environmental significance under mild or neutral leaching conditions. Only available Mn was found to be of a high enough concentration in the Waterberg coal slurry to be of moderate environmental concern. The rest of the elements were found to pose a low to negligible threat to the environment under mild leaching conditions, as they are not likely to be leached to levels high enough to exceed drinking water limits.

Table 47 Elemental and salinity risk potential of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) in drinking water based on neutral leach conditions

*Environmental significance	Maximum Risk Potential Factor (RPFi)/ 1000	Sample A	Sample B	Sample C
Very high	>10 000			
High	A:1 000 – 10 000 B: 100 – 1 000 C: 10 – 100			
Moderate	1 - 10	Mn		
Low	0.1 - 1	S, Ca, Sb, Pb	Sb, S	Sb, S
Non-strategic	< 0.1	Se, B, Cd, U, Fe, Mg, Tl, As, Ni, Hg, Mo, Ba, Al, Co, Sr, Zn, Cr, Th, Si, K, Ti, Cu, V, Ce, V, Li, Be	Mn, Se, Ca, B, Pb, Cd, Al, Tl, Ba, As, Mo, U, Ni, Si, Fe, Ti, Mg, K, Sr, Na, Co, Cr, Cu, Th, V, Zn, Li, Ce	Al, Se, Ni, Pb, Fe, B, As, Zn, Mn, U, Co, Cr, Mo, Ba, Cd, Si, Ti, Ca, Mg, K, Sr, Na, Be, Cu, Th, V, Li, Tl, Ce

** Elements not analysed; Cs, Cs, Dy, Eu, Er, Ga, Ge, Gd, Hf, Ho, In, La, Lu, Nd, Pr, Rb, Sc, Sm, Tb, Ta, Te, Tm, Y, and Yb*

Risk Potential for Drinking Water: Acid Leach Conditions

Similarly, the results in Table 48 indicate that no elements were found to be of high to very high environmental significance under acidic leach conditions. However, Fe and Pb for all three coal wastes, are shown to have the potential to pose a moderate risk to water sources if coal wastes are exposed to acidic conditions. In addition to Fe and Pb, Mn in the Waterberg coal slurry leached under acidic conditions can also be of moderate environmental significance. Elements of potential low environmental significance under acid leach include S^-, Sb, Ca, As, Ba, Se, Al, Cr and Mo. The rest of the assessed elements were found to be of negligible threat to the environment as they are not leached to levels high enough to be toxic in drinking water.

Table 48 Elemental and salinity risk potential of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) in drinking water based on acidic leach concentration

*Environmental significance	Maximum Risk Potential Factor (RPFi)/ 1000	Sample A	Sample B	Sample C
Very high	>10 000			
High	A:1 000 – 10 000 B: 100 – 1 000 C: 10 – 100			
Moderate	1 - 10	Mn, Fe, Pb	Fe, Pb	Pb, Fe
Low	0.1 - 1	S, Sb, Ca, As, Ba, Se, Al	Sb, Al, S, Mn, As	Sb, S, Al, Mo, Cr
Non-strategic	< 0.1	Ni, B, Cd, Tl, Mo, Hg, U, Mg, Co, V, Sr, Zn, Cr, Cu, Si, Th, K, Li, Na, P, Ti, Sn, Be	Se, Ni, Ba, Cd, Hg, B, Tl, Ca, Co, Mo, U, P, Cr, V, Li, Zn, Mg, Cu, Sr, Si, K, Ti, Na, Sn, Be	Ni, Se, As, Cd, B, Hg, Tl, U, Ba, Mn, V, Zn, Li, Co, Th, Na, Be, Si, K, P, Sr, Ca, Mg, Ti, Sn

** Elements not analysed; Cs, Cs, Dy, Eu, Er, Ga, Ge, Gd, Hf, Ho, In, La, Lu, Nd, Pr, Rb, Sc, Sm, Tb, Ta, Te, Tm, Y, and Yb*

Risk Potential for Drinking Water: Oxidising Conditions

The results in Table 49 show that Fe was the only metal evaluated to be of high environmental significance under oxidising leach conditions in Waterberg coal slurry and Witbank coal discards. S, Pb and Sb are of moderate risk for all samples. Other elements evaluated to be of moderate risk are Mn and As in the Waterberg coal slurry, and Fe, Al, and Hg in the Witbank coal slurry. The remainder of the elements analysed were found to be of low to negligible risk, even under relatively aggressive oxidising conditions.

Table 49 Elemental and Salinity risk potential of coal waste samples A (Waterberg slurry), B (Witbank slurry) and C (Witbank discards) in drinking water based on potential bioavailable concentration under oxidising leach

Environmental significance	Maximum Risk Potential Factor (RPFi)/ 1000	Sample A	Sample B	Sample C
Very high	>10 000			
High	A:1 000 – 10 000 B: 100 – 1 000 C: 10 - 100	Fe		Fe
Moderate	1 - 10	S, Mn, Pb, Sb, As	Fe, Pb, S, Sb, Al, Hg	S, Pb, Sb
Low	0.1 - 1	Se, Hg, Al, Ba, Ca, Ni, Mo, B, U, V, Cd	As, Se, Ba, Mn, Ni, U	Hg, As, Mo, Al, Se, Cr, Ni
Non-strategic	< 0.1	Cd, Tl, Co, Cr, Mg, Th, Cu, Zn, Y, Sr, Sc, Sm, Gd, Dy, Nd, Ti, Si, Ce, Er, Li, Tb, Yb, Ho, Pr, Eu, K, Cs, Ga, Tm, Te, Na, P, Be	Mo, B, Cd, Th, Cr, V, P, Ca, Co, Tl, Ce, Nd, La, Y, Cu, Sr, Si, Ti, Mg, Na, Zn, Li, Sn, Cs, Ga, Hf, Sc, Sm, Eu, Tb, Yb, Pr, Gd, Dy, Ho, Er, Tm	U, Th, Cd, Ba, Tl, Ce, Mn, Cu, V, Zn, Li, La, Nd, Si, Ti, Ca, Mg, P, K, Na, Be, Sn, Cs, Ga, Hf, Sc, Sm, Eu, Tb, Yb, Pr, Gd, Dy, Ho, Er, Tm

Risk Potential for Soil

The risk potential environmental significance ranking results for oxidising leach conditions are presented in Table 50 while the detailed data on all three leach conditions is presented in Appendix C.2.3. The risk potential factors (RPFi) under water and acid leach were all below 0.1 (see Appendix C.2.3.) thus the elements were evaluated to be of no environmental concern on soils under these leaching conditions. However, under oxidising leach conditions S salts in Waterberg coal slurry and Witbank discards were evaluated to have the potential to pose a moderate risk on soils but the S salts risk potential in Witbank coal slurry was ranked as low. Other elements were available in concentrations too low to be a threat to soil quality.

Table 50 Elemental and salinity risk potential of coal waste samples A (Waterberg slurry), B (Witbank slurry) and C (Witbank discards) on soil based on potential total bioavailable concentration

Environmental significance	Maximum Risk Potential Factor (RPFi)/ 1000	Sample A	Sample B	Sample C
Very high	>10 000			
High	A:1 000 – 10 000 B: 100 – 1 000 C: 10 – 100			
Moderate	1 - 10	S		S
Low	0.1 - 1		S	
Non-strategic	< 0.1	As, Pb, Cu, Hg, Ba, Co, Cr, Ni, V, Zn, Cd	Pb, Hg, As, Cu, Mn, Co, Cr, Ni, V, Zn, Cd	Pb, Cr, Hg, As, Mn, Co, Cu, Ni, V, Zn, Cd

The elemental and salinity risk assessment tested hypothesis 2 which states:

- The coal processing waste generated from different coalfields and processing operations in South Africa have the potential to cause environmental impacts of varying magnitudes from ARD and elevated concentration of toxic elements and salts owing to their different geochemical properties.

The results proved the hypothesis to be true as evidenced by the difference in the environmental significance and/or risk potential factors of the elements found in the three coal wastes. The environmental significance and risk potential factors were determined by the toxicity and bioavailability of the elements which in turn were determined by the geochemical properties that affect concentration, occurrence and leaching behaviour of the elements. Even the Waterberg sample which was found to be NAF also pose an elemental and salinity risk to drinking water and soil.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Reliable characterisation data linking the coal waste leaching behaviour, mineralogy and physio-chemical properties to their possible ARD, elemental and salinity risks is essential to design, justify and implement mitigation measures. Although there are several characterising techniques to characterise the physiochemical properties and potential environmental impacts of mine wastes, their application to coal and coal wastes in South Africa is limited and surrounded by uncertainty owing to the complex nature of coal wastes. In order to comprehensively and consistently characterise the potential environmental impacts of coal processing wastes, the reliability of the characterisation methods needs to be evaluated. Furthermore, the risk potential data needs to be validated using various but appropriate evaluation techniques. As outlined in Chapter 1, the objective of this study is to determine the reliability of coal waste characterisation techniques and interpretation of the data in terms of environmental risk potential. The objective was accomplished through experimental work to answer the following research questions:

- How reliable and reproducible are the commonly used total sulphur and sulphur speciation tests and how much sulphur and what are the forms in coal processing wastes?
- How accurate are the commonly used elemental analysis techniques and what are the elemental compositions of the coal processing waste?
- What is the ARD potential of coal wastes using conventional static tests and biokinetic tests?
- How does extended boil NAG tests validate the ARD potential classification by the conventional static tests?
- How does the sulphur species behave under static tests and what is the implication on ARD potential
- What is the leaching behaviour of the coal waste elements under disposal conditions and the environmental impact risk of salts and elements mobilized under disposal conditions?
- How does the mineralogy of the coal waste influence the environmental risk of the coal wastes?

The experimental work was conducted to synthesize risk assessment criteria with physiochemical and leaching data to evaluate potential ARD, elemental and salinity risks of three coal waste samples obtained from different processing units of collieries in Waterberg and Witbank coalfields. The reliability of analytical techniques used to determine total sulphur and elemental compositions was evaluated on a coal standard SARM 19 followed by analysis on the coal waste samples. The ACARP C15034 and ISO 157:1996 protocols commonly used to evaluate sulphur forms were compared and evaluated using the

coal waste samples and coal standard. Conventional ABA and NAG tests were enhanced through extended boil NAG tests and the ARD potential validated through mineralogy based theoretical ARD and biokinetic shake flask tests. The leaching behaviour of sulphur forms under static ARD tests was further studied, as well the leaching behaviour of elements under various leaching conditions. Then the elemental and salinity risks associated with coal processing waste evaluated for neutral, acidic and oxidising leach conditions.

6.1. Research Outcomes

The research outcomes to answer the research questions are presented in the following sections:

Total Sulphur and Sulphur Forms

Both methods used to determine total sulphur in the coal standard SARM 19, were found to be accurate (± 3.1– 12.5 % RSE) and precise (± 0.01-0.03 % standard error), but in addition to being reproducible, Leco analysis proved to be more reliable compared to the Eschka method. The coal processing wastes used in this study were evaluated to have < 2 % total sulphur, which according to literature is typical of South African coals to have low sulphur content. The sulphur in the coal wastes was found to exist in different forms i.e. sulphides, sulphates and organic sulphur. The results showed pyrite as the major species forming between 52-61 % of the total sulphur while sulphate sulphur ranges between 12-26 % and organic/low-risk sulphur range between 23-43 %. Both the ACARP C15034 and ISO 157:1996 protocols gave comparable results, but the latter consistently evaluated slightly higher sulphate in all samples and lower pyritic sulphur in the coal slurry wastes which could be as a result of partial solubilisation of pyritic sulphur under aggressive conditions in HCl extraction of sulphates. The results also showed the ACARP C15034 protocol to be more repeatable (±0.02 % standard error) particularly for the determination of sulphates compared to the ISO 157:1996 protocol (±0.06 % standard error). Furthermore, the ACARP C15034 protocol identifies sulphates that are acid-forming, unlike ISO 157 method. Therefore, in samples containing other acid-forming sulphates, the ACARP C15034 method gives a better estimation of the acid-producing potential of the coal waste samples compared to ISO 157:1996.

Element Concentrations

In testing reliability of analytical techniques used for elemental analysis, inter-laboratory reproducibility was not tested and reliability was based on accuracy for a particular lab and the results do not necessarily show the accuracy of the analytical technique. Accuracy and precision evaluated for each analytical technique varied from element to element but WDXRF analysis at Stellenbosch University could analyse most of the major elements accurately within 5% RSE except Mg and Mn. Similarly, LA-ICP-MS analysis at Stellenbosch University could analyse most of the trace and minor elements accurately and precisely within ± 10 % RSE except As, Cs, Ge, Tb, Se, Mo, Zn and Sb. Contrastingly the accuracy and precision of ICP-MS, ICP-OES and FAAS analyses at the University of Cape Town were out of ±

10 % RSE range for most elements. Reliability of analytical techniques could have been influenced by systematic and random errors such as calibration, detection limits, sample preparation and homogeneity. The concentration of elements in the three coal wastes varied from sample to sample. Elements in the three coal wastes found to be major elements (i.e above 0.1 wt. %). are Al, Ca, Fe, K, Mg, Si and Ti, while Ba, Mn, Na, P, Sr and Zr were evaluated to be minor elements (i.e 0.1-0.01 wt. %) and the rest as trace elements (i.e below 0.01 wt. %). Analysis on the coal processing wastes showed the concentration of Sb, Cr, Cu, Ni, and Zn in all the three coal wastes as well as Th in the Witbank coal wastes to exceed the range reported in SA coals.

Acid Rock Drainage Potential

The ARD classification of the coal processing waste sample was shown to be a function of the acid generating potential (AP) and acid neutralising potential (NP) of the samples. However different testing methods evaluated different values for AP and NP factors. The net acid-producing potential (NAPP) value evaluated in ABA tests was shown to be dependent on the sulphur species used to calculate maximum potential acidity (MPA). In the Waterberg coal slurry, the NP was higher than AP thus classifying the sample as non-acid-forming (NAF) (with a capacity of -68.6 to -46.8 kg H_2SO_4/Ton) regardless of whether total sulphur or acid-forming sulphur is used to calculate the AP. Contrastingly in the Witbank coal discards, AP was in excess of the NP, thus classifying the sample as potentially acid-forming (PAF) (with a capacity of 9.2-25.9 kg H_2SO_4/Ton) despite the sulphur species considered for calculating MPA. There was no significant difference of AP and NP for the Witbank coal slurry thus causing uncertainty with the ARD classification by the combined static tests. NAPP calculated from acid-forming sulphur classifies the sample as uncertain (UC) but when NAPP is based on total sulphur, the sample is classified as PAF (the NAPP ranged between -12.1 and 9.9 kg H_2SO_4/Ton). However, the calculated ARD based on mineralogy classified the Witbank coal slurry as PAF.

The biokinetic shake flask tests validated the presence of fast-moderate weathering acid neutralising minerals in the Waterberg coal slurry which caused pH to increase to above 7 soon after commencing the tests under uncontrolled pH conditions. However, the controlled pH conditions also showed the sample becomes acid-forming only when the acid neutralising capacity has been exhausted. The biokinetic shake flask tests also showed both samples from Witbank to be net acid generating from the onset of the tests. The tests also showed the net acid generation particularly of Witbank coal slurry to vary with time as a result of the weathering rate of the acid neutralising minerals.

Comparison of the ARD testing methods shows the chemical ANC test as part of the ABA test protocol overestimated the available acid neutralising capacity of the sample. This was evident from the ANC tests on the biokinetic tests and is confirmed by the QEMSCAN results which indicate that much of the NP is associated with slow weathering silicates and is unlikely to be available to neutralise acid

generated by oxidative dissolution of sulphide under disposal conditions, even under worst-case conditions.

Effects of Organic Acids on ARD Potential

The effects of organic acids evaluated from extended boil NAG tests influenced the significant change of NAG pH of the Witbank coal slurry from 3.9 to 5.2 but pH changed only slightly from 2.52- 2.56 in Witbank coal discards. The increase in extended boil NAG pH caused a shift of the ARD potential classification of the Witbank coal slurry from PAF to UC but the Witbank coal discards remained PAF after considering the extended boil NAG pH. This indicates the organic acid can cause an overestimation of the net acid generating capacity of some coal wastes.

Behaviour of Sulphur Species Under ARD Static Tests

The studies on the behaviour of the sulphur species under ABA and NAG tests showed 21 %, 50 % and 17 % of the pyritic sulphur in Waterberg coal slurry, Witbank coal slurry and Witbank coal discards respectively, solubilised under ANC tests. This shows some of the pyritic sulphur is readily soluble in acid and can cause an under-estimation of the ANC capacity of the coal wastes. On the other hand, 53 %, 38 % and 99 % of the low-risk sulphur in Waterberg coal slurry, Witbank coal slurry and Witbank coal discards respectively converted to leachate sulphate under NAG tests. These results indicate the aggressive NAG conditions could have caused the partial conversion of low-risk sulphur to acidity thus causing an overestimation of the NAG capacity. Partial solubilisation of pyritic sulphur and conversion of low-risk sulphur are possibly some factors that contribute to the uncertainty of ARD potential classification by static tests.

Element Mobility and Risk Potential

The potential risk posed by metals, metalloids and non-metals mobilised under neutral, acidic and oxidising leach conditions were ranked and scored in terms of environmental significance. Under neutral leach conditions, of the analysed elements, only Mn, Ca and Pb in Waterberg coal slurry, as well as Sb and S in all coal wastes, can be mobilised to concentrations that pose a potential threat in drinking water. Fe and Pb in all three coal wastes, as well as Mn in Waterberg coal slurry, were found to have the potential to be leached under acidic conditions to pose a moderate risk in drinking water sources. While S, Sb, Ca, As, Ba, Se, Al, Cr and Mo were shown to pose a low-risk potential to drinking water under acid leach. The results indicate under oxidising leach conditions Fe, S, Pb, Sb, Mn, As, Al and Hg can be mobilized to levels considered as high-moderate environmental significance to drinking water sources. While Se, Ca, Ni, Mo, B, U, V, Cd, Ba and Cr have the potential to be a low threat to drinking water quality under oxidising leach conditions. The risk potential of all the analysed elements in the coal wastes were evaluated to be of no environmental concern on soils under neutral and acidic leaching conditions. However, under oxidising leach conditions, SO_4^{2-} salts (from S concentrations) in

Waterberg coal slurry and Witbank discards were found to have the potential to pose a moderate risk on soils but the SO_4^{2-} salts risk potential in Witbank coal slurry is ranked as of low significance.

Mineralogical Composition and Environmental Risks

Generally, the main constituents in coal processing wastes evaluated from QEMSCAN and QXRD analysis were found to be coal, carbominerite, kaolinite, quartz and K-feldspar with quantities differing between samples as well as analysing method. Other constituents in the coal wastes are carbonates (predominantly calcite and dolomite), gypsum, pyrite, chalcopyrite, jarosite, amphiboles, mica/muscovite, Fe-oxyhydroxides, apatite and rutile. Parity curves comparing major elements concentration from mineralogy analysis against element concentration by WDXRF shows QEMSCAN underestimating Ca, Mg and Fe in the coal slurry wastes particularly the Waterberg sample indicating possible underestimating of carbonates such as calcite, dolomite and siderite. The parity curves also showed QEMSCAN evaluated higher Al concentration than WDXRF for Witbank coal discards indicating a possible overestimation of kaolinite. QXRD underestimated all the major elements with the exception of Fe, K and Ca in Witbank coal discards as well as Mg in all coal wastes compared to the WDXRF results. This indicates the QXRD could have analysed dolomite more accurately but overestimated coal and underestimated mineral matter including calcite. In addition, comparison of sulphur species evaluated by mineralogy analysis compared to both ISO 157:1996 and ACARP C15034 protocols show both QXRD and QEMSCAN underestimated soluble sulphates in all the coal wastes. The results also show the mineralogy analysis overestimated pyrite for Witbank coal wastes but slightly underestimated the pyrite in Waterberg coal slurry.

The mineralogical composition can be used to calculate the acid generating potential (AP) and acid neutralising potential (NP) of the coal wastes, but the results are affected by the accuracy of the mineralogy analysing methods. Thus, underestimation of carbonates causes underestimation of NP in Waterberg coal slurry while overestimation of pyrite causes overestimation of AP in the Witbank coal wastes. However, the Waterberg coal slurry by having more NP (from calcite, dolomite, amphiboles, mica and K-feldspar) than AP (from pyrite) was classified as NAF by both static tests and ARD potential calculated from mineralogy. While the acid buffering from the K-feldspar, apatite and mica in Witbank coal slurry and discards is not adequate to neutralise all the acidity from the acid-forming sulphur. The biokinetic shake flask tests results also showed the net acid generation behaviour to be time-related depending on the weathering rate of acid neutralising and acid generating minerals. Hence the initial pH increase observed on commencing the biokinetic shake flask can be attributed to dissolving carbonates (calcite and dolomite) and fast weathering amphiboles such as wollastonite. While the slight increase in pH observed later between day 40 and 100 can be attributed to slow weathering minerals like K-feldspar and mica according to mineralogy results.

The ranking and scoring of the risk potential of elements and salts is based on their potential availability as well as toxicity. The potential availability was shown to be linked to the mineralogy of the coal wastes which determines the level of element enrichment as well as the phase hosting the elements. The proportion of elements that are considered to be potentially available are those hosted in water-soluble, exchangeable, carbonates, Fe/Mn oxides, sulphides and organic phases of the coal wastes. While proportions of the elements hosted by inert phases like kaolinite, quartz and rutile remained in the residual phase are considered potentially unavailable to the environment.

6.2. Concluding Remarks

The main objective of this study was to evaluate the applicability of characterisation techniques and assess the potential ARD, salt and elemental risks of coal processing wastes. The physiochemical properties and risk potential assessment has shown that coal processing wastes even from the same coalfield can be both different and similar in characteristics. The coal wastes elemental compositions can be in similar ranges but they can vary quite considerably in the relative concentrations of minerals, and in their acid generating properties. This study has also shown that chemical static ABA and NAG tests are simple and fast tools for evaluating ARD potential of coal processing wastes, but the classification of some samples may be uncertain. Presence of different sulphur species and their conversion can cause overestimation or underestimation of the NAPP, while effects of organic acids can cause an overestimation of NAG capacity. The characterisation of ARD potential can be enhanced through extended boil NAG tests to account for the organic acids effect. The mineralogical ARD and biokinetic tests are important tools that can be used for validating and complementing static chemical tests allowing consist and reliable classification of the ARD potential of coal wastes. Furthermore, the biokinetic shake flask tests are a relatively fast and cheap method that shows the time-related net acid generating behaviour of the samples incorporating the effects of microbial catalysis on ARD formation. However, the reliability of the mineralogical ARD potential is dependent on the accuracy of the mineralogy analysis.

The study also showed the total sulphur in coal wastes can be reliably evaluated from the existing combustion and gravimetric standard methods; Leco and Eschka method, but the sulphur exists in various forms. Both the ISO157:1996 and the ACARP C15034 protocols have been evaluated to be tools that can precisely determine the sulphur species but the ACARP C15034 can further distinguish acid-forming sulphates unlike the ISO 157:1996 protocol. Therefore, the ACARP protocol is a better tool for sulphur speciation for coal wastes with acid-forming sulphates, but it can underestimate the MPA for samples with high contents of jarosite which according to the protocol is considered low-risk sulphur although it is acid-forming. Due to limitations of each analysing technique used for element analysis not one analytical technique by itself is ideal for comprehensive and reliable element analysis in coal wastes, therefore, a combination of techniques gives more reliable characterisation data. Sequential chemical extractions coupled with ranking and scoring model proved to be essential tools

that can evaluate the water and soil-related risk potential of metals, metalloids and non-metals found in coal processing wastes under various leach conditions.

The outcomes of this research provide evidence that the coal processing wastes generated in South Africa have the potential to pose environmental impacts from ARD, toxic elements and salts which can be quantified and validated using a combination of existing characterisation tools. Uncertainty of ARD risk should lead to greater caution to overcome specific limitations by the commonly used static tests. This study can therefore provide a basis for South African regulatory bodies to standardise the characterisation of the potential environmental risks posed by coal processing wastes. The reliable and consistent characterisation data will be fundamental in the design and implementation of sustainable coal waste management and risk mitigation strategies. Furthermore, the characterisation data gives a basis for value recovery of useful coal wastes' constituents such as kaolinite, pyrite and residual coal which can be used as feedstock in other processes.

6.3. Recommendations

Based on the results obtained in this study the following are recommended:

- For comprehensive and reliable characterisation of the elemental composition of coal processing wastes, it is recommended to combine analytical techniques; WDXRF, LA-ICP-MS, ICP-OES and ICP-MS as the accuracy of techniques differ from element to element. It is also recommended to add to the characterisation toolbox techniques like selective ion electrode capable of detecting the halogens as they are elements of environmental concern likely to be found in coal wastes.
- It is also recommended to standardize sample preparation for FAAS, ICP-MS and ICP-OES to achieve complete solubilisation without volatisation of elements. This will allow accurate and consistent determination of elemental composition including volatile elements like Hg, Se and Sb which are not accurately analysed by LA-ICP-MS.
- Further studies on the behaviour of acid neutralizing minerals under different ARD tests is recommended to understand how the behaviour affects the ARD potential. This will enable selection of appropriate static tests for evaluating ARD potential of coal wastes.
- The batch shake flask tests do not truly resemble the disposal scenario as the flow is likely to be semi-continuous or continuous in the dump scenario. Executing the biokinetic tests under conditions imitating the disposal scenario like the flow throw and draw and fill conditions will give valuable information on the net acid generation rates of different samples. Further study of the sulphur species behaviour under dump disposal ARD conditions will enlighten on which sulphur species to consider when calculating the acid-producing potential of coal waste samples.
- Although SCE provides information on the leaching behaviour of elements and salts under different environmental conditions, the leaching behaviour under ARD test conditions imitating the dump scenario needs to be further analysed and the elemental and salinity risks evaluated.

- The coal processing wastes contain silica (quartz) and pyrite, thus it is recommended to characterise coal waste for their potential to cause dust related impacts like silicosis.
- Further development of the QEMSCAN mineral list is recommended to allow identification of some mineral phases such as soluble sulphates
- Analytical results showed the enrichment of elements as well as the presence of potentially usable and economically valuable constituencies such as residual coal, pyrite and kaolinite. Further studies are recommended for value recovery and recycling of these minerals and elements.
- The results obtained in this study are subject to the particular samples and not representative of all South African coal processing wastes. Application of the tests methods on a larger number of coal wastes from different sources and origins is recommended to optimise the toolbox for characterising the potential environmental risks of coal wastes.

REFERENCES

Ahern, C., McElnea, A. and Sullivan, L. (2004) *Acid Sulfate Soils Laboratory Methods Guidelines*. Queensland, Australia: Department of Natural Resources, Mines and Energy, Indooroopilly. doi: QNRME04149.

Ahmadi, A. , Khezri, M., Akbar, A. and Askari, M. (2015) 'Bioleaching of copper , nickel and cobalt from the low grade sul fi dic tailing of Golgohar Iron Mine , Iran', *Hydrometallurgy*. Elsevier B.V., 154, pp. 1–8. doi: 10.1016/j.hydromet.2015.03.006.

van Alphen, C. (2007) 'Automated mineralogical analysis of coal and ash products - Challenges and requirements', *Minerals Engineering*, 20(5), pp. 496–505. doi: 10.1016/j.mineng.2006.12.013.

APHA. (2005) *Standard methods for the examination of water and waste water, 21st edn.*. Washington, DC: American Public Health Association.

Baedecker, P. A. (ed.) (1987) *Methods for Geochemical Analysis*. Denver: U.S. Geological Survey Bulletin 1770. doi: I 19:3:1770.

Baffi, C., Bettinelli, M., Beone, G. M. and Spezia, S. (2002) 'Comparison of different analytical procedures in the determination of trace elements in lichens', *Chemosphere*, 48, pp. 299–306. doi: PII: S0045-6535(02)00094-2.

Baker, L. (2011) *Governing electricity in South Africa: wind, coal and power struggles.* 15. Available at: www.clean-development.com.

Banerjee, D. (2014) 'Acid drainage potential from coal mine wastes: Environmental assessment through static and kinetic tests', *International Journal of Environmental Science and Technology*, 11(5), pp. 1365–1378. doi: 10.1007/s13762-013-0292-2.

Baysal, A. and Akman, S. (2011) 'A practical method for the determination of sulphur in coal samples by high-resolution continuum source flame atomic absorption spectrometry', *Talanta*. Elsevier B.V., 85(5), pp. 2662–2665. doi: 10.1016/j.talanta.2011.08.038.

Becker, J. S. and Dietze, H. (2003) 'State-of-the-art in inorganic mass spectrometry for analysis of high-purity materials', *Internal Journal of Mass Spectrometry*, 228, pp. 127–150. doi: 10.1016/S1387-3806(03)00270-7.

Belaid, M., Falcon, R., Vainikka, P. and Patsa, K. V.. (2013) 'Potential and Technical basis for Utilising Coal Beneficiation Discards in Power Generation by Applying Circulating Fluidised Bed Boilers', in *2nd International Conference on Chemical, Ecology and Environmental Sciences*. London, UK, pp. 260–265.

Bell, F. G., Bullock, S. E. T., Hälbich, T. F. J. and Lindsay, P.. (2001) 'Environmental impacts associated with an abandoned mine in the Witbank Coalfield, South Africa', *International Journal of Coal Geology*, 45(2–3), pp. 195–216. doi: http://dx.doi.org/10.1016/S0166-5162(00)00033-1.

Bergh, K. (The F. F. F. (2013) 'Distribution of trace metal elements - South African coals', *Inside Mining*, 6(10), pp. 12–14.

Boon, M. and Heijnen, J. J. (1998) 'Chemical oxidation kinetics of pyrite in bioleaching processes', *Hydrometallurgy*, 48, pp. 27–41. doi: PII: S0304-386X(01)00224-9.

Broadhurst, J. L., Maluleke, W. J. and Blottnitz, H. Von (2009) 'Comparison and Application of Sequential Chemical Extraction Techniques for Metal Speciation in Sulphidic Copper Tailings 1', in *Securing the Future and 8th ICARD*. Skellefteå, Sweden, pp. 1–10.

Broadhurst, J. L. and Petrie, J. (2010) 'Ranking and scoring potential environmental risks from solid mineral wastes', *Minerals Engineering*, 23, pp. 182–191. doi: 10.1016/j.mineng.2009.09.008.

Bryan, C. G. (2006) 'A study of the microbiological populations of mine wastes', PhD Thesis, School of Biological Sciences, University of Wales.

Cairncross, B. (2001) 'An overview of the Permian (Karoo) coal deposits of southern Africa', *Journal of African Earth Sciences*, 33(2001), pp. 529–562. doi: 10.1016/S0899-5362(01)00088-4.

Caroli, S., Mazzeo, A. F., Laurenzi, A., Senofonte, O. and Violante, N. (1988) 'Determination of Sulphur in Coal Products by Inductively Coupled Plasma Atomic Emission Spectrometry *', *Analytical Atomic Spectrometry*, 3(January), pp. 245–248.

Cline, J. D. (1969) 'Spectrophotometric determination of hydrogen sulfide in natural waters', *Department of Oceanography, University of Washington*, pp. 454–458.

Dale, L. (ACARP N. 02) (2006) *Trace elements in coal*. Available at: www.acarp.com.au.

Dang, Z., Liu, C. and Haigh, M. J. (2002) 'Mobility of heavy metals associated with the natural weathering of coal mine spoils', *Environmental Pollution*, 118(3), pp. 419–426. doi: 10.1016/S0269-7491(01)00285-8.

Department of Environmental Affairs (2012) *National Norms and Standards for the Remediation of Contaminated Land and Soil Quality, Government Gazette*. South Africa. doi: http://dx.doi.org/9771682584003-32963.

Department of Minerals and Energy (2001) 'National Inventory Discard And Duff Coal – 2001 Summary Report', *Energy*, (June 2002), pp. 1–31.

Department of Water Affairs & Forestry (1996) *South African water quality guidelines domestic use*.

Second edi. Pretoria: Department of Water Affairs and Forestry.

Deysel, L. M. and Vermeulen, D. (2015) 'A Detailed ABA Study of the Coal-Bearing Formations in the Waterberg Coalfield, Limpopo Province, South Africa', in *10th International Conference on Acid Rock Drainage & IMWA Annual Conference*, pp. 1–10.

Dold, B. (2017) 'Acid rock drainage prediction: A critical review', *Journal of Geochemical Exploration*. Elsevier B.V., 172, pp. 120–132. doi: 10.1016/j.gexplo.2016.09.014.

Dyantyi, N. (2014) 'Application of mineralogy in the interpretation of laboratory scale acid rock drainage (ARD) prediction tests: A gold case study', MSc Dissertation, University of Cape Town.

Eberhard, A. (2011) 'The future of South African coal: Market, investment, and policy challenges', *Program on Energy and Sustainable Development*, (January), p. 20,21,30. doi: 10.1017/CBO9781316136058.005.

Eskom (2016) *Fact Sheet Coal in South Africa*. Available at: www.eskom.co.za.

European Commision (1998) *EUR 17980- technical coal research: Coal conversion Characterisation of sulphur in coal and coal products by standard and non-standard methods*. Luxembourg: Office for Official Publications of the European Communities.

Falcon, R. and Ham, A. J. (1988) 'Characteristics of Southern African Coals.', *Journal of The South African Institute of Mining and Metallurgy*, 88(5), pp. 145–161.

Fan, G., Zhang, D. and Wang, X. (2014) 'Reduction and utilization of coal mine waste rock in China: A case study in Tiefa coalfield', *Resources, Conservation and Recycling*. Elsevier B.V., 83, pp. 24–33. doi: 10.1016/j.resconrec.2013.12.001.

Fey, D.L., 2003. Acid-Base Accounting, in: Billings Symposium / ASMR Annual Meeting Assessing the Potential of Mine-Waste Piles Workshop

Finkelman, R. B. (1999) 'Trace Elements in Coal Environmental and Health Significance', *Biological Trace Element Research*, 67, pp. 197–204.

Finkelman, R. B. and Gross, P. M. K. (1999) 'The types of data needed for assessing the environmental and human health impacts of coal', *International Journal of Coal Geology*, 40(2–3), pp. 91–101. doi: 10.1016/S0166-5162(98)00061-5.

French, D. and Ward, C. R. (2009) 'The application of advanced mineralogical techniques to coal combustion product characterisation', in *3rd World of Coal Ash, WOCA Conference - Proceedings*. Lexington, KY, USA, pp. 1–28. Available at: http://www.scopus.com/inward/record.url?eid=2-s2.0-74849125981&partnerID=tZOtx3y1.

Fundikwa, B. (2015) 'Environmental Performance Assessment of Froth Flotation for Coal Recovery and Sulfur Removal from Ultrafine Coal Waste', MSc Dissertation, University of Cape Town.

Gleyzes, C., Tellier, S. and Astruc, M. (2002) 'Fractionation studies of trace elements in contaminated soils n sediments.pdf', *Trac-Trends in Analytical Chemistry*, 21(6–7), pp. 451–467. doi: S0165-9936(02)00603-9.

Gluskoter, H. J. (1974) 'Inorganic sulfur in coal', *Illinois State Geological Survey*, pp. 94–98.

Hall, G. E. M., Gauthier, G., Pelchart, J. -C., Pelchart, P. and Vaive, J. E. (1996) 'Application of a sequential extraction scheme to ten geological certified reference materials for the determination of 20 elements', *Journal of Analytical Atomic Spectrometry*, 11(September), p. 787. doi: 10.1039/ja9961100787.

Hall, I. (2013) 'South African Coal Roadmap: Mapping the Future of South Africa ' s Coal industry', in *2nd Limpopo Coalfields Conference*, pp. 1–29.

Hancox, P. J. and Goetz, A. E. (2014) 'South Africa's coalfields - A 2014 perspective', *International Journal of Coal Geology*, 132, pp. 170–254. doi: 10.1016/j.coal.2014.06.019.

Hansford, G. S. and Vargas, T. (2001) 'Chemical and electrochemical basis of bioleaching processes', *Hydrometallurgy*, 59, pp. 135–145. doi: PII: S0304-386X 00 00166-3 Ž.

Hesketh, A. H., Broadhurst, J. L., Bryan, C. G., van Hille, R. P. and Harrison, S. T. L. (2010) 'Biokinetic test for the characterisation of AMD generation potential of sulfide mineral wastes', *Hydrometallurgy*. Elsevier B.V., 104(3–4), pp. 459–464. doi: 10.1016/j.hydromet.2010.01.015.

Hornberger, R. J., Brady, K. B. C., Cuddeback, J. E., White, W. B., Scheetz, B. E., Telliard, W. A., Parsons, S. C., Loop, C. M., Bergstresser, T. W., McCracken Jr. C. R. and Wood, D. (2004) 'Refinement of Adti-Wp2 Standard Weathering Procedures, and Evaluation of Particle Size and Surface Area Effects Upon Leaching Rates: Part 1: Laboratory Evaluation of Method Performance', *Journal American Society of Mining and Reclamation*, 2004(1), pp. 916–947. doi: 10.21000/JASMR04010916.

Horsfall, D. W. (1980) 'A general review of coal preparation in South Africa', *The South African Institute of Mining and Metallurgy*, August, pp. 257–268.

Huggins, F. E. (2002) 'Overview of analytical methods for inorganic constituents in coal', *International Journal of Coal Geology*, 50(1–4), pp. 169–214. doi: 10.1016/S0166-5162(02)00118-0.

International Energy Agency (2017) *Key world energy statistics*, *International Energy Agency*. Paris, France. doi: 10.1017/CBO9781107415324.004.

IRMA (2016) 'IRMA Standard for Responsible Mining IRMA-STD-001 Draft v2.0', *Intiatjve for Responsibke Mining Assurance*, April, pp. 1–291. Available at: www,responsiblemining.net.

Iroala, O. J. (2014) ‘Combining froth flotation with reflux classification to mitigate ARD generating potential of the Waterberg and Witbank coal ultrafines via sulfide removal’, MSc Dissertation, University of Cape Town.

Iwashita, A., Nakajima, T., Takanashi, H., Fujita, Y. and Yamashita, T. (2006) ‘Effect of pretreatment conditions on the determination of major and trace elements in coal fly ash using ICP-AES’, *Fuel*, 85, pp. 257–263. doi: 10.1016/j.fuel.2005.04.034.

Iwashita, A., Nakajima, T., Takanashi, H., Fujita, Y. and Yamashita, T. (2007) ‘Determination of trace elements in coal and coal fly ash by joint-use of ICP-AES and atomic absorption spectrometry’, *Talanta*, 71, pp. 251–257. doi: 10.1016/j.talanta.2006.03.053.

Jeffrey, L. (2005) ‘Characterization of the coal resources of South Africa’, *Journal of the South African Institute of Mining and Metallurgy*, (September 2004), pp. 7–9. Available at: http://www.lostcauseinc.com/pdf/document-1.pdf.

Johnson, D. B., Kanao, T. and Hedrich, S. (2012) ‘Redox transformations of iron at extremely low pH : fundamental and applied aspects’, *Frontiers in Microbiology*, 3(96), pp. 1–13. doi: 10.3389/fmicb.2012.00096.

Kalenga, P. M. (2011) ‘Determination and characterization of sulphur in South African coal’, MSc Dissertation, University of Witswatersrand.

Kazadi Mbamba, C., Harrison, S. T. L., Franzidis, J. -P. and Broadhurst, J. L. (2012) ‘Mitigating acid rock drainage risks while recovering low-sulfur coal from ultrafine colliery wastes using froth flotation’, *Minerals Engineering*. Elsevier Ltd, 29, pp. 13–21. doi: 10.1016/j.mineng.2012.02.001.

Komadel, P. and Stucki, J. W. (1988) ‘Quantitative assay of minerals for Fe^{2+} and Fe3+ using 1,10-phenanthroline: III. A rapid photochemical method’, *Clays and Clay Minerals*. vol. 36, pp. 379-381.

Kotelo, L. O. (2013) ‘Characterising the acid mine drainage potential of fine coal wastes’, MSc Dissertation, University of Cape Town.

Laban, K. L. and Atkin, B. P. (2000) ‘The direct determination of the forms of sulphur in coal using microwave digestion and i . c . p-a . e . s analysis’, *Fuel*, 79, pp. 173–180.

Lapakko, K. (International I. for E. and D. (2002) *Metal Mine Rock and Waste Characterization Tools : An Overview*. Minesota, US. Available at: www.mackay.unr.edu/adti.

Lawrence, R. W. and Scheske, M. (1997) ‘A method to calculate the neutralization potential of mining wastes’, *Environmental Geology*, 32(2), pp. 100–106.

Liu, H., Gu, G. and Xu, Y. (2011) ‘Hydrometallurgy Surface properties of pyrite in the course of bioleaching by pure culture of Acidithiobacillus ferrooxidans and a mixed culture of Acidithiobacillus

ferrooxidans and Acidithiobacillus thiooxidans', *Hydrometallurgy*. Elsevier B.V., 108(1–2), pp. 143–148. doi: 10.1016/j.hydromet.2011.03.010.

Mamba, B., Rietveld, L. and Verberk, J. (2008) 'SA Drinking Water Standards under the microscope', *The Water Wheel*, February, pp. 24–27.

McCarthy, T. S. (2011) 'The impact of acid mine drainage in South Africa', *South African Journal of Science*, 107(5/6), pp. 1–7. doi: 10.4102/sajs.v107i5/6.712.

Miller, S. (2008) *ACARP Project C15034: Development of ARD Assessment for Coal Process Wastes, Environmental Geochemistry International Pty Ltd*. Balmain NSW, Australia. doi: A BN 1 2 0 0 3 79 3 4 8 6.

Miller, S. D., Stewart, W. S., Rusdinar, Y., Schumann, J. M., Ciccarelli, J. M., Li, J., Roger, S. T. and Smart, C. (2010) 'Science of the Total Environment Methods for estimation of long-term non-carbonate neutralisation of acid rock drainage', *Science of the Total Environment, The*. Elsevier B.V., 408(9), pp. 2129–2135. doi: 10.1016/j.scitotenv.2010.01.011.

Mior, R., Morés, S., Welz, B., Carasek, E. and de Andrade, J. B. (2013) 'Determination of sulfur in coal using direct solid sampling and high-resolution continuum source molecular absorption spectrometry of the CS molecule in a graphite furnace', *Talanta*, 106, pp. 368–374. doi: 10.1016/j.talanta.2013.01.004.

Misz-Kennan, M. and Fabianska, M. J. (2011) 'Application of organic petrology and geochemistry to coal waste studies', *International Journal of Coal Geology*, 88(1), pp. 1–23. doi: 10.1016/j.coal.2011.07.001.

Mittermüller, M., Saatz, J. and Daus, B. (2016) 'A sequential extraction procedure to evaluate the mobilization behavior of rare earth elements in soils and tailings materials', *Chemosphere*. Elsevier Ltd, 147, pp. 155–162. doi: 10.1016/j.chemosphere.2015.12.101.

Mohring, R. P. (2001) 'Keynote Address : Coal mining – the future', *Forecast*, (February), pp. 19–24.

Morin, K. A. and Hutt, N. M. (1998) *Kinetic tests and risk assessment for ARD, 5th Annual BC Metal Leaching and ARD Workshop*. 5th. Vancouver, Canada. Available at: http://www.mdag.com/downloads/M0003 - MDAG 1998 ARD Risk Paper.pdf.

Munnik, V. (Mvula T. (2010) *The Social and Environmental Consequences of Coal Mining in South Africa A Case Study, Environmental Monitoring Group*. Cape Town , South Africa.

Nemati, M. and Webb, C. (1997) 'A Kinetic Model for Biological Oxidation of Ferrous Iron by Thiobacillus ferrooxidans', *Biotechnology and Bioengineering*, 53(5), pp. 478–486. doi: CCC 0006-3592/97/050478-09.

O'Brien, G., Jenkins, B., Esterle, J. and Beath, H. (2003) 'Coal characterisation by automated coal petrography', *Fuel*, 82(9), pp. 1067–1073. doi: 10.1016/S0016-2361(02)00428-3.

Oelofse, S. (Department of E. A. and T. (DEAT)) (2008) *Emerging Issues Paper : Mine Water Pollution, Environment & tourism*. doi: ISBN NO: 978-0-9814178-5-1.

Olson, G. J., Brierley, J. and Brierley, C. (2003) 'Bioleaching review part B : Progress in bioleaching : applications of microbial processes by the minerals industries', *Appl Microbiol Biotechnol*, 63, pp. 249–257. doi: 10.1007/s00253-003-1404-6.

Opitz, A. K. B., Broadhurst, J. L. and Harrison, S. T. L. (2015) 'Assessing Environmental Risks Associated with Ultrafine Coal Wastes Using Laboratory-Scale Tests', *Advanced Materials Research*, 1130, pp. 635–639. doi: 10.4028/www.scientific.net/AMR.1130.635.

Opitz , A,K, B. (2013) 'An investigation into accelerated leaching for the purpose of ARD mitigation', MSc Dissertation, University of Cape Town.

Paktunc, A. D. (1999) 'Mineralogical constraints on the determination of neutralization potential and prediction of acid', *Environmental Geology*, 39(December), pp. 103–112.

Parbhakar-fox, A. and Lottermoser, B. G. (2015) 'A critical review of acid rock drainage prediction methods and practices', *Minerals Engineering*. Elsevier Ltd, 82, pp. 107–124. doi: 10.1016/j.mineng.2015.03.015.

Parbhakar-fox, A., Walters, S. and Bradshaw, D. (2011) 'Development of a textural index for the prediction of acid rock drainage', *Minerals Engineering*, doi: 10.1016/j.mineng.2011.04.019.

PerkinElmer Inc. (2004) *The 30-Minute Guide to ICP-MS*. 006355F_01. Waltham, USA. Available at: www.perkinelmer.com.

Pinetown, K. L., Ward, C. R. and van der Westhuizen, W. A. (2007) 'Quantitative evaluation of minerals in coal deposits in the Witbank and Highveld Coalfields, and the potential impact on acid mine drainage', *International Journal of Coal Geology*, 70(1–3 SPEC. ISS.), pp. 166–183. doi: 10.1016/j.coal.2006.02.013.

Pone, J. D. N. *et al.* (2007) 'The spontaneous combustion of coal and its by-products in the Witbank and Sasolburg coalfields of South Africa', *International Journal of Coal Geology*, 72(2), pp. 124–140. doi: 10.1016/j.coal.2007.01.001.

Prevost, X. (2010) 'A clean future for coal', *Inside Mining*, April/May, pp. 14–17.

Rawlings, D. E., Tributsch, H. and Hansford, G. (1999) 'Reasons why â€™ Leptospirillum â€™ -like species rather than Thiobacillus ferrooxidans are the dominant iron-oxidizing bacteria in many commercial processes for the biooxidation of pyrite and related ores', *Microbiology*, 145, pp. 5–13.

Reddick, J. (2006) '*An investigation of cleaner production opportunities in the South African coal*', MSc Dissertation, University of Cape Town.

Reddick, J. F., Von Blottnitz, H. and Kothuis, B. (2007) 'A cleaner production assessment of the ultra-fine coal waste generated in South Africa', *Journal of the Southern African Institute of Mining and Metallurgy*, 107(12), pp. 811–816.

Richardson, J. F. and Harker, J. H. (2002) *Coulson and Richardson's Chemical Engineering Volume 2, Fifth edition Particle technology & Separation Processes*. 5th edn. Oxford: Butterworth-Heineman. doi: 10.1002/1521-3773(20010316)40:6<9823::AID-ANIE9823>3.3.CO;2-C.

Rodriguez, Y., Ballester, A., Blázquez, M. L., González, F. and Muñoz, J. A. (2003) 'New information on the pyrite bioleaching mechanism at low and high temperature', *Hydrometallurgy*, 71, pp. 37–46. doi: 10.1016/S0304-386X(03)00172-5.

Rodushkin, I., Axelsson, M. D. and Burman, E. (2000) 'Multielement analysis of coal by ICP techniques using solution nebulization and laser ablation', *Talanta*, 51, pp. 743–759.

Rohwerder, T., Gehrke, T., Kinzler, K. and Sand, W. (2003) 'Bioleaching review part A : Progress in bioleaching : fundamentals and mechanisms of bacterial metal sulfide oxidation', *Appl Microbiol Biotechnol*, 63, pp. 239–248. doi: 10.1007/s00253-003-1448-7.

SACRM (2011) *Overivew of the South African Coal Value Chain, South African Coal Roadmap*.

Sanyika, N. and Ngcobo, S. (2014) 'Assessing the environmental implications of using froth flotation for mitigating acid rock drainage risks associated with fine coal waste', BSc Project, University of Cape Town.

Schumann, R., Stewart, W., Miller, S., Kawashima, N., Li, J. and Smart, R. (2012) 'Acid-base accounting assessment of mine wastes using the chromium reducible sulfur method', *Science of the Total Environment, The*. Elsevier B.V., 424, pp. 289–296. doi: 10.1016/j.scitotenv.2012.02.010.

Silva, L. F. O., Izquierdo, M., Querol, X., Finkelman, R. B., Oliveira, M. L., Wollenschlager, M., Towler, M., Pérea-López, R. and Macias, F. (2011) 'Leaching of potential hazardous elements of coal cleaning rejects', *Environ Monit Assesz*, 175, pp. 109–126. doi: 10.1007/s10661-010-1497-1.

Smart, R., Skinner, B., Levay, G., Gerson, A., Thomas, J., Sobieraj, H., Schumann, R., Weisner, C. and Weber, P. (2002) *AMIRA International ARD Test Handbook Project P387A Prediction & Kinetic Control of Acid Mine Drainage*. Melbourne, Australia: Ian Wark Research Institute. doi: ACN 004 448 266.

Speight, J. (2005) *Handbook of Coal Analysis, Handbook on coal analysis*. Edited by J. . Winefordner. JOHN WILEY & SONS.INC.

Stewart, W., Miller, S., Kawashima, N., Li, J. and Smart, R. (2009) 'Development of Prediction Methods for ARD Assessment of Coal Process Wastes', *8th International Conference on Acid Rock Drainage*, 8th Intern, pp. 1–14.

Sun, Y., Qi, G., Lei, X., Xu, H., Li, L., Yuan, C. and Wang, Y. (2015) 'Distribution and mode of occurrence of uranium in bottom ash derived from high-germanium coals', *Journal of Environmental Sciences (China)*. Elsevier B.V., pp. 1–8. doi: 10.1016/j.jes.2015.07.009.

Swaine, D. J. (2000) 'Why trace elements are important', *Fuel Processing Technology*, 65–66, pp. 21–33. doi: PII: S0378-3820 99 00073-9.

Szczepanska, J. and Twardowska, I. (1999) 'Distribution and environmental impact of coal-mining wastes in Upper Silesia, Poland', *Environmental Geology*, 38(3), pp. 249–258. doi: 10.1007/s002540050422.

Tessier, A., Campbell, P. G. C. and Bisson, M. (1979) 'Sequential Extraction Procedure for the Speciation of Particulate Trace Metals', *Analytical Chemistry*, 51(7), pp. 844–851. doi: 10.1021/ac50043a017.

The South African Coal Processing Society. (2011) *Coal Preparation in South Africa*. 4th English Edition Reprinted 2011 ISBN 0-620-28565-6 ed. Pietermaritzburg - 3577: Printed by Intrepid Printers (Pty) Ltd.

Tuttle, M., Briggs, P. and Berry, C. (2003) 'A Method to Separate Phases of Sulphur in Mine-Waste piles and Natural Alteration Zones, and to Use Sulphur Isotopic Compositions to Investigate Release of', *Sixth International Conference …*. Available at: http://crustal.cr.usgs.gov/projects/aqueous_geochemistry/pdfs/ICARD_Tuttle.pdf.

Tyler, G. (no date) *ICP Optical Emission Specroscopy Technical Note 05: ICP-OES , ICP-MS and AAS Techniques Compared*. 5. Longjumeau, France. Available at: www.jyhoriba.com.

Vassilev, S. V and Vassileva, C. G. (1997) 'Geochemistry of coals, coal ashes and combustion wastes from coal-fired power stations', *Fuel Processing Technology*, 51(1–2), pp. 19–45. doi: 10.1016/S0378-3820(96)01082-X.

Vontorová, J., Matějka, V., Dědková, K. and Praus, P. (2013) 'The method for determination of sulfur content in nanocomposites', *NANOCON*, 10, pp. 16–18.

Wagner, N. J. and Hlatshwayo, B. (2005) 'The occurrence of potentially hazardous trace elements in five Highveld coals, South Africa', *International Journal of Coal Geology*, 63(3–4), pp. 228–246. doi: 10.1016/j.coal.2005.02.014.

Wang, J., Nakazato, T., Sakanishi, K., Yamada, O., Tao, H. and Saito, I. (2004) 'Microwave digestion

with HNO 3 / H 2 O 2 mixture at high temperatures for determination of trace elements in coal by ICP-OES and ICP-MS', *Analytica Chimica Acta*, 514, pp. 115–124. doi: 10.1016/j.aca.2004.03.040.

Wang, J., Nakazato, T., Sakanishi, K., Yamada, O., Tao, H. and Saito, I. (2006) 'Single-step microwave digestion with HNO 3 alone for determination of trace elements in coal by ICP spectrometry', *Talanta*, 68, pp. 1584–1590. doi: 10.1016/j.talanta.2005.08.034.

Ward, C. R. (2002) 'Analysis and significance of mineral matter in coal seams', *International Journal of Coal Geology*, 50(1–4), pp. 135–168. doi: 10.1016/S0166-5162(02)00117-9.

Watkins, T., Ridley, M. K., Poignet, B. M. A. and Willia, J. P. (1995) 'Determination of rare-earth elements in coal using microwave digestion and gradient ion chromatography', *Chemical Geology*, 121, pp. 273–283.

Weber, P. A., Thomas, J. E., Skinner, W. M. and Smart, R. St. C. (2004) 'Improved acid neutralisation capacity assessment of iron carbonates by titration and theoretical calculation', *Applied Geochemistry*, 19, pp. 687–694. doi: 10.1016/j.apgeochem.2003.09.002.

Weston, A. (2011) 'Work-related lung diseases.', *IARC scientific publications*, (163), pp. 387–405. Available at: http://www.scopus.com/inward/record.url?eid=2-s2.0-84867288891&partnerID=40&md5=03e5c9a76c6680f0d7a57e9a71dcb0f2.

Xu, Y., Iwashita, A. and Nakajima, T. (2005) 'Effect of HF addition on the microwave-assisted acid-digestion for the determination of metals in coal by inductively coupled plasma-atomic emission spectrometry', *Talanta*, 66, pp. 58–64. doi: 10.1016/j.talanta.2004.09.018.

Yahya, A. and Johnson, D. B. (2002) 'Bioleaching of pyrite at low pH and low redox potentials by novel mesophilic Gram-positive bacteria', *Hydrometallurgy*, 63, pp. 181–188. doi: PII: S0304-386X(01)00224-9.

Zhang, J., Ren, D., Zhu, Y., Chou, C. -L., Zeng, R. and Zheng, B. (2004) 'Mineral matter and potentially hazardous trace elements in coals from Qianxi Fault Depression Area in southwestern Guizhou , China', *International Journal of Coal Geology*, 57, pp. 49–61. doi: 10.1016/j.coal.2003.07.001.

Zhao, B. (2012) 'Environmental assessment of Durban Navigation Colliery discard dumps in the Klip River coalfield, Kwazulu-Natal Province of South Africa', *Environmental Earth Sciences*, 67(3), pp. 743–757. doi: 10.1007/s12665-012-1533-2.

Zhu, Q. (2014) *Coal sampling and analysis standards*. London, UK: IEA Clean Coal Centre. Available at: www.iea-coal.org.

Zimmerman, A. J. and Weindorf, D. C. (2010) 'Heavy metal and trace metal analysis in soil by sequential extraction: a review of procedures.', *International journal of analytical chemistry*, 2010, p.

387803. doi: 10.1155/2010/387803.

Websites

Winter, M. (1993-2018) 'Abundance in Earth's crust, ' The University of Sheffield and the WebElements Ltd, UK. Retrieved from https://www.webelements.com/periodicity/abund_crust_a/

APPENDIX A

MATERIALS AND METHODS

A.1. QEMSCAN Analysis

Procedure

1. Weigh 100 g of dry carnauba wax in a 500 ml glass beaker.
2. Put the beaker in the microwave and melt the wax to dark yellow liquid.
3. Weigh out 0.2 g of sample and place in each 25 mm mould oiled with mould release spray oil
4. Add approximately 8.5 g of hot wax to the mould and stir quickly in a figure of 8 pattern.
5. Place the moulds in a 60 ^{O}C oven to cure for 40 min, then takeout and allow cooling to room temperature.
6. Take out the wax sample from the 25 mm mould and place in a 30 mm mould and fill up the 30 mm mould with epoxy resin.
7. Leave the mould in a pressure pot to settle overnight.
8. Add a printed label and a further resin to the back of the mould before allowing the mould to cure to dryness in the oven at 30 ^{O}C.
9. Remove the block from the mould then polish using a series of grinding and polishing with sand paper until 1 µm polish. Carefully rinse and lightly soap the block between each grinding and polishing step to remove grits and scratches.
10. After polishing soaping and rinsing the blocks, place them in the ultrasonic bath for approximately 10 minutes. Clean them once more with excess ethanol paying attention to avoid scratching the surface.
11. Leave the blocks for at least 1 hour in the oven set at 30º C to allow the blocks to dry.
12. Check the quality of the final polish under an optical microscope ensuring that there are no plucked grains, large differences in relief, cracked / or grungy looking grains on the block's surface.
13. Carbon-coat the samples using the Emitech carbon evaporator to allow diffusion of electrons off the surface of the sample during detection. Then analyse the coated blocks by QEMSCAN.

A.2. Total Sulphur Standard Eschka Method (ISO/ SANS 334:1992)

Reagents

- Eschka mixture
- 36 % HCl
- 2 g /L potassium sulphate (K_2SO_4) solution (dry the K_2SO_4 at 105 – 110 ^{O}C before dissolving)
- 85 g / L barium chloride ($BaCl_2$) solution (filtered before use)
- 1 g / L Methyl red indicator solution
- 25 % ammonia (NH_3) solution
- 17 g/L Silver nitrate ($AgNO_3$) solution

Table 51 Eschka method - test portion for coal

Expected total sulphur content (wt. %)	**Mass of test portion (g)**
< 5	1.0
5 - 10	0.5
>10	0.25

NB* All mass weighed to the nearest 0.1 mg

A.2.1. Ignition and Recovering the Residue

Procedure

1. Cover the bottom of the crucible uniformly with 0.5 g weighed of the Eschka mixture.
2. Mix intimately appropriate amount (from table 1) of the sample with 2.5 g of the Eschka mixture and transfer to the crucible. Cover the mixture with 1.0 g of the Eschka mixture.
3. Place the charged crucible in a cold muffle furnace and raise the temperature to 800 ± 25^{O}C and maintain at this temperature for 90 minutes.
4. Remove the crucibles and place in a desiccator to cool.
5. Transfer the ignited mixture from the crucible to a 400 ml beaker containing 25 -30 ml of water and if there are unburnt particles present repeat the test from step 1.
6. Wash the crucible thoroughly with about 50 ml of hot water and add the washings to the contents of the beaker.

A.2.2. Extraction and Precipitation of Barium Sulphate

1. Place a watch glass on the beaker and while tilting the watch glass, carefully add enough HCl to dissolve the solid matter (17 ml will normally be required), warming the contents of the beaker to effect solution.
2. Boil for 5 minutes to expel carbon dioxide and filter (medium- textured, doubly acid-washed filter paper or filter paper pad is recommended for quick filtration), collecting the filtrate in a 400 ml conical beaker.

3. Wash the filter with five 20 ml portions of hot water.
4. Add 2-3 drops of methyl red indicator solution to the combined filtrate and washings and then cautiously add the ammonia solution until the colour of the indicator changes and a trace of precipitation is formed.
5. Add enough HCl to just re-dissolve the precipitate and then add 1 ml in excess.
6. Dilute the solution if necessary to approximately 200 ml and cover the beaker with a watch glass.
7. Heat the covered beaker until the solution boils and then reduce the heating slightly until ebullition of the solution ceases.
8. Add 10 ml of the cold $BaCl_2$ solution from a pipette with a delivery time of approximately 20 seconds, so that the $BaCl_2$ solution falls into the centre of the hot solution, while it is being agitated.
9. Keep the solution just below boiling point for 30 minutes
10. Filter the solution using one of the techniques:

a. By gravity through an ash-less, close textured, doubly acid washed filter paper of diameter 100-125 mm. Carefully fold the filter paper and fit it into a long stemmed 60^O funnel, so that the stem remains full of liquid during the filtration.

b. By gravity through a filter-paper pad prepared from ash-less, close textured, doubly acid washed filter paper.

c. By suction through a pad of filtration mineral fibre in a Gooch crucible. Before commencing the filtration, dry the Gooch crucible pad for 1 hour at 130 ^{O}C ± 10 ^{O}C and weigh to the nearest 0.1 mg

11. Wash the precipitate with hot water, using not more than 250 ml, until the last 20 ml of the washings give not more than a faint opalescence with the silver nitrate solution.
12. If technique a. or b. is used for filtration, place the wet filter paper or pad (add to the pad 2 halves of filter paper used to successively wipe the funnel) in a previously ignited and weighed crucible. Place crucible on a flat plate and insert into a muffled furnace at a temperature of 800 ^{O}C ± 25 ^{O}C and heat for 15 minutes. Cool in a desiccator and reweigh.
13. If technique c. is used for filtration, dry the Gooch crucible and pad for 1 hour at 130 ^{O}C ± 10 ^{O}C, cool in a desiccator and reweigh.

Blank test

1. Carry out the same procedure for the ignition and residue recovery but omitting the test portion.
2. Follow the extraction and precipitation of $BaSO_4$ procedure but pipetting 25.0 ml of potassium sulphate solution to the filtrate before adding the methyl red indicator solution.

Calculation

$$S\ \% = \frac{13.74\ (m_2\ -\ m_3 + 0.03348\ \rho_{K2SO4}\ )}{m1} \qquad (50)$$

Where:

- m_1 is the test portion mass expressed in grams
- m_2 is the determined $BaSO_4$ mass, expressed in grams
- m_3 is the $BaSO_4$ in the blank, expressed in grams
- ρ_{K2SO4} is the mass concentration expressed in grams per litre, of the potassium sulphate solution

The result is reported on an air-dried basis, as the mean of duplicate determinations to the nearest 0.1 % (m/m).

Precision

The duplicate determinations should not differ by more than 0.05 % absolute.

A.3. Sulphur Forms Assessment

A.3.1. ISO 157:1996 Protocol

Sample preparation

Grind about 25 g of the sample to below 75 µm and ensure the moisture content is in equilibrium with the laboratory atmosphere. Before the test mix the sample thoroughly for at least 1 minute, preferably by mechanical means.

Acid Digestion / Extraction

Reagents

- Concentrated HCl approximately 36 % (m/m)
- 15 % HCl made by diluting 420 ml concentrated acid (36 % m/m) to 1 L with distilled water
- 9 % HNO_3 made by diluting 130 ml of concentrated acid (approximately 70 % m/m) to 1 L with distilled water

NB – Care must be exercised when handling the reagents, many of which are toxic and corrosive.

Procedure

1. Weigh out sample according to table below

Table 52 ISO 157:1996 method - test portion for coal

Total sulphur content (wt. %)	Mass of sample (g)
< 0.7	8
0.7 - 2.0	5
>0.7	2

2. After transferring the sample to a 250 ml Erlenmeyer flask, add 50 ml of 15 % HCl and fit a cold-finger condenser into the neck of the flask.
3. Boil for 30 minutes ensuring that a slow stream of water is passing the cold finger.
4. Remove the condenser and thoroughly rinse back into the flask.

5. Filter the mixture through a medium-textured, doubly acid-washed filter paper into a tall-form beaker.
6. Wash the residue three times with the 15 % HCl and rinse three times using a total volume of 30 ml of hot distilled water.
7. Preserve the filtrate for sulphates sulphur analysis. Immediately transfer the washed, undissolved residue and filter paper to a 250 ml Erlenmeyer flask, add 50 ml of the dilute nitric acid and retain for the pyritic sulphur determination.

Sulphate Sulphur Determination

Reagents

- H_2O_2 approximately 30 % m/m
- Methyl red indicator solution made by dissolving 1 g of 2-(4-dimethylaminophenylazo) benzoic acid, sodium salt (methyl red) in 1 L of water.
- Concentrated NH_3 solution (not less than 25 % (m/m)).
- Concentrated HCl (approximately 36 % (m/m)).
- 2 g/L K_2SO_4
- 85 g/L $BaCl_2$ solution filtered before use through a close-textured, doubly acid washed filter paper or filter pad.
- 17 g/L $AgNO_3$ stored in a dark glass bottle

Procedure

1. Add 5 ml of 30 % H_2O_2 to the filtrate from step 5 and boil for 5 minutes to convert all the soluble iron to Fe^{3+}.
2. To the hot solution, add 2-3 drops of methyl red indicator followed by dropwise addition of 25 % NH_3 solution until the solution is just alkaline (yellow colour), then add 5 additional drops.
3. Filter the resultant precipitate on a toughened fast filter paper into a 250 ml beaker and wash thoroughly with hot water, discarding the precipitate.
4. Cautiously add 36 % HCl dropwise until the colour change to pink is observed, then add a further 1 ml in excess. The solution volume should be between 150 and 250 ml.
5. Add 25 ml of 2 g/L K_2SO_4 from a one-mark pipette and cover beaker with a watch glass and apply heat until the solution boils and then reduce the heating slightly until ebullition ceases.
6. Add 10 ml of 85 g/L $BaCl_2$ solution from a pipette with a delivery time of approximately 20 seconds, held so that the $BaCl_2$ falls into the centre of the hot solution, whilst this is being agitated. Keep the solution just below boiling point without agitation for 30 minutes.
7. Filter the solution either by gravity through an ash-less, close textured, doubly acid-washed filter paper or filter paper pad, or by suction through a pad of mineral fibre used for filtration in a Gooch

crucible (before filtration dry the Gooch crucible and pad for 1 hour at 130 ^{O}C ± 10 ^{O}C and weigh them).

8. Wash the precipitate with hot water, using not more than 250 ml, until the last 20 ml of the washing give not more than a faint opalescence with 17 g/L $AgNO_3$.Amount of sulphate sulphur in the precipitate is determined gravimetrically.
9. If filter was by gravity, place the wet filter paper or pad in the previously ignited and weighed crucible on the cold flat plate and insert it into a muffle furnace for 15 minutes at 800 ^{O}C ± 25 ^{O}C. cool in a desiccator and reweigh. If filter was by suction dry the Gooch crucible and pad for 1 hour at 130 ^{O}C ± 10 ^{O}C and reweigh them.
10. Prepare a blank solution by following steps 1-9 but omitting the test filtrate. Using a pipette add 25 ml of the K_2SO_4 solution to the filtrate before adding the methyl red indicator.

Calculation:

The sulphate sulphur content $W_{S,s}$ of the sample expressed as a percentage by mass is given by the equation

$$W_{S,s} = \frac{m_2 - m_3}{m_1} \times 13.74 \qquad (51)$$

Where;

- m_1 is the test portion mass, in grams used in HCl extraction
- m_2 is the $BaSO_4$ mass in grams of found in the determination
- m_3 is the $BaSO_4$ in the blank mass expressed as grams

Report the result as the mean of duplicate determinations, to the nearest 0.01 % (m/m)

Pyritic Sulphur Determination

Procedure

1. Take the 250 ml conical flask retained from the HCl extraction and macerate the residue and filter paper immersed in the HNO_3, with a flat ended glass rod, rinsing the rod on withdrawal.
2. Fit the cold finger condenser into the neck of the flask and boil the mixture for half an hour, ensuring that a slow stream of water is passing through the cold finger.
3. Remove the condenser, rinse thoroughly into the conical flask and filter the mixture through a medium-textured, doubly acid washed filter paper into a beaker.
4. Wash the residue three times with dilute HNO_3 solution and use 30 ml of hot water to rinse the residues three times. Discard the undissolved residue.
5. Add 5 ml of 30 % H_2O_2 to the filtrate and boil for 5 minutes to destroy any coloration arising from the decomposition of the coal.
6. After cooling the solution, iron content is analysed by one of three methods:

a) Atomic absorption spectroscopy (AAS)
b) Titrimetry
c) Colorimetry

7. The iron content is then back calculated assuming a stoichiometry where 1 mole of pyrite (MW = 87.84) per mole of Fe (MW = 55.84) is used.

A.3.2. ACARP C15034 Protocol

Reagents

- Zinc acetate solution (for digestion) made by dissolving 60 g of zinc acetate in 1.5 L deionised water
- 1 % Zinc acetate solution (for S^- analysis) made by dissolving 10 g of zinc acetate in 1 L deionised water
- 95 % Ethanol solution
- Technical grade chromium powder
- Standardised 6 M HCl made by slowly adding approximately 585 ml of 32 % HCl to 400 ml of deionised water and diluting to 1 L with deionised water
- N, N-dimethyl-ρ-phenylene diamine dihydrochloride (DMPD) solution made by dissolving 2 g of DMPD in 500 ml of 6 M HCl solution
- Ferric Chloride ($FeCl_3.6H_2O$) solution made by dissolving 8 g of $FeCl_3.6H_2O$ in 500 ml of 6 M HCl
- Sulphide stock solution (100 mg/L) made by dissolving 750 mg of $Na_2S.9H_2O$ in 1 L deionised water
- Standardised 1 M KCl made by dissolving 74.5513 g of KCl in 1 L deionised water
- Standardised 0.1 M NaOH

Pyritic Sulphur Determination Procedure According to the CRS Method

1. Weigh out 0.500 g (to the nearest 0.000) of sample into a 250 ml double-neck round bottom digestion flask and include a blank in each batch.
2. To 2.0 g of the chromium powder in the digestion flask add 10 ml of 95 % ethanol and wet the sample by swirling.
3. In a fume-hood set up the apparatus (as shown in Figure 50) by placing the digestion flask in the heating mantle and connecting to the condenser. Then attach the pressure equalising funnel making sure the gas flow arm is facing the condensers and that the solution tap is shut. Attach Pasteur pipette to the outlet tube at the top of the condenser and insert it into a 100 ml Erlenmeyer flask containing 50 ml zinc acetate solution.
4. Ensuring there are no leaks, turn on the water to flow around the condenser. Add 60 ml of 6 M HCl to the glass dispenser in the pressure equalising funnel.

5. Turn on the N_2 supply flow to the pressure equalising funnel adjusting the flowrate to 3 bubbles/second in the zinc acetate solution. Continue purging the system with N_2 gas for 3 minutes.
6. Release a trickle of HCl acid slowly into the round-bottomed flask.
7. Allow the contents to react for 2 min before switching on the heating mantle with the knob set to achieve a gentle boil. Ensure there is sufficient reflux in the condenser and allow 20 min digestion of the digestion flask contents.
8. Remove the Erlenmeyer flask and use wash bottle deionised water to wash an ZnS on the Pasteur pipette into the Erlenmeyer flask.

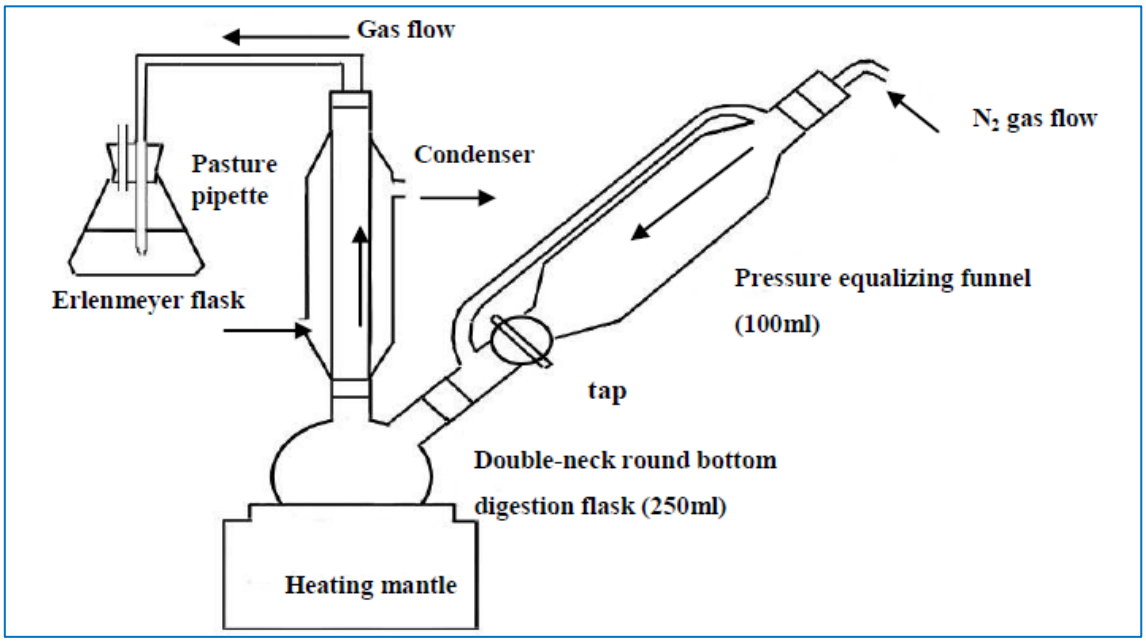

Figure 50 CRS set up (Ahern et al., 2004)

Sulphide Analysis

The sulphide concentration in the ZnS solution in the Erlenmeyer flask is analysed by a UV-Vis spectrophotometer according to the method by Cline (1969)

a) Using Table 53 for dilutions:
b) Pipette 200 µL of 1 % zinc acetate into a test tube.
c) Add 20 µL of sample.
d) Top up the test tube contents to 5 ml with deionised water.
e) Add 0.5 ml of N, N-dimethyl-p-phenylene diamine dihydrochloric solution.
f) Add 0.5 ml of ferric chloride solution.
g) Vortex (10-20 s), allow 5 minutes for blue colour to develop.
h) Read absorbance at 670 nm after setting it to zero with a blank.
i) Calculate the sulphide concentration from a standard curve gradient of 0.84 nm / (mg/ L).

Table 53 Dilution factors for sulphide analysis (Cline, 1969)

Sulphide concentration (µmole / litre)	Diamine concentration (g / 500 ml)	Ferric concentration (g / 500 ml)	Dilution factor (ml : ml)	Path length (cm)
1 – 3	0.5	0.75	1:1	10
3 – 40	2.0	3.0	1:1	1
40 – 250	8.0	12.0	2:25	1
250 – 1000	20.0	30.0	1:50	1

The KCl Extraction Procedure

1. Prior to the test, ensure the 1 M KCl solution is inert by purging the solution for half an hour with with argon gas.
2. To the 2.00 g of pulverised sample (-75 µm) in the 125ml plastic bottle add 80 ml of the inert 1 M KCl solution.
3. Remove oxygen in the bottle's head space by purging with nitrogen or argon gas.
4. After sealing and shaking the bottle, further mix the contents by tumbling in a centrifuge for 1 hour.
5. Filter the sample through a 0.45µm filter paper soon after removing the bottle from the centrifuge.
6. Test the pH of the filtered solution and if pH exceeds 7, take a 30-40ml portion of the filtered liquor for determination of acid sulphate by titrating to pH 7 with 0.1 M NaOH.
7. Analyse the remaining portion of the filtered solution for soluble sulphates using ICP-OES (this was replaced by the turbidity sulphate method).

Calculation:

The KCl acid sulphate S is calculated from the equation

$$KCl\ Acid\ Sulphate\ S\ (\%) = \frac{Vol_{NaOH} \times Mol_{NaOH} \times Vol_{Extract} \times {}^{32.06}/_{2}}{Wt_{Samp} \times Vol_{Titrated} \times 10} \quad (52)$$

Where:

- Vol_{NaOH} is the titration volume of NaOH required to bring the extract solution to pH 7
- Mol_{NaOH} is molar concentration of NaOH in mol/L
- $Vol_{Extract}$ is the volume of the original extract solution in ml (80 ml)
- Wt_{Samp} is the weight of sample used for original extraction in g (approx. 2g)
- $Vol_{Titrated}$ is the volume of the solution aliquot actually titrated in ml (30-40 ml)

The S species are differentiated as:

Pyritic S (%) = CRS (%)

Acid Sulphate = KCl acid sulphate S

Non-Acid Sulphate S = KCl S – KCl Acid Sulphate S

Low-risk S Forms = Total S – (CRS + KCl S)

Sulphate Analysis (Turbidity Method)

Reagents

- Conditioning solution made by dissolving 75 g NaCl, 30 ml of 32 % HCl, 50 ml glycerol and 100 ml ethanol in 300 ml deionised water
- $BaCl_2$ (20-30 mesh or finer)
- Standard sulphate solution of 100 mg /L made by dissolution of 0.1479 g Na_2SO_4 in 1 L of deionised water

Procedure

1. Centrifuge or filter samples to remove suspended solids.
2. Add 5 ml of appropriately diluted sample to a test tube.
3. Add 0.25 ml conditioning reagent, followed by one micro scoop of finely ground $BaCl_2$.
4. Mix on a vortex mixer for 1 min.
5. Read absorbance at 420 nm.
6. The absorbance values can be translated to sulphate concentration using a sulphate standard curve (0-50 mg/L SO_4^{2-}).

Calculations

The KCl extractible S is calculated as follows:

$$S\ (wt\ \%) = \frac{(32.06/96.06) \times Conc_{SO4} \times Vol_{KCl} \times 100\ \%}{1000 \times Sample\ weight} \qquad (53)$$

Where

- $Conc_{so4}$ is sulphate concentration in mg/ L,
- Vol_{KCl} is the initial volume 80 ml expressed as L (0.08 L)
- Sample weight is the amount of sample used for extraction i.e. 2 g

NB for residues from ARD static tests digestion S (wt %) are multiplied by weight loss factor calculated as follows:

$$Weight\ loss\ factor = 1 - \left((initial\ mass - final\ mass)/initial\ mass\right) \qquad (54)$$

Where initial mass is the amount of sample digested under static tests and final mass is the mass of the residue after drying

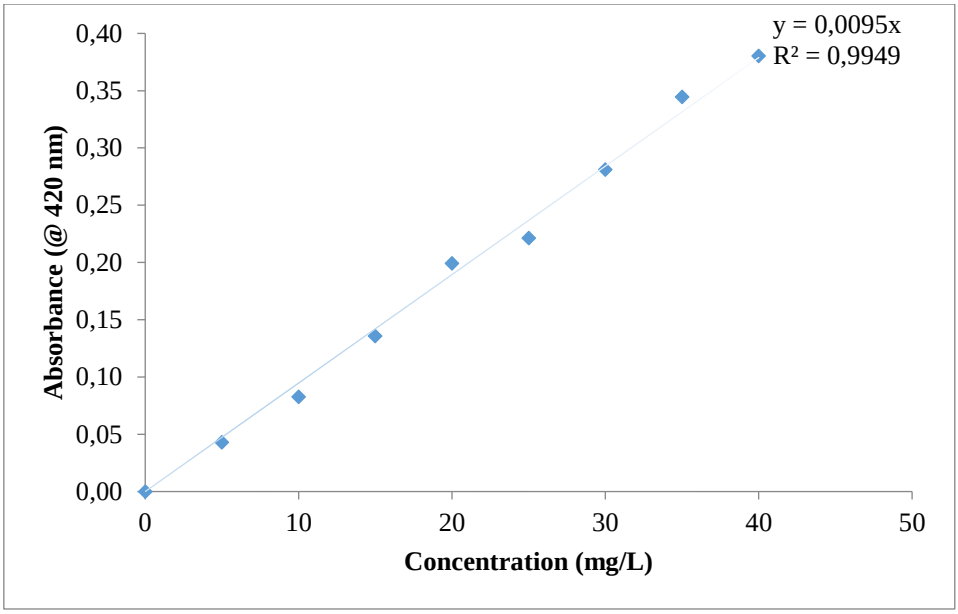

Figure 51 Sulphate standard curve

A.4. Characterisation of ARD Potential

A.4.1. ABA and NAG Tests

Reagents

- Deionised water
- Standardized 0.5M NaOH solution made by dissolving 20.0 g of NaOH granules in 1 litre deionised water
- Standardized 0.1 M NaOH solution made by diluting 0.5 M NaOH 1:4 with deionized water and
- Certified grade 0.1 M HCl solution
- Certified grade 0.1 M NaOH solution
- Standardized 0.5 M HCl solution made by diluting 42 ml concentrated HCl (36 % m/m) to 1 L with deionized water
- Standardized 0.1 M HCl solution made by diluting 0.5 M HCl 1:4 with deionised water
- 25 % HCl solution made by diluting concentrated acid 1:3 with deionised water
- 30 % H_2O_2 solution
- 15 % H_2O_2 made by diluting 30 % H_2O_2 1:1 with deionised water

NB H_2O_2 solution should be at room temperature and of pH between 4.5 and 6.0. If pH is below 4.5 bring it up to above 4.5 by adding dilute NaOH solution made up by adding 1 g NaOH to 100 ml deionized H_2O.

Reagent standardisation

- NaOH solution is standardised by titrating 50 ml of certified 0.1 N HCl to pH 7 with the prepared 0.1 N NaOH. Normality of the NaOH is calculated using the equation:

$$N_2 = \frac{N_1 V_1}{V_2} \qquad (55)$$

Where:

V_1 = Volume of HCl used.

N_1 = Normality of HCl used.

V_2 = Volume of NaOH used.

N_2 = Calculated Normality of NaOH

- HCl solution is standardised by titrating 20 ml of certified 0.1 NaOH to pH 7 with the prepared 0.1 N HCl. Normality of the HCl is calculated using the equation:

$$N_1 = \frac{N_2 V_2}{V_1} \qquad (56)$$

Where:

V_2 = Volume of NaOH used.

N_2 = Normality of NaOH used.

V_1 = Volume of HCl used.

N_1 = Calculated Normality of HCl.

A.4.2. Incremental H_2O_2 Modified Sobek ANC Test

Fizz Rating

Procedure

1. Place approximately 0.5 g of pulverised sample on a watch glass or piece of aluminium foil.
2. 0ne or two drops of 25% HCl added to the sample.
3. Bubbles or fizzing sound indicate the presence of $CaCO_3$. The fizz or bubbling is rated as indicated in the table below.

Table 54 Fizz ratings and associated acid quantities and concentrations to be used in the ANC

Reaction	Fizz rating	HCl molarity (M)	HCl volume (ml)	NaOH molarity (M)
None	0	0.5	4	0.1
Slight	1	0.5	8	0.1
Moderate	2	0.5	20	0.5
Strong	3	0.5	40	0.5
Very Strong	4	0.1	40	0.5
Carbonate	5	0.1	60	0.5

Digestion

Procedure (Weber et al., 2004)

1. In a 250 ml conical flask, place approximately 2.00 g of dry pulverised sample.
2. Carefully add HCl (appropriate volume and concentration) to each beaker. The volume and concentration of HCl is based on the fizz rating.
3. Flush the sample on the flask sides to the bottom with 20 ml deionised water.
4. Heat the flask contents at 90 ^{O}C for 1-2 hours and allow to cool for 1 hour at room temperature.
5. Top up the solution to 125 ml with deionised water.
6. Check solution's pH, if in the range 0.8 – 1.5, then proceed with the titration.

The reaction is complete when no gas evolution is visible and particles settle evenly over the bottom of the flask.

Table 55 Guidelines for adjusting the pH within the target range prior to back titration (Smart et al. 2002)

pH of mixture	Remarks
pH> 1.5	Too little acid was added to the sample, add more acid to match the next fizz rating on the same sample portion or repeat the test on a new portion of the sample using reagent amounts stipulated by the next fizz rating unless the previous fizz rate was 0
pH< 0.8	Indicates possibility of addition of excess acid unless a fizz rate of 5 was used. Using reagent amounts stipulated by a lower fizz rate is recommended.

Back Titration

1. Filter ANC digest solution.
2. Titrate the filtered solution with NaOH (using a burette) to pH 4.5.
3. Add 10 drops of 30 % H_2O_2 and allow to react for 15 minutes.
4. Measure pH and if it dropped, back titrate with NaOH to pH 4.5.
5. Repeat addition of H_2O_2 and back titration as described in steps 3-4 until pH is constant after step 3.

6. Back titrate with NaOH to pH 7.0.
7. Add 10 drops of 30 % H_2O_2 and allow to react for 15 minutes.
8. Measure pH and if it dropped, back titrate with NaOH to pH 7.0.
9. Repeat addition of H_2O_2 and back titration as described in steps 6 and8 until pH is constant after step 7 (no pH change to 1 decimal places in 15 minutes).
10. Leave the solution for 24 hours.
11. Measure pH and if pH dropped, back titrate to pH 7.0.
12. Add 10 drops of 30 % H_2O_2, and leave for approximately 24 hours.
13. Repeat addition of H_2O_2 and back titration as described in steps 10 to 12 over 72 hours.
14. The ANC is calculated per:

$$ANC = \frac{[(Volume_{HCl} - (Volume_{NaOH} * C)) * M_{acid}] * 49}{W_{sample}} \quad (57)$$

Where:

M_{acid} is the molarity (or normality) of HCl (M), W_{sample}, the mass of digested sample (g) and "C" taking molarity factor for NaOH and HCl solutions which is calculated as:

$$C = \frac{Volume_{HCl\ in\ blank}}{Volume_{NaOH\ titrated\ in\ blank}} \quad (58)$$

49 is a conversion factor to express ANC in kg H_2SO_4/Ton.

A.4.3. Conventional Single Addition NAG Tests

NAG tests are based on simultaneous acid–forming reaction (rapid oxidation of sulphide sulphur by H_2O_2) and acid neutralising reaction.

Procedure (Smart et al. 2002)

1. In a 500 ml conical flask, place approximately 2.50 g of dry pulverised sample.
2. After weighing the flask and contents, carefully add 250 ml of 15 % H_2O_2 to the conical flask. Record the mass again after addition of H_2O_2.
3. Place the flask in a fume hood after covering it with a watch glass and let the contents to react for 24 hours. Rapid and vigorous NAG reactions can "boil-over".
4. Measure the pre-boil NAG_{pH}.
5. After the reaction, bring the flask to a gentle boil on a hot plate for at least 2 hours or until effervescence ceases. Occasional topping with deionised water is required to keep a constant volume.
6. Allow the samples to cool to room temperature.
7. Flush the sample on the flask sides to the bottom with deionised to give a final volume of 250 ml.
8. Measure the solution's after boil NAG pH (NAG_{pH}).

9. Filter the NAG solution and preserve filtrate for titration and residues for further analysis.
10. While stirring, titrate solution to pH 4.5 and 7.0, with NaOH of molarity determined on NAG_{pH} as follows:
    - When NAG_{pH} is > 2 titrate with 0.10M NaOH
    - When NAG_{pH} is ≤ 2 titrate with 0.50M NaOH
11. The NAG is calculated based on the quantity of NaOH consumed in the titration.

Calculation

$$NAG = \frac{49 \times V \times M}{W} \qquad (59)$$

Where:

V is the total of NaOH used (ml)

M is the molarity (calculated from standardisation) of the NaOH solution

W is the mass in grams of digested sample.

49 is a conversion factor to express NAG capacity in kg H_2SO_4/Ton.

A.4.4. Extended Boil NAG Tests (ACARP Project C15034)

Procedure (Miller, 2008)

1. Do a standard NAG test (steps 1 to 9 of the single addition NAG).
2. If the NAG_{pH} is ≤ 4.5 split the filtrate into:
    - Sample A 100 ml – for extended boil
    - Sample B 100 ml- for solution assay
    - Sample C 50 ml – stored as reserve in case of follow up requirement
3. Carry out extended boiling step on sample A (vigorous boiling of the solution on a hot plate for 3-4 hours).
4. Cool the sample and measure pH.
5. If Ext Boil NAG_{pH} < 4.5 the sample is likely to be PAF and carry out Calculated NAG procedure on sample B. Sample B is assayed for concentrations of anions and cations of S, Ca, Mg, Na, K and Cl and the NAG value calculated as follows:

$$Acid\ component = \left[{}^{[S]}/_{32.06}\right] \times \left[{}^{Vol_{NAG}}/_{Wt_{samp}}\right] \times 98.07 \qquad (60)$$

$$Neutralising\ Component = \left[\left({}^{[Ca]}/_{40.1}\right) + \left({}^{[Mg]}/_{24.3}\right) + 0.5 \times \left({}^{[Na]}/_{22.9}\right) + 0.5 \times \left({}^{[K]}/_{39.1}\right) - 0.5 \times \left({}^{[Cl]}/_{33.45}\right)\right] \times \left[{}^{Vol_{NAG}}/_{Wt_{samp}}\right] \times 98.07 \qquad (61)$$

$$Calculated\ NAG\ Acidity = (Acid\ Component) - (Neutralising\ Component) \qquad (62)$$

Where

- Concentration of S, Ca, Mg, Na, K, and Cl are in mg/L
- Vol_{NAG} is the volume of the original NAG solution in litres (normally 0.25 L)
- Wt_{sample} is the weight of the sample used in the original NAG test in grams (normally 2.5 g)
- Calculated NAG Acidity is in units kg H_2SO_4 per Ton (Calculated NAG≤0 means sample is likely to be NAF and otherwise means sample is likely to be PAF)

The Extended Boil protocol is as follows:

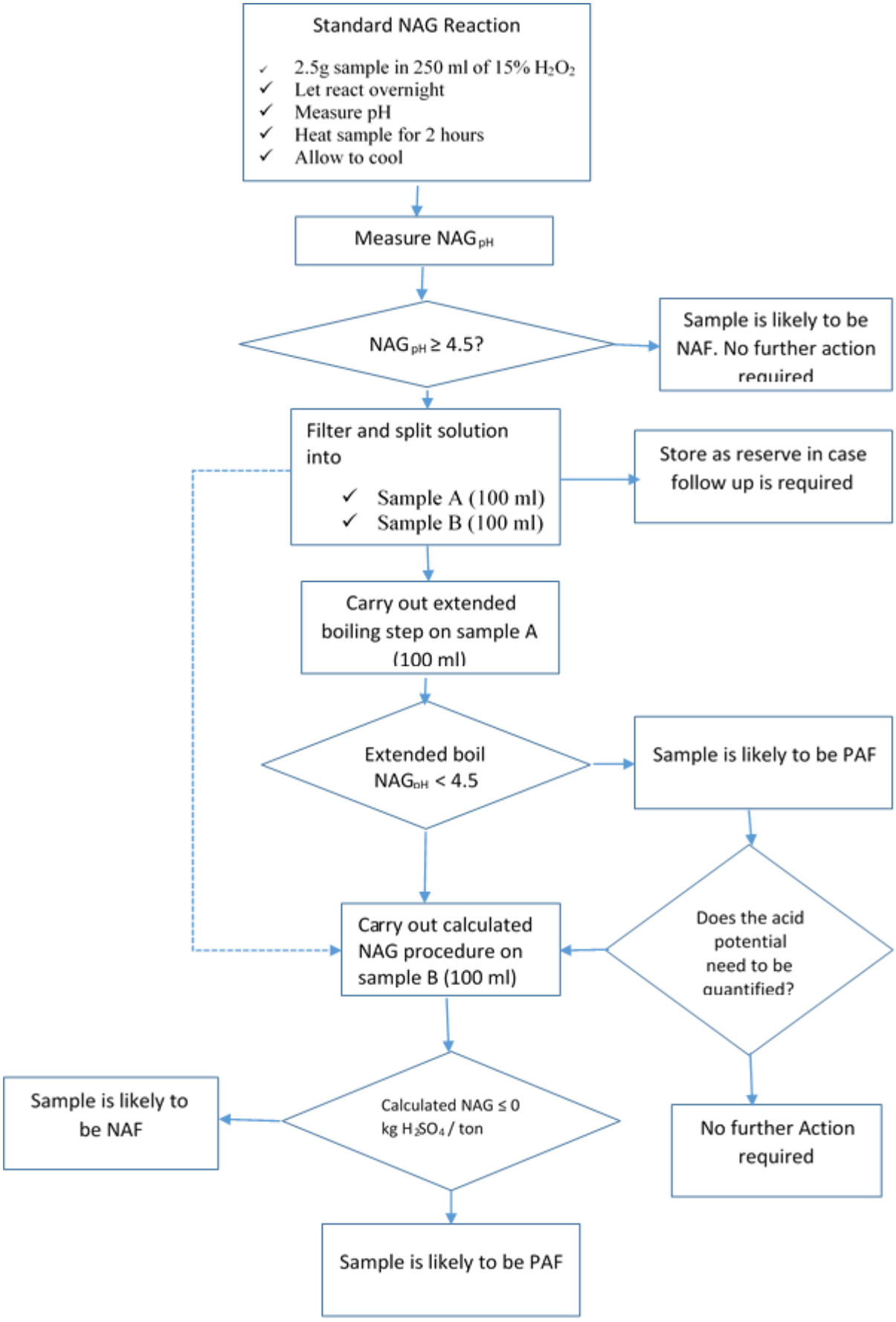

Figure 52 Extended Boil NAG protocol

A.4.5. Batch Shake Flask Tests (Hesketh *et al.*, 2010)

Reagent and equipment

- Autotrophic basal salt medium (ABS)
- 250ml Erlenmeyer flasks
- 7.5g milled sample (100% below 75 µm) per flask
- 96 – 98 % concentrated H_2SO_4 acid
- 0.5 M H_2SO_4 acid

Test Conditions

The inoculated biokinetic tests will be run at the same time to have the same initial inoculum conditions. The non-inoculated tests will be run after the sampling intervals have reduced for the inoculated tests

- inoculated with controlled pH
- inoculated with uncontrolled pH
- non-inoculated with controlled pH
- non-inoculated with uncontrolled pH

Inoculum Preparation

Procedure

1. Equal volumes (to give a cell concentration of 10^9 cells/ ml) of mesophilic mixed culture dominated by *Lesptospirrilum ferriphilum* (iron oxidiser) will be co-cultured with *Acidthiobacilus caldus* (sulphur oxidiser). The cultures will be obtained from the 35ºC stock reactor and bioleaching stock reactor respectively in FeS lab (CeBER).
2. Culture control flasks (3) containing 7.5 g pyrite and 150 ml ABS solution will be inoculated with 10^9 cells and run at 37 ^{O}C and 150 rpm to monitor cell growth.

ABS Media Preparation

1. Make 1 Litre 50x solution by dissolving 7.5 g $(NH4)_2SO_4$, 7.5 g $Na_2SO_4.10H_2O$, 2.5 g KCl, 25 g $MgSO_4.7H_2O$, 2.5 g KH_2PO4 and $Ca(NO_3)_2.4H_2O$ in deionised water.
2. The 50x stock solution to will be diluted to make 1x ABS solution.

Shake Flask Operation

1. Sterilize flasks covered with cotton plugs and aluminium foil by autoclaving.
2. Adjust the pH of ABS using concentrated 96-98 % H_2SO_4 to pH 2.
3. Sterilize the ABS solution in an autoclave.
4. Add 7.5g of the sample to the flask under laminar flow.
5. Add 150 ml ABS solution using a sterile measuring cylinder to the sterile 250 ml Erlenmeyer flasks.

6. Inoculate with appropriate volume of mixed culture of iron and sulphur oxidising micro-organisms to give cell concentration of 10^9 (skip this step for abiotic flasks).
7. Record the mass of each flask and do the initial sampling before placing on a shaking incubator at 150 rpm at 37 ^{O}C.
8. Follow the sampling procedure every day until the pH stabilises and/or redox potential is above 650 mV (approximately 2 weeks) then adjust sampling instances to 2-4 days.
9. At the end of the tests ARD static tests would be done on the residues.

Sampling

1. Remove flasks from shaker.
2. Measure mass and correct for water loss from evaporation using deionised water for uncontrolled pH.
3. For pH controlled tests measure mass and pH. Titrate the flask solution to pH 2 using 0.5 M H_2SO_4 if pH is above 2 and record the volume of acid used and the new mass. If pH is below 2 make up to the initial mass using acidified water of pH 2.
4. Leave flasks and allow the solids to settle to the bottom and pipette 0.5 ml of the flask solution and store in Eppendorf tubes for elemental analysis using ICP by Analytical laboratory at UCT.
5. Record the pH and redox potential of the flask.
6. Remove an aliquot from the Eppendorf tube and perform elemental analysis (ferrous assay is conducted using the 1-10 phenanthroline method (Komadel and Stucki 1988) and sulphate analysis (using turbidity from barium chloride addition). Perform cell count on the aliquots from control flasks to monitor cell growth.
7. Replace flasks on shaking incubator.
8. Repeat sampling at intervals depending on data required.

Experimental Set-up


x 3

Biotic pH controlled:

7.5 g & -75 µm sample, 10^9 cells, 150 ml media, 37^{O}C, 150 rpm


x 3

Biotic pH uncontrolled:

7.5 g & -75 µm sample, 10^9 cells, 150 ml media, 37^{O}C, 150 rpm


x 3

Abiotic pH uncontrolled:

7.5 g & -75 µm sample, 150 ml media, 37^{O}C, 150 rpm


x 3

Abiotic pH controlled:

7.5 g & -75 µm sample, 150 ml media, 37^{O}C, 150 rpm

Culture control:

7.5 g pyrite, 150 ml media, 10^9 cells, 37^{O}C, 150 rpm

Iron Assay by Spectrophotometry with 1-10 Phenathroline

Reagents

- Standard Fe^{2+} stock solution (100 mg/L Fe^{2+}) made by lowly adding 20 ml concentrated H_2SO_4 to 50 ml of deionised water and dissolve 497.629 mg of $FeSO_4.7H_2O$. Dilute to 1000 ml with deionised water and mix thoroughly. Standard solutions of lower concentration are obtained by dilution.

- 1-10 Phenathroline indicator solution made by dissolving 2127.708 mg of 1-10 Phenathroline (as $C_{12}H_8N_2.H_2O$) in about 100 ml of deionised water. Dilute with deionised water to 1000 ml mark. This gives a 1-10 Phenathroline in excess of the stoichiometric requirements.
- Ammonium acetate buffer solution made by dissolving 250 g of ammonium acetate ($NH_4C_2H_3O_2$) in 150 ml of deionised water. Add 700 ml of concentrated glacial acetic acid.

Procedure

- Filter all turbid samples before analysis.
- Prepare a standard curve ranging from 0-50 mg L Fe^{2+}. The absorbance of the 50 mg/L standard should be around 2 absorbance units, yielding a slope of around 0.04.

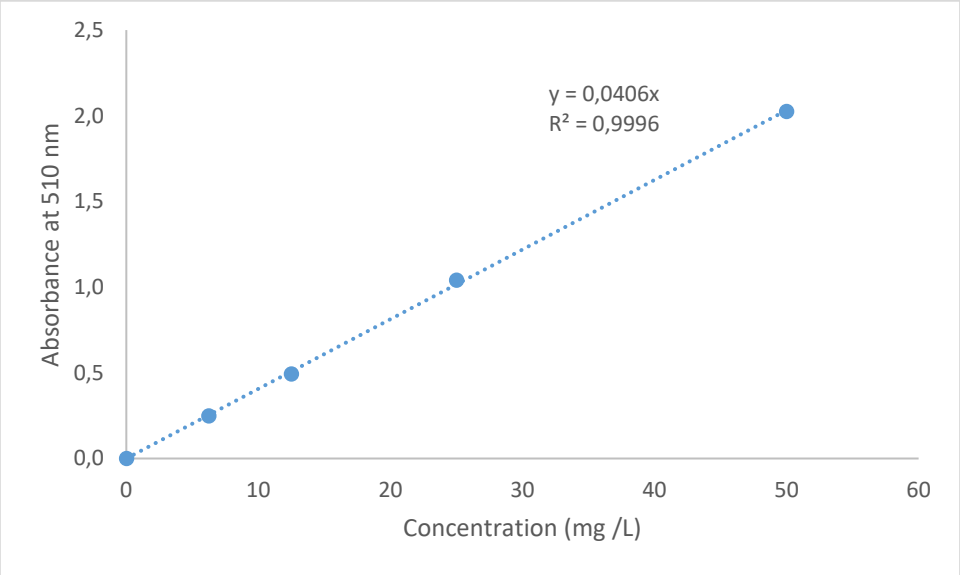

Figure 53 Ferrous (Fe^{2+}) standard curve

Ferrous iron

1. Add 2 ml acetate buffer to a clean test tube. It is essential that the test tubes are clean as an iron residue will affect the results.
2. Add 2 ml 1-10 Phenathroline solution.
3. Add 1 ml of sample and mix by vortexing. Dilutions can be performed in the test tube by first adding a volume of deionised water, then sufficient volume of the sample to make up 1 ml in total (i.e. 980 µL deionised water and 20 µL sample).
4. Prepare a blank comprising 2 ml acetate buffer, 2 ml Phenathroline solution and 1 ml of deionised water. Use this to auto zero the spectrophotometer.
5. Allow 5 min for the reaction to occur then read the absorbance at 510 nm.
6. If total values are required return the volume of the cuvette to the test tube after measuring the absorbance.

Total iron

1. Add 1 micro scoop (small spatula tip) of hydroxylamine to the test tubes including the blank.
2. Vortex for 10-20 s to ensure all hydroxylamine has dissolved.
3. Allow a minimum of 5 min for the colour to develop.
4. Re-zero the spectrophotometer with the blank + hydroxylamine. This should a value of 0.01-0.04 prior to zeroing. If the absorbance value is greater than 0.04 it indicates some contamination. Prepare a fresh blank.
5. Measure absorbance at 510 nm.
6. Do not use the same cuvette as was used for the ferrous assays.

ANC and Total Sulphur Tests on Biokinetic Residues

1. Filter the contents of the shake flask and wash the residues three times with 30 ml deionised water.
2. Dry the residues at 37 ^{O}C until the residue mass is constant.
3. Calculate the weight loss from the original 7.5 g and split the residues for Leco analysis and ARD static tests.
4. Contact the total sulphur analysis and ARD static tests as described in Section 4.1 and 4.2 and multiply the results by the weight loss factor.
5. Calculate the reduction in ANC and total sulphur relative to the feed.

A.5. Sequential Chemical Extractions

Scheme B (Broadhurst, Maluleke and Blottnitz, 2009)

Step 1: Water-soluble Fraction

1. Weigh 1 g of tailing sample into 50 ml screw-up centrifuge tube.
2. Add 40 ml of deionised water.
3. Continuously shake the mixture for 1 hr at room temperature.
4. Centrifuge and decant supernatant liquid into a labelled test tube.
5. Wash the residue with 5 ml deionised water, vortex and centrifuge again twice. Add the supernatant rinse to the test tube. ***N.B: do this twice.***

Step 2: Exchangeable Fraction (Ammonium acetate Leach)

1. To the residue from step 1, add 20 ml of 1 M NH4-acetate solution brought to pH 4.5 by 1M acetic acid.
2. Vortex contents for 5-10 s.
3. Cap and place in an orbital shaker for 2 hrs.
4. Centrifuge and decant the supernatant liquid into a labelled test tube.
5. Rinse the residue with 5 ml of deionised water, vortex and centrifuge again. Add the supernatant rinse to the test tube. ***N.B: do this twice.***
6. Make up to the 30 ml mark and analyse.

Step 3: Carbonate Fraction

1. To the residue from step 2, add 20 ml of 1.0 M CH_3COONa solution brought to pH 4.5 with 1.0 M acetic acid.
2. Vortex contents for 5-10 s.
3. Cap and place in an orbital shaker for 2 hrs.
4. Centrifuge and decant the supernatant liquid into a labelled test tube.
5. Rinse the residue with 5 ml of deionised water, vortex and centrifuge again. Add the supernatant rinse to the test tube. ***N.B: do this twice.***
6. Make up to the 30 ml mark and analyse.

Step 4: Amorphous Fe Oxide Fraction

1. To the residue from step 3, add 20 ml of 0.25 M $NH_2OH.HCl$ solution adjusted to pH 2.0 with 0.25 M HCl at 50 ^{O}C.
2. Cap and shake for 2 hrs in darkness.
3. Centrifuge and decant the supernatant liquid into a labelled test tube.
4. Rinse the residue with 5 ml of deionised water, vortex and centrifuge again. Add the supernatant rinse to the test tube. ***N.B: do this twice.***
5. Make up to the 30 ml mark and analyse.

Step 5: Crystalline Fe Oxide Fraction

1. To the residue from step 4, add 30 ml of 2.0 M $NH_2OH.HCl$ solution brought to pH 2.0 by 25% CH_3COOH at 90 ^{O}C.
2. Cap and shake for 3 hrs in darkness.
3. Centrifuge and decant the supernatant liquid into a labelled test tube.
4. Rinse the residue with 5 ml of deionised water, vortex and centrifuge again. Add the supernatant rinse to the test tube. ***N.B: do this twice.***
5. Make up to the 40 ml mark and analyse.

Step 6: Elements in Sulphide Phases (4 M $KClO_3$, HCl and HNO_3) Fraction

1. Add to the residue from step 5, 750 mg of $KClO_3$ and 5 ml of 12 M HCl.
2. Cap and vortex (exercise caution, content may froth).
3. Add a further 10 ml of HCl.
4. Cap and vortex.
5. After 30 min add 15 ml of deionised water.
6. Cap and vortex and centrifuge for 10 min.
7. Decant supernatant liquid into a labelled test tube.
8. To the residue add 10 ml of 4 M HNO_3.
9. Cap and vortex.

10. Place in a water bath at 90 ^{O}C for 20 min.
11. Vortex and centrifuge for 10 min.
12. Decant the supernatant liquid into the previously labelled test tube (i.e. mixing the $KClO_3$/HCl extracts with the HNO_3 leachate).
13. Rinse the residue with 5 ml of deionised water, vortex and centrifuge again. Add the supernatant rinse to the test tube. ***N.B: do this twice.***
14. Make up to the 50 ml mark and analyse.

Step 7: Residual Fraction

Residues from stage 6 were mixed with deionised and poured out of the centrifuge tubes into pre-weighed petri dishes. The centrifuge tubes were further rinsed with deionised water until all the sample was taken out of the centrifuge tubes. The unclosed petri dishes were put in the 80 ^{O}C oven for the samples to dry. The petri dishes were weighed every 6 hours, until there were no weight losses after 4 days. The petri dishes were weighed and the residues were sent for XRF and LA-ICP-MS analysis.

APPENDIX B

RESULTS: CHARACTERISATION OF PHYSIO-CHEMICAL PROPERTIES

B.1. Physical Analysis

B.1.1. Particle Size Distribution

Table 56 Particle size distribution for coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

	Sample A		Sample B		Sample C	
Aperture Size (mm)	**Average Mass Retained (%)**	**Average Cumulative Passing (%)**	**Average Mass Retained (%)**	**Average Cumulative Passing (%)**	**Average Mass Retained (%)**	**Average Cumulative Passing (%)**
31.500					48.0 ± 1.0	100.0 ± 0.0
22.400					7.8 ± 0.1	52.0 ± 1.0
16.000					8.9 ± 0.2	44.1 ± 1.0
11.200					9.4 ± 0.4	35.3 ± 1.1
8.000					6.7 ± 0.2	25.9 ± 0.7
5.600					4.6 ± 0.1	19.2 ± 1.0
4.000					2.9 ± 0.1	14.6 ± 0.9
2.000					4.8 ± 0.5	11.7 ± 0.8
1.000					2.7 ± 0.3	6.9 ± 0.3
0.710			2.9 ± 0.3	100.0 ± 0.0	0.8 ± 0.0	4.3 ± 0.0
0.425			5.1 ± 0.2	97.1 ± 0.3	1.1 ± 0.0	3.5 ± 0.0
0.300			5.0 ± 0.7	92.0 ± 0.1	0.6 ± 0.0	2.4 ± 0.1
0.212	14.9 ± 0.1	100.0 ± 0.0	8.8 ± 0.3	87.0 ± 0.8	0.5 ± 0.0	1.9 ± 0.1
0.150	27.5 ± 0.1	85.1 ± 0.1	8.5 ± 0.3	78.1 ± 1.0	0.4 ± 0.0	1.4 ± 0.0
0.106	19.1 ± 0.2	57.6 ± 0.0	9.9 ± 0.4	69.7 ± 1.4	0.3 ± 0.0	1.0 ± 0.0
0.075	14.4 ± 0.1	38.5 ± 0.2	12.7 ± 1.6	59.8 ± 1.8	0.2 ± 0.0	0.8 ± 0.0
0.053	8.1 ± 0.7	24.1 ± 0.1	16.5 ± 2.0	47.1 ± 3.4	0.2 ± 0.0	0.6 ± 0.0
0.038	5.8 ± 0.6	16.0 ± 0.7	8.7 ± 0.5	30.6 ± 1.4	0.0 ± 0.0	0.4 ± 0.0
0.025	10.2 ± 0.2	10.2 ± 0.2	21.9 ± 1.9	21.9 ± 1.9	0.4 ± 0.1	0.5 ± 0.1
0.000	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Total	**100.0**		**100.0**		**100.0**	

B.1.2. Ash Analysis

Table 57 Ash analysis per size fraction for coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

	Sample A		Sample B		Sample C	
Aperture Size (mm)	**Average Ash Content (%)**	**Cumulative Ash Content (%)**	**Average Ash Content (%)**	**Cumulative Ash Content (%)**	**Average Ash Content (%)**	**Cumulative Ash Content (%)**
31.500					70.5 ± 0.0	33.9 ± 0.0
22.400					53.1 ± 0.0	4.2 ± 0.0
16.000					52.4 ± 0.0	4.6 ± 0.0
11.200					55.8 ± 0.0	5.3 ± 0.0
8.000					57.4 ± 0.0	3.9 ± 0.0
5.600					59.7 ± 0.0	2.7 ± 0.0
4.000					62.2 ± 0.0	1.8 ± 0.0
2.000					62.4 ± 0.0	3.0 ± 0.0
1.000					63.2 ± 0.0	1.7 ± 0.0
0.710			34.5 ± 0.0	1.0 ± 0.0	55.9 ± 0.0	0.4 ± 0.0
0.425			27.1 ± 0.0	1.4 ± 0.0	50.1 ± 0.0	0.5 ± 0.0
0.300			30.4 ± 0.0	1.5 ± 0.0	50.5 ± 0.0	0.3 ± 0.0
0.212	35.2 ± 0.0	5.3 ± 0.0	33.8 ± 0.0	3.0 ± 0.0	53.0 ± 0.0	0.2 ± 0.0
0.150	37.8 ± 0.0	10.4 ± 0.0	35.6 ± 0.0	3.0 ± 0.0	55.9 ± 0.0	0.2 ± 0.0
0.106	46.3 ± 0.0	8.9 ± 0.0	37.4 ± 0.0	3.7 ± 0.0	56.0 ± 0.0	0.1 ± 0.0
0.075	52.7 ± 0.0	7.6 ± 0.0	43.2 ± 0.0	5.5 ± 0.0	55.5 ± 0.0	0.1 ± 0.0
0.053	63.3 ± 0.0	5.1 ± 0.0	46.2 ± 0.0	7.6 ± 0.0	56.3 ± 0.0	0.1 ± 0.0
0.038	69.4 ± 0.0	4.0 ± 0.0	48.0 ± 0.0	4.2 ± 0.0	52.1 ± 0.0	0.0 ± 0.0
0.025	77.0 ± 0.0	7.8 ± 0.0	49.3 ± 0.0	10.8 ± 0.0	53.7 ± 0.0	0.1 ± 0.0
Total		**49.1 ± 0.0**		**41.7 ± 0.0**		**63.2 ± 0.0**

B.2. Total Sulphur

Table 58 Total sulphur contents in coal standard SARM 19 and coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Sample	Leco- UCT				Leco- ALS				Eschka			
	Total S (%)	Mean (%)	Std Dev	Std Error	Total S (%)	Mean (%)	Std Dev	Std Error	Total S (%)	Mean (%)	Std Dev	Std Error
SARM 19	1.33	**1.34**	0.02	0.01	1.56	**1.54**	0.06	0.03	1.33	**1.30**	0.04	0.02
	1.34				1.47				1.26			
	1.36				1.58				1.32			
A	1.57	**1.54**	0.03	0.02	1.78	**1.84**	0.13	0.08	1.89	**1.89**	0.02	0.01
	1.55				1.75				1.91			
	1.51				1.99				1.87			
B	0.98	**1.02**	0.05	0.02	1.17	**1.06**	0.1	0.06	1.07	**1.11**	0.09	0.05
	1.00				0.98				1.21			
	1.02				1.03				1.06			
C					2.02	**1.94**	0.11	0.08				
					1.86							

B.3. Sulphur Forms Assessment

Table 59 Distribution of sulphur forms in coal standard SARM 19 and of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Sulphur forms	Proportion of sulphur form (%) in total sulphur							
	Sample A		Sample B		Sample C		SARM 19	
	ACARP	ISO	ACARP	ISO	ACARP	ISO	ACARP	ISO
CRS / Pyritic	61.3 ± 0.7	56.3 ± 1.8	51.6 ± 0.3	39.3 ± 1.2	52.7 ± 2.5	56.4 ± 0.4	52.4 ± 0.3	47.3n± 0.7
acid sulphate	0.0	-	1.2 ± 0.1	-	11.7 ± 0.8	-	0.54 ± 0.1	-
non-acid sulphate	17.3 ± 0.4	-	17.4 ± 0.5	-	0.00	-	18.4 ± 1.6	-
Total sulphate	17.3 ± 0.4	20.3 ± 5.5	18.6± 0.5	17.9 ± 1.2	11.7 ± 0.8	15.7 ± 2.5	18.9 ± 1.6	25.6 ± 1.3
low-risk / organic	21.4	23.4 ± 3.8	29.8	42.8 ± 4.1	35.5	27.8 ± 6.0	28.7	27.1 ± 3.4

B.4. Mineralogy Analysis

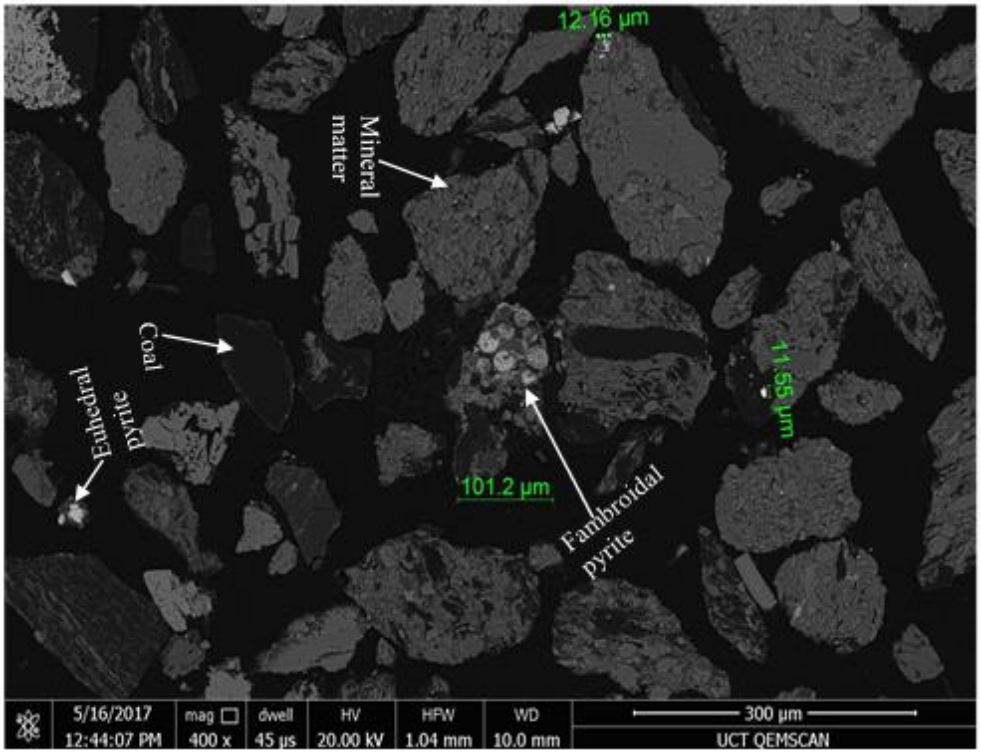

Figure 54 QEMSCAN images showing mineral distribution and association in Waterberg coal slurry

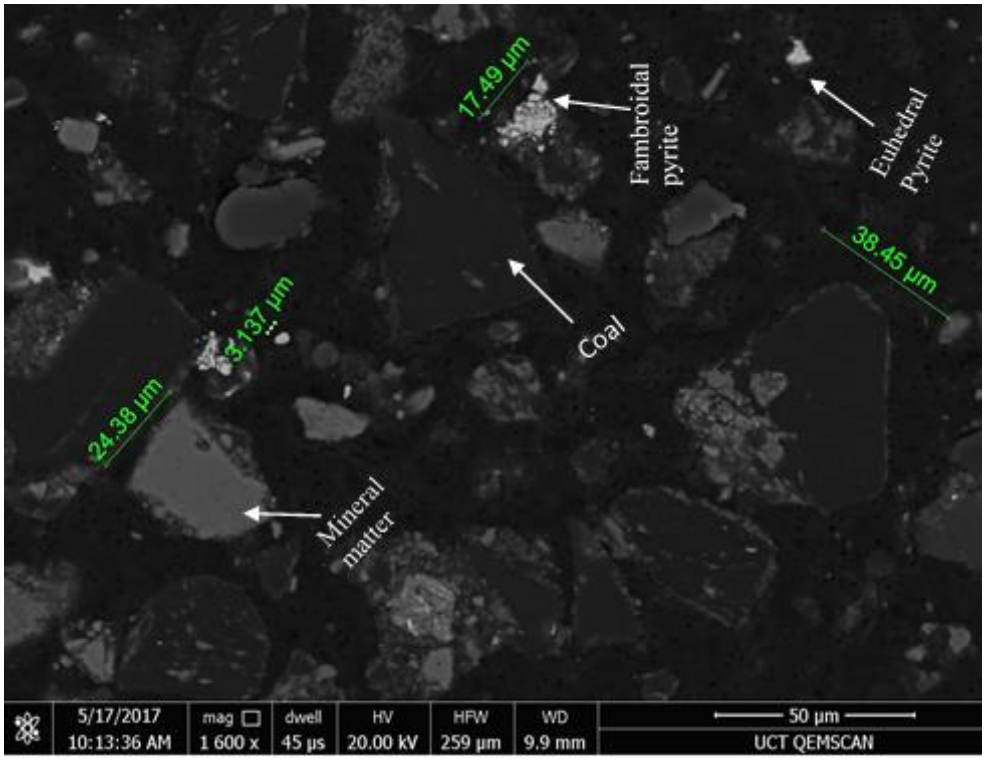

Figure 55 QEMSCAN images showing mineral distribution and association in Witbank coal slurry

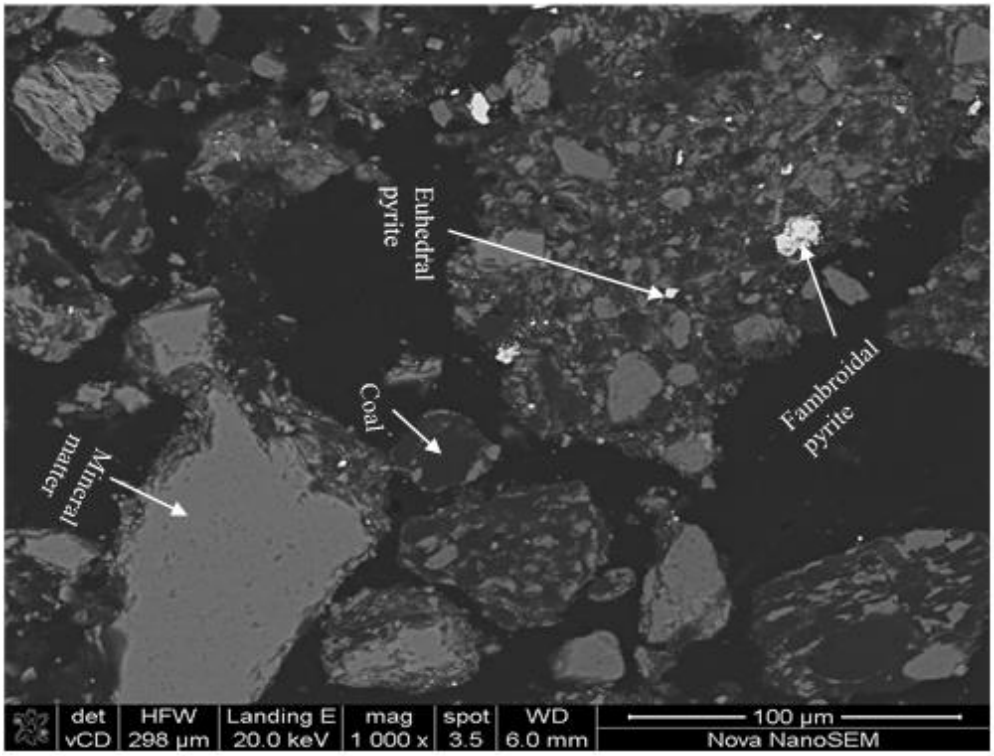

Figure 56 NanoSEM images showing mineral distribution and association in Witbank coal discards

B.5. Element Composition and Deportment

B.6.Table 60 Deportment of major elements in Waterberg coal slurry based on QEMSCAN mineralogical analysis

Mineral	Deportment of major elements (%)							
	Si	Al	Fe	Ti	Ca	Mg	K	S
Calcite	-	-	-	-	56.20	-	-	-
Amphibole	1.30	0.01	0.23	-	23.56	53.06	-	-
K-feldspar	2.96	5.33	0.81	-	6.68	0.01	47.81	-
Muscovite	0.81	2.33	0.14	-	-	16.93	11.65	-
Fe-oxyhydroxide	0.38	-	35.26	1.13	-	-	-	-
Kaolinite	43.62	87.83	0.02	-	-	-	-	-
Apatite	0.00	-	-	-	0.83	-	-	-
Quartz	38.92	4.02	-	-	0.03	-	40.34	-
Rutile	0.04	0.04	0.01	98.30	-	-	0.20	-
Siderite	-	-	0.99	-	-	-	-	-
Gypsum	-	-	-	-	12.65	-	-	4.82
Jarosite	-	-	-	-	-	-	-	0.05
Sphalerite	-	-	0.01	-	-	-	-	0.10
Chalcopyrite	-	-	1.66	-	-	-	-	3.28
Pyrite	-	-	60.88	-	-	-	-	54.27
Carbominerite	11.95	0.1-2	-	-	-	-	-	22.75
Coal	-	-	-	-	-	-	-	14.72
Other	0.02	0.31	0.00	0.57	0.06	30.00	-	0.01

Table 61 Deportment of major elements in Witbank coal slurry based on QEMSCAN mineralogical analysis

Mineral	Deportment of major elements (%)							
	Si	Al	Fe	Ti	Ca	Mg	K	S
Calcite	-	-	-	-	2.00	-	-	-
Amphibole	0.06	0.01	0.14	-	1.09	60.76	-	-
K-feldspar	1.32	0.56	1.24	-	3.65	-	86.72	-
Muscovite	0.56	0.80	0.01	-	-	4.42	13.28	-
Fe-oxyhydroxide	0.07	-	15.42	-	-	-	-	-
Kaolinite	83.12	96.56	-	-	-	-	-	-
Apatite	-	-	-	-	69.19	-	-	-
Quartz	11.21	-	-	-	-	-	-	-
Rutile	0.03	0.00	-	100.00	-	-	-	-
Siderite	-	-	0.57	-	-	-	-	-
Gypsum	0.06	-	-	-	24.07	-	-	1.06
Sphalerite	-	-	0.03	-	-	-	-	0.09
Chalcopyrite	-	-	-	-	-	-	-	-
Pyrite	-	-	82.59	-	-	-	-	56.46
carbominerite	3.53	1.98	-	-	-	-	-	17.70
Coal	-	-	-	-	-	-	-	24.69
Other	0.04	0.08	-	-	-	34.82	-	-

Table 62 Deportment of major elements in Witbank coal discards based on QEMSCAN mineralogical analysis

Mineral	Deportment of major elements (%)							
	Si	Al	Fe	Ti	Ca	Mg	K	S
Calcite	-	-	-	-	-	-	-	-
Amphibole	0.01	-	0.05	-	3.73	31.23	-	-
K-feldspar	2.30	1.30	0.42	-	5.77	-	73.96	-
Muscovite	0.40	0.97	0.01	-	-	11.37	25.93	-
Fe-oxyhydroxide	0.01	-	5.27	-	-	-	-	-
Kaolinite	65.12	97.67	0.00	-	-	-	-	-
Apatite	-	-	-	-	89.55	-	-	-
Quartz	27.76	-	-	-	-	-	-	-
Rutile	0.08	0.01	-	100.00	-	-	0.11	-
Siderite	-	-	-	-	-	-	-	-
Gypsum	0.00	-	-	-	0.96	-	-	0.01
Sphalerite	-	-	0.01	-	-	-	-	0.12
Chalcopyrite	-	-	10.29	-	-	-	-	9.84
Pyrite	-	-	83.94	-	-	-	-	70.27
carbominerite	4.28	-	-	-	-	-	-	4.72
Coal	-	-	-	-	-	-	-	15.03
Other	0.04	0.06	-	-	-	57.40	-	0.00

Table 63 Deportment of major elements in Waterberg coal slurry based on QXRD mineralogical analysis

Mineral	Deportment of major elements (%)						
	Si	Al	Fe	Ca	Mg	K	S
Calcite	-	-	-	34.52	-	-	-
Dolomite	-	-	-	54.39	100.00	-	-
Fe-oxyhydroxide	-	-	71.58	-	-	-	-
Kaolinite	30.35	100.00	-	-	-	-	-
Quartz	69.65	-	-	-	-	-	-
Siderite	-	-	3.06	-	-	-	-
Gypsum	-	-	-	11.09	-	-	28.80
Jarosite	-	-	12.16	-	-	100.00	16.74
Pyrite	-	-	13.19	-	-	-	54.46

Table 64 Deportment of major elements in Witbank coal slurry based on QXRD mineralogical analysis

Mineral	Deportment of major elements (%)						
	Si	Al	Fe	Ca	Mg	K	S
Calcite	-	-	-	1.95	-	-	-
Dolomite	-	-	-	2.96	4.23	-	-
Fe-oxyhydroxide	-	-	33.45	-	-	-	-
Kaolinite	63.51	100.00	-	-	-	-	-
Quartz	36.49	-	-	-	-	-	-
Siderite	-	-	0.00	-	-	-	-
Gypsum	-	-	-	-	-	-	23.46
Jarosite	-	-	57.96	-	-	100.00	41.53
Pyrite	-	-	8.59	-	-	-	18.46
Epsomite	-	-	-	95.09	95.77	-	16.55

Table 65 Deportment of major elements in Witbank coal discards based on QXRD mineralogical analysis

Mineral	Deportment of major elements (%)						
	Si	Al	Fe	Ca	Mg	K	S
K-feldspar	1.54	3.92	-	100.00	-	-	-
Mica	-	0.64	3.08	-	100.00	100.00	-
Fe-oxyhydroxide	-	-	40.50	-	-	-	-
Kaolinite	35.53	95.43	-	-	-	-	-
Quartz	62.22	-	-	-	-	-	-
Pyrite	-	-	56.42	-	-	-	100.00

B.6. Comparison of Chemical and Mineralogical Results

B.6.1. Assay Reconciliation on Major Elements

Table 66 Assay reconciliation of WDXRF and QEMSCAN on the major elements of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Element	Mass (%) in sample					
	Sample A		Sample B		Sample C	
	WDXRF	QEMSCAN	WDXRF	QEMSCAN	WDXRF	QEMSCAN
Al	4.24	4.33	6.97	6.99	8.15	8.68
Ca	2.73	0.99	0.59	0.12	0.04	0.01
Fe	3.65	2.75	1.64	1.48	1.70	1.55
K	0.45	0.43	0.28	0.20	0.23	0.16
Mg	0.65	0.02	0.02	0.01	0.04	0.00
S	1.84	1.60	1.06	1.08	1.94	1.87
Si	13.32	13.36	10.52	10.52	22.07	22.01
Ti	0.24	0.10	0.46	0.36	0.59	0.79

Table 67 Assay reconciliation of QXRD and QEMSCAN on the major elements of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Element	Mass (%) in sample					
	Sample A		Sample B		Sample C	
	QXRD	QEMSCAN	QXRD	QEMSCAN	QXRD	QEMSCAN
Al	3.42	4.33	5.74	6.99	7.33	8.68
Ca	1.52	0.99	0.21	0.12	0.21	0.01
Fe	1.68	2.75	1.25	1.48	1.58	1.55
K	0.05	0.43	0.17	0.20	0.07	0.16
Mg	0.50	0.02	0.09	0.01	0.11	0.00
S	0.47	1.60	0.67	1.08	1.03	1.87
Si	11.74	13.36	9.40	10.52	20.50	22.01
Ti		0.10		0.36		0.79

Table 68 Assay reconciliation of WDXRF and QXRD on the major elements of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Element	Mass (%) in sample					
	Sample A		Sample B		Sample C	
	WDXRF	QXRD	WDXRF	QXRD	WDXRF	QXRD
Al	4.24	3.42	6.97	5.74	8.15	7.33
Ca	2.70	1.52	0.59	0.21	0.04	0.21
Fe	3.65	1.68	1.64	1.25	1.70	1.58
K	0.45	0.05	0.28	0.17	0.23	0.07
Mg	0.65	0.50	0.02	0.09	0.04	0.11
S	1.84	0.47	1.06	0.67	1.94	1.03
Si	13.32	11.74	10.52	9.40	22.07	20.50
Ti	0.24		0.46		0.59	

B.6.2. Assays Reconciliation on Sulphur Forms

Table 69 Assay reconciliation of QEMSCAN and ACARP C15034 on the sulphur forms of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Sulphur form	Proportion of sulphur form (%) in total sulphur					
	Sample A		Sample B		Sample C	
	QEMSCAN	ACARP	QEMSCAN	ACARP	QEMSCAN	ACARP
Coal/ low-risk S	37.47	21.39	42.39	29.75	19.75	35.53
Sulphide/CRS S	57.65	61.32	56.55	51.60	80.24	52.74
Total sulphate S	4.86	17.29	1.06	18.65	0.01	11.73

Table 70 Assay reconciliation of QEMSCAN and ISO 157:1996 on the sulphur forms of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Sulphur form	**Proportion of sulphur form (%) in total sulphur**					
	Sample A		**Sample B**		**Sample C**	
	QEMSCAN	ISO	QEMSCAN	ISO	QEMSCAN	ISO
Coal/ organic S	37.47	23.37	42.39	42.77	19.75	27.84
Sulphide/ pyritic S	57.65	56.34	56.55	39.31	80.24	56.44
Total sulphate S	4.86	20.29	1.06	17.92	0.01	15.72

APPENDIX C

RESULTS: POTENTIAL RISK ASSESSMENT

C.1. ARD Potential Assessment

C.1.1. ARD Tests Classification Criteria

Table 71 ARD potential classification criteria of different methods adapted from (Paktunc, 1999; Smart *et al.*, 2002)

ARD prediction tests	Result	Units	Classification guideline
Acid Base Accounting	NAPP > 20	kg H_2SO_4/Ton	Potentially acid-forming (PAF)
	-20< NAPP<20	kg H_2SO_4/Ton	Uncertain (UC)
	NAPP<-20	kg H_2SO_4/Ton	Non-acid-forming (NAF)
Net Acid Generation	NAG pH < 4.5 & NAG >5	kg H_2SO_4/Ton	Potentially acid-forming (PAF)
	NAG pH < 4.5 & NAG=5	kg H_2SO_4/Ton	Potentially acid-forming with low capacity (PAF-LC)
	NAG pH > 4	pH	Non-acid-forming (NAF)
Combined static tests	NAG pH < 4.5 and NAPP > 0		Potentially acid-forming (PAF)
	NAG pH > 4.5 and NAPP <0		Non-acid-forming (NAF)
	NAG pH>4.5 and NAPP>0 or NAG pH<4.5 and NAPP<0		Uncertain (UC)
Mineralogy ARD calculation	NAPP>0	kg H_2SO_4/Ton	Potentially acid-forming (PAF)/
	NAPP<0	kg H_2SO_4/Ton	Non-acid-forming (NAF)

C.1.2. Conversion and Deportment of Sulphur Species under ARD Static Tests

Table 72 Conversion of sulphur species in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) under ARD static test conditions

S Forms	Mass (%) of sulphur form in sample								
	Sample A			Sample B			Sample C		
	Feed	ANC	NAG	Feed	ANC	NAG	Feed	ANC	NAG
CRS	1.13 ±0.01	0.89 ±0.00	0.00 ±0.00	0.55 ±0.00	0.28 ±0.00	0.01 ±0.00	1.02 ±0.03	0.84 ±0.04	0.01 ±0.01
Acid sulphate	0.00 ±0.00	0.09 ±0.00	0.01 ±0.00	0.01 ±0.00	0.12 ±0.00	0.02 ±0.00	0.23 ±0.01	0.11 ±0.01	0.19 ±0.01
Non-acid sulphate	0.32 ±0.00	0.02 ±0.00	0.01 ±0.01	0.18 ±0.01	0.03 ±0.00	0.01 ±0.00	-	0.02 ±0.00	0.01 ±0.00
Leachate sulphate		0.30 ±0.00	1.65 ±0.00	-	0.28 ±0.01	0.91 ±0.01	-	0.35 ±0.00	1.72 ±0.00
low-risk	0.39 ±0.00	0.53 ±0.06	0.17 ±0.03	0.32 ±0.00	0.36 ±0.02	0.11 ±0.04	0.69 ±0.00	0.61±0.03	0.01 ±0.03
Total	1.84	1.84	1.84	1.06	1.06	1.06	1.94	1.94	1.94

C.1.3. Theoretical ARD Calculated from Mineralogy

Table 73 Neutralization potential (NP) contributed by K-feldspars in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) calculated from QEMSCAN mineralogy results

Mineral phase	Sample A	Sample B	Sample C	Sample A	Sample B	Sample C
K-feldspars	Mineral Mass (%)			NP (kg H_2SO_4/ Ton)		
Orthoclase ($KAlSi_3O_8$)	0.00	0.27	0.70	0.07	3.85	9.86
Garnet-almandine ($Fe^{2+}{}_3Al_2(SiO_4)_3$)	0.03	0.03	0.01	0.13	0.14	0.05
Grossular ($Ca_3Al_2(SiO_4)_3$)	0.10	0.01		2.14	0.18	
K-Al Silicate (assumed 1:1:1 ratio)	0.42	0.13	0.14	34.94	10.72	11.69
K-Silicate-Quartz (assumed 1:1:1 ratio)		0.13	0.81	0.00	0.60	3.72
Sanidine ($K_{0.75}Na_{0.25}AlSi_3O_8$)	0.74			10.55		
Plagioclase ($Na_{0.5}Ca_{0.5}Si_3AlO_8$	0.00			0.03		
Albite ($Na_{0.95}Ca_{0.05}Al_{1.05}Si_{2.95}O_8$)	0.03			0.51		
Anorthite (($Na_{0.05}Ca_{0.95}Al_{1.95}Si_{2.05}O_8$)	0.02			0.33		
Total				**48.68**	**15.48**	**25.33**

Table 74 Neutralization potential (NP) contributed by amphiboles in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) calculated from QEMSCAN mineralogy results

Mineral Phase	**Sample A**	**Sample B**	**Sample C**	**Sample A**	**Sample B**	**Sample C**
Amphiboles	**Mineral Mass (%)**			**NP (kg H_2SO_4/ Ton)**		
Serpentine ($Mg_{2.25}Fe^{2+}_{0.75}(Si_2O_5)(OH)_4$)	0.02	0.01		0.28	0.09	
Tremolite ($Ca_2Mg_5(Si_8O_{22})(OH)_2$)		0.01	0.01	0.00	0.10	0.05
Chlorite ($Mg_{3.75}Fe^{2+}_{1.25}Si_3Al_2O_{10}(OH)_8$)	0.01	0.01		0.21	0.39	
Olivine ($Mg_{1.6}Fe^{2+}_{0.4}(SiO_4)$)	0.01		0.00	0.07		0.01
Fe-Olivine ($Fe^{2+}_2SiO_4$)			0.00			
Pyroxene ($CaMg(Si_2O_6)$)	0.00			0.04		
Hornblende ($Ca_{1.7}Mg_{3.5}Fe_{1.3}Al_{1.3}Si_7O_{22}(OH)_{22}$)	0.01			0.52		
WollasTonite ($CaSiO_3$)	0.67			5.62		
Forsterite ($Mg_2(SiO_4)$)	0.01			0.21		
Epidote ($Ca_2Fe^{3+}_{2.25}Al_{0.75}(SiO_4)_3(OH)$)	0.00			0.01		
Lizardite (($Mg_3Si_2O_5(OH)_4$)	0.00			0.10		
Talc ($Mg_3Si_4O_{10}(OH)_2$)	0.00			0.01		
Total				**7.06**	**0.59**	**0.06**

Table 75 Neutralization potential (NP) contributed by Fe-oxyhydroxides in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) calculated from QEMSCAN mineralogy results

Mineral phase	**Sample A**	**Sample B**	**Sample C**	**Sample A**	**Sample B**	**Sample C**
Fe-oxyhydroxides	**Mineral Mass (%)**			**NP (kg H_2SO_4/ Ton)**		
Goethite ($Fe^{3+}O(OH)$)	1.07	0.24	0.10			
Magnetite ($Fe^{3+}Fe^{2+}O_4$)	0.18	0.13				
Hematite ($Fe^{3+}_2O_3$)	0.14		0.00			
Chromite ($Fe^{2+}Cr_2O_4$)	0.00		0.09	0.02		0.79
Total				**0.02**	**0.00**	**0.79**

C.1.4. Batch Shake Flask Tests

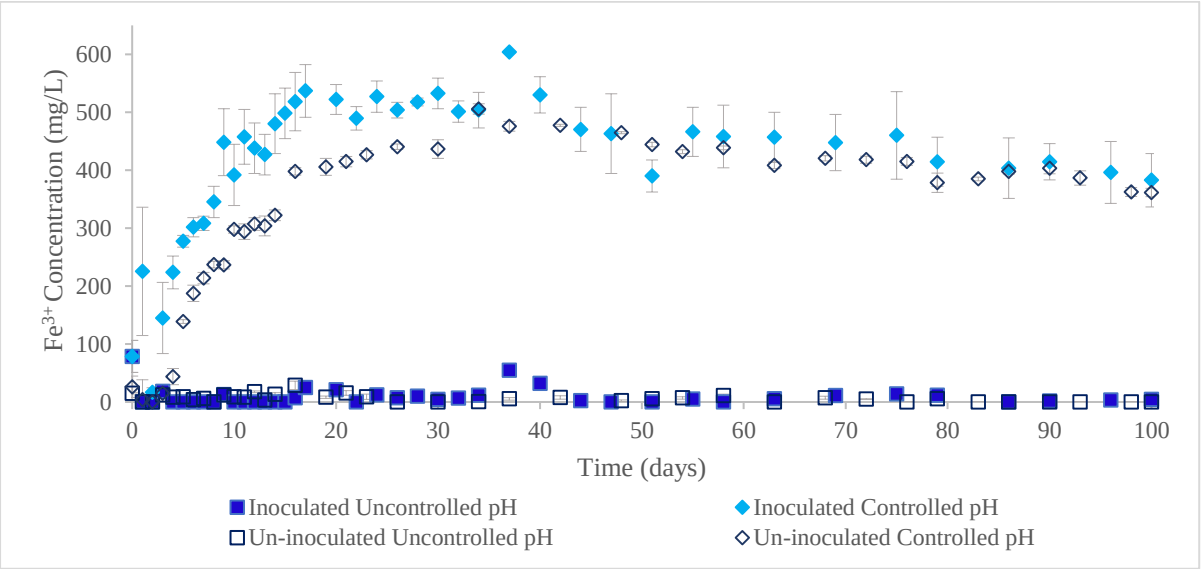

Figure 57 Ferric iron (Fe^{3+}) concentration profile of Waterberg coal slurry under biokinetic test conditions

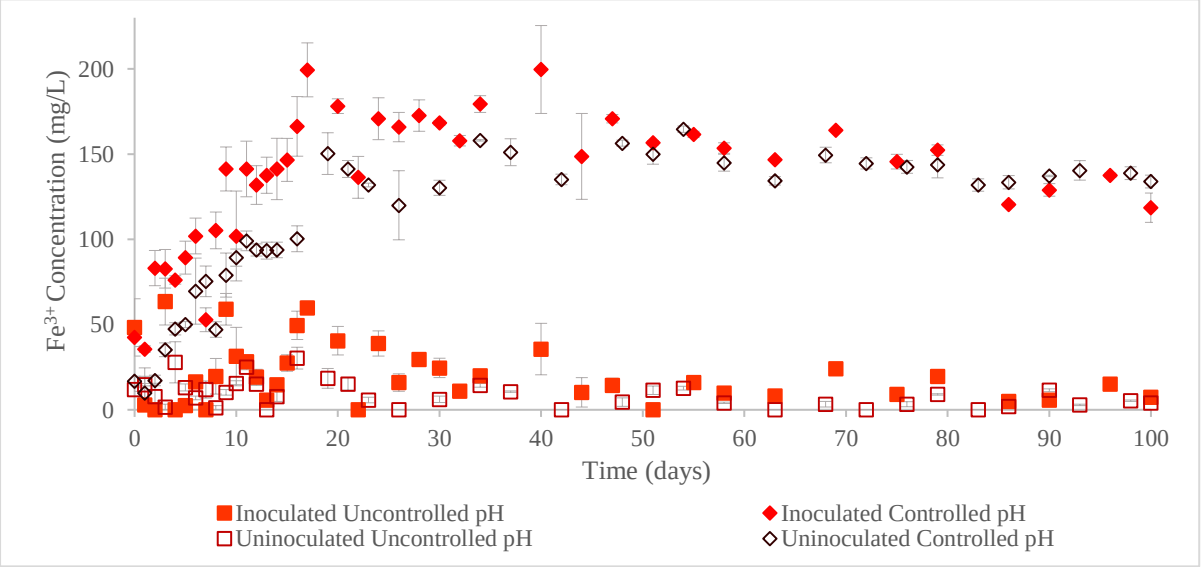

Figure 58 Ferric iron (Fe^{3+}) concentration profile of Witbank coal slurry under biokinetic test conditions

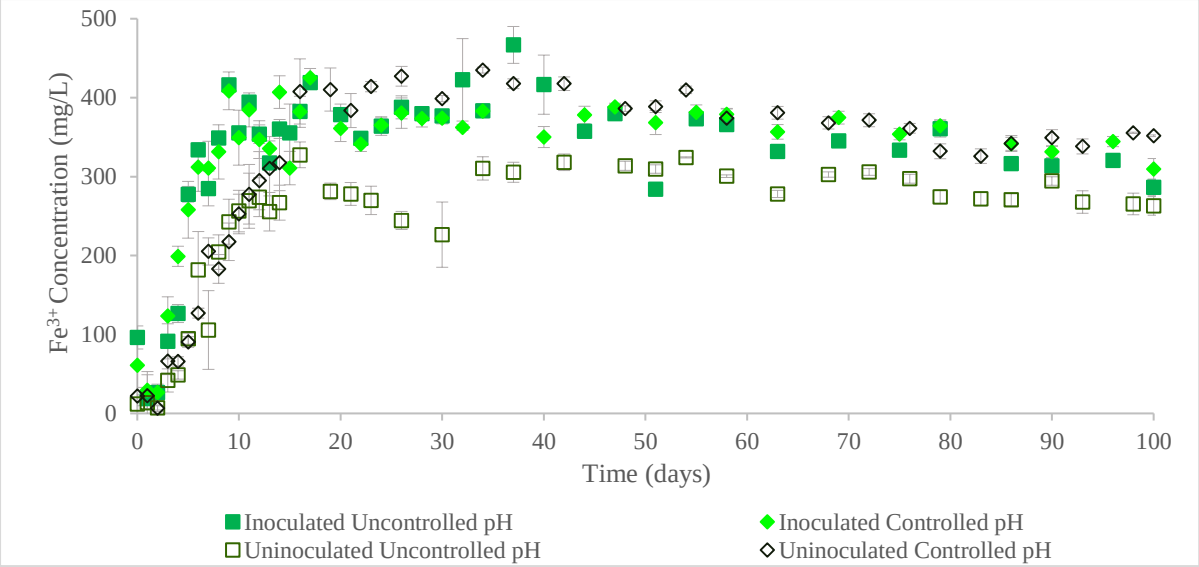

Figure 59 Ferric iron (Fe^{3+}) concentration profile of Witbank coal slurry under biokinetic test conditions

Table 76 Acid neutralising potential of coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) determined from biokinetic ARD tests

Sample	Volume H_2SO_4 inoculated (ml)	Volume H_2SO_4 un-inoculated (ml)	Density 0.5M H_2SO_4 (g / ml)	Mass of sample (g)	ANC (kg H_2SO_4 / Ton)
A	14.75	14.25	1.03	7.50	68.66 ± 0.25
B	4.153	4.01	1.03	7.50	19.63 ± 0.07
C	0.4	0.318	1.03	7.50	11.26 ± 0.13

C.2. Elemental and Salinity Risk Assessment

C.2.1. Hazard Potential

Table 77 Total concentration (TCi), Background concentration (BCi) and maximum allowed concentration (ARCi) of major and minor elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

	Sample A	**Sample B**	**Sample C**			
	TCi (mg/kg)	TCi (mg/kg)	TCi (mg/kg)	***BCi (mg/kg)	*ARCi (mg/kg)	**ARCi (mg/kg)
Major Elements						
Al	42420.76	69668.68	81469.22	82000.00	0.10	-
Ca	27338.26	5938.11	431.99	50000.00	32.00	-
Fe	36498.88	16351.15	17473.99	63000.00	0.30	-
K	4542.20	2839.99	2285.78	15000.00	50.00	-
Mg	6538.27	1178.92	364.50	29000.00	30.00	-
S	55131.13	31760.32	58127.39	420.00	500.00	4000
Si	133190.17	105203.94	220661.91	270000.00	5.00	-
Ti	2429.24	4613.57	5876.80	6600.00	5.00	-
Minor Elements						
Ba	1040.00	1084.27	351.72	340.00	1.00	-
Mn	593.15	102.95	42.44	1100.00	0.05	740
Na	300.69	241.72	bdl	23000.00	200.00	-
P	132.67	942.50	279.81	1000.00	5.00	-
Sr	158.35	480.80	121.28	360.00	7.00	-
Zr	160.85	248.00	359.68	130.00	-	-

** Maximum allowed concentration in drinking water guidelines* (Department of Water Affairs and Forestry, 1996; Mamba et al., 2008; IRMA, 2016)

*** Based on maximum allowed concentration in soil guidelines* (Department of Environmental Affairs, 2012)

**** Background concentration from crustal abundance (["Abundance in Earth's Crust". WebElements.com](WebElements.com))*

Table 78 Total concentration (TCi), Background concentration (BCi) and maximum allowed concentration (ARCi) of trace elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards)

Element	Sample A	Sample B	Sample C			
	TCi (mg/kg)	TCi (mg/kg)	TCi (mg/kg)	***BCi (mg/kg)	*ARCi (mg/kg)	**ARCi (mg/kg)
As	7.86	4.49	6.94	2.10	0.01	5.80
Bi	0.42	0.24	0.79	0.03	-	-
Cd	0.28	0.06	0.30	0.15	0.01	7.50
Ce	53.92	90.35	72.13	60.00	1.00	-
Co	15.92	12.13	6.12	30.00	0.10	300
Cr	82.10	87.50	199.87	140.00	0.05	6.50
Cs	3.75	3.75	3.57	1.90	-	-
Cu	32.75	34.85	42.72	68.00	1.00	16.00
Dy	6.05	5.96	5.32	6.20	1.00	-
Er	3.22	3.46	3.26	3.00	1.00	-
Eu	1.11	1.27	1.03	1.80	1.00	-
Ga	13.04	19.29	19.89	19.00	-	-
Gd	6.11	5.92	4.87	5.20	1.00	-
Ge	2.18	3.24	< 2.18	1.40	-	-
Hf	4.32	6.58	10.42	3.30	-	-
Ho	1.17	1.25	1.14	1.20	1.00	-
In	0.09	0.08	0.28	0.16	-	-
La	25.57	44.12	34.08	34.00	1.00	-
Lu	0.44	0.49	0.49	-	1.00	-
Mo	3.39	2.88	8.20	1.10	0.05	-
Nb	14.14	20.96	24.77	17.00	-	-
Nd	25.70	35.25	26.84	33.00	1.00	-
Ni	34.15	31.05	29.05	90.00	0.02	91.00
Pb	26.06	23.00	33.24	10.00	0.01	20.00
Pr	6.27	9.20	7.44	8.70	1.00	-
Rb	32.40	20.03	17.87	60.00	-	-
Sb	1.67	1.15	0.88	0.20	0.01	-
Sc	16.20	14.48	12.28	26.00	1.00	-
Se	1.34	1.25	1.55	0.05	0.04	-
Sm	6.47	7.05	5.23	6.00	1.00	-
Sn	4.55	3.34	5.73	2.20	5.00	-
Ta	0.83	1.50	1.84	1.70	-	-
Tb	0.97	0.94	0.85	0.94	1.00	-
Te	< 0.5	< 0.5	< 0.5	0.00	0.02	-
Th	10.77	20.12	20.14	6.00	0.23	-
Tl	0.20	0.08	0.22	0.53	0.00	-
Tm	0.45	0.50	0.50	0.45	1.00	-
U	3.84	5.43	4.75	1.80	0.02	-
V	80.55	69.20	59.15	190.00	0.10	150.00
Y	31.74	33.20	29.33	29.00	1.00	-
Yb	2.87	0.17	3.47	2.80	1.00	-
Zn	80.25	32.15	50.50	79.00	5.00	240.00

C.2.2. Element Partitioning and Availability

Table 79 Sequential chemical extraction partitioning and recovery results for Waterberg coal slurry

Element	% of Total Extracted							
	*F1	F2	F3	F4	F5	F6	F7	Recovery
Si	0.0	-	0.0		0.4	0.5	99.0	104.4
Al	0.0	0.4	0.1	0.1	1.5	2.3	95.6	100.8
Fe	bdl	1.3	0.4	0.2	24.4	64.0	9.7	93.2
Ti	0.0	0.0	0.0	0.0	0.0	10.0	89.9	110.2
Ca	14.2	65.0	14.2	1.3	4.4	bdl	1.0	85.6
Mg	6.2	36.6	24.9	2.2	6.3	3.6	20.2	82.9
P	0.0	bdl	1.1	bdl	bdl	bdl	98.9	99.1
K	bdl	2.2	1.1	1.1	3.0	0.0	92.7	85.0
S	15.5	4.1	0.5	0.5	1.6	54.6	23.2	100.0
Mn	1.9	39.7	12.5	12.6	24.9	8.3	bdl	102.5
Ba	0.2	2.9	3.3	3.1	11.9	9.3	69.4	108.2
Sr	5.5	34.8	8.8	6.7	3.9	2.0	38.3	104.1
Na	7.3	0.0	-	-	49.8	24.9	18.0	106.8
As	0.1	3.0	0.6	0.3	19.5	50.9	25.6	130.6
Co	0.2	18.3	3.5	3.8	19.7	39.6	14.8	103.2
Cr	0.0	0.7	0.2	0.1	3.9	12.1	83.0	98.1
Cu	0.4	0.0	0.4	0.8	19.4	60.3	18.7	112.4
Ni	0.2	8.2	2.5	4.2	21.3	33.6	29.9	102.2
Pb	0.0	12.2	4.0	2.2	51.8	18.1	11.6	109.4
Th	0.0	2.5	1.0	0.0	0.1	38.7	57.7	100.6
U	0.1	13.4	2.5	0.0	2.4	27.5	54.1	104.1
V	0.0	1.0	0.2	1.0	7.8	42.0	47.9	107.5
Zn	4.5	13.1	2.2	2.7	13.4	34.6	29.5	127.0
Mo	0.3	9.5	4.2	0.6	12.1	53.7	19.7	133.0
Sb	3.6	11.2	4.6	5.4	9.2	39.6	26.4	160.8
Se	3.3	12.9	4.3	1.0	6.1	31.3	41.1	154.2
Sn	0.0	0.0	0.0	0.0	0.0	50.2	49.8	100.6
Cd	0.2	37.3	3.3	3.0	6.8	13.8	35.6	148.7
Tl	1.1	25.3	4.5	9.8	22.5	36.7	0.0	136.7

** F1-water-soluble fraction, F2-exchangeable fraction, F3-carbonate fraction, F4-amorphous Fe-oxide fraction, F5-crystalline Fe-oxide fraction, F6-organics and sulphides, F7-residual fraction*

Table 80 Sequential chemical extraction partitioning and recovery results for Witbank coal slurry

Element	% of Total Extracted							
	*F1	F2	F3	F4	F5	F6	F7	Recovery
Si	0.0	bdl	0.0	0.1	0.4	0.7	98.8	94.2
Al	0.0	0.4	0.2	0.4	2.5	3.1	93.3	86.3
Fe	0.0	0.5	0.2	6.0	42.6	34.7	16.1	94.2
Ti	bdl	0.0	0.0	0.0	0.0	1.5	98.5	100.9
Ca	40.3	37.1	11.2	5.2	1.6	bdl	4.6	92.2
Mg	25.4	20.1	11.8	1.4	3.0	bdl	38.2	116.1
P	0.0	bdl	0.5	bdl	11.0	28.4	60.1	90.3
K	bdl	1.1	1.7	0.7	3.4	0.0	91.8	121.4
S	22.3	1.5	0.4	0.4	5.3	43.0	27.1	100.0
Mn	15.9	38.1	14.0	9.6	15.5	6.9	bdl	103.1
Ba	0.3	3.0	1.9	3.0	6.1	29.3	56.4	94.0
Sr	0.9	1.3	0.5	0.7	3.2	29.3	64.2	91.2
Na	14.1	bdl	0.0	0.0	54.9	21.7	9.3	162.9
As	0.4	3.0	0.7	1.1	16.7	37.1	41.0	155.8
Co	0.9	4.7	4.6	19.5	30.3	15.4	24.6	84.0
Cr	0.0	0.9	0.3	0.2	4.1	15.1	79.4	82.4
Cu	0.1	0.0	0.3	0.9	16.5	50.9	31.3	113.7
Ni	0.5	4.1	3.6	9.2	19.9	18.0	44.7	97.2
Pb	0.0	2.6	2.1	1.8	32.0	38.3	23.2	144.4
Th	0.0	0.3	0.2	0.0	0.0	42.7	56.8	89.3
U	0.0	4.4	1.8	0.1	1.6	30.9	61.2	96.2
V	0.0	0.1	0.0	0.4	7.1	24.6	67.7	100.7
Zn	2.3	4.7	3.1	12.4	24.5	28.4	24.6	133.6
Mo	0.2	8.1	1.4	0.6	10.4	43.5	35.8	123.6
Sb	20.5	15.2	8.3	9.1	11.6	35.2	0.0	143.3
Se	1.6	18.3	2.6	1.2	7.4	68.9	0.0	97.2
Sn	0.0	0.0	0.0	0.0	0.0	22.5	77.5	130.2
Cd	0.7	35.4	9.7	12.6	20.9	20.7	0.0	153.8
Tl	4.6	35.4	8.3	10.4	25.7	15.5	0.0	200.8

** F1-water-soluble fraction, F2-exchangeable fraction, F3-carbonate fraction, F4-amorphous Fe-oxide fraction, F5-crystalline Fe-oxide fraction, F6-organics and sulphides, F7-residual fraction*

Table 81 Sequential chemical extraction partitioning and recovery results for Witbank coal discards

Element	% of Total Extracted							
	*F1	F2	F3	F4	F5	F6	F7	Recovery
Si	0.0	bdl	0.0	0.0	0.2	0.3	99.5	99.7
Al	0.5	0.2	0.0	0.1	0.7	1.5	97.0	93.7
Fe	0.1	3.4	0.7	9.8	13.3	61.3	11.4	96.8
Ti	0.0	0.0	0.0	0.0	0.0	0.4	99.5	92.9
Ca	53.6	8.2	bdl	bdl	bdl	bdl	38.3	94.6
Mg	18.3	bdl	bdl	bdl	bdl	bdl	81.7	126.3
P	bdl	bdl	0.7	bdl	6.0	17.9	75.4	90.5
K	bdl	1.9	3.7	2.8	4.8	0.0	86.8	100.5
S	9.1	2.2	0.6	1.8	3.7	59.4	23.2	100.0
Mn	20.4	6.3	0.9	4.3	3.0	1.8	63.4	148.1
Ba	1.0	3.6	2.4	2.7	7.7	17.2	65.4	114.4
Sr	1.1	1.2	0.6	0.9	4.9	23.6	67.7	99.7
Na	0.6	bdl	0.0	85.1	7.3	7.0	0.0	-
As	0.3	10.9	2.0	3.5	11.6	71.6	0.0	57.9
Co	39.2	4.3	1.1	4.7	4.2	18.9	27.7	102.0
Cr	0.8	2.5	0.5	9.4	18.3	9.0	59.4	117.3
Cu	12.0	0.0	3.6	5.7	14.0	53.3	11.4	59.1
Ni	18.2	2.0	0.6	8.8	2.7	16.7	50.9	104.5
Pb	0.3	4.7	3.4	12.7	52.3	14.6	12.0	84.5
Th	0.2	2.3	0.6	0.0	1.1	43.7	52.1	88.3
U	4.4	3.8	0.6	0.2	2.4	17.3	71.3	95.9
V	0.0	1.0	0.1	2.2	4.7	17.3	74.8	100.1
Zn	42.1	22.9	1.7	2.1	2.2	9.2	19.8	149.3
Mo	0.0	3.9	0.7	2.3	27.1	34.5	31.5	110.3
Sb	20.9	13.8	9.2	7.2	11.0	14.0	23.9	190.5
Se	2.5	24.6	3.9	2.5	5.9	60.6	0.0	52.0
Sn	0.0	0.0	0.0	0.0	0.0	37.4	62.6	31.6
Cd	13.5	16.9	2.3	2.0	3.2	13.8	48.4	115.4
Tl	0.4	6.6	0.7	11.4	19.3	17.9	43.7	147.7

** F1-water-soluble fraction, F2-exchangeable fraction, F3-carbonate fraction, F4-amorphous Fe-oxide fraction, F5-crystalline Fe-oxide fraction, F6-organics and sulphides, F7-residual fraction*

Table 82 Potentially available concentration of trace elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) under oxidising leach conditions

Element	Available concentration (mg/kg)		
	Sample A	Sample B	Sample C
Ce	8.19	36.53	33.64
Cs	0.60	1.54	1.64
Ga	2.36	4.28	2.65
Hf	0.00	0.59	1.74
La	2.67	15.88	14.35
Rb	2.99	4.96	4.74
Sc	10.14	7.05	3.84
Sm	3.91	3.82	3.13
Eu	0.62	0.62	0.51
Nb	1.34	2.14	2.04
Ta	0.00	0.00	0.00
Tb	0.62	0.36	0.31
Y	18.70	15.44	8.73
Yb	1.02	0.00	0.66
Pr	1.22	3.72	3.70
Nd	9.08	17.52	15.25
Gd	4.09	3.11	2.53
Dy	3.93	2.89	1.81
Ho	0.59	0.53	0.28
Er	1.60	1.37	0.88
Tm	0.14	0.12	0.05
Lu	0.16	0.11	0.04
Te	0.00	0.00	0.00
In	0.00	0.00	0.00
Bi	0.32	0.09	0.69

C.2.3. Risk Potential

Table 83 Risk potential posed on drinking water by analysed major and minor elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) under neutral leach conditions

	Sample A			Sample B			Sample C		
	EFi	**EnFi**	**HPFi / 1000**	**EFi**	**EnFi**	**HPFi / 1000**	**EFi**	**EnFi**	**HPFi / 1000**
Major elements									
Si	10.71	0.00	0.00	5.42	0.00	0.00	4.95	0.00	0.00
Al	1659.79	0.00	0.00	2169.66	0.00	0.01	5567.66	0.01	0.04
Fe	1457.50	0.01	0.01	252.80	0.00	0.00	1994.39	0.01	0.02
Ti	0.15	0.00	0.00	0.09	0.00	0.00	0.08	0.00	0.00
Ca	579.37	0.37	0.21	132.38	0.08	0.01	7.89	0.01	0.00
Mg	77.26	0.08	0.01	20.79	0.02	0.00	2.80	0.00	0.00
P	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	1.70	0.01	0.00	1.61	0.01	0.00	0.90	0.00	0.00
S	21.64	25.76	0.56	15.10	17.98	0.27	13.11	15.61	0.20
Minor elements									
Mn	5067.30	0.23	1.17	1145.95	0.05	0.06	334.88	0.02	0.01
Ba	34.48	0.10	0.00	29.72	0.09	0.00	14.80	0.04	0.00
Sr	9.48	0.18	0.00	1.34	0.03	0.00	0.39	0.01	0.00
Na	0.12	0.00	0.00	0.28	0.00	0.00	0.04	0.00	0.00

Table 84 Risk potential posed on drinking water by analysed trace elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) under neutral leach conditions

Element	Sample A			Sample B			Sample C		
	EFi	EnFi	HPFi / 1000	EFi	EnFi	HPFi / 1000	EFi	EnFi	HPFi / 1000
As	32.21	0.15	0.00	23.58	0.11	0.00	44.98	0.21	0.01
Be	0.00	0.00	0.00	0.00	0.00	0.00	3.09	0.10	0.00
Co	30.56	0.10	0.00	5.73	0.02	0.00	27.16	0.09	0.00
Cr	11.87	0.00	0.00	12.99	0.00	0.00	70.86	0.03	0.00
Cu	0.17	0.00	0.00	0.03	0.00	0.00	3.04	0.04	0.00
Ni	146.82	0.03	0.00	69.95	0.02	0.00	307.11	0.07	0.02
Pb	348.46	0.35	0.12	87.91	0.09	0.01	140.15	0.14	0.02
Th	1.17	0.04	0.00	0.26	0.01	0.00	1.91	0.07	0.00
U	35.96	0.30	0.01	15.39	0.13	0.00	24.77	0.21	0.01
V	8.84	0.00	0.00	1.00	0.00	0.00	5.79	0.00	0.00
Zn	3.58	0.23	0.00	0.60	0.04	0.00	9.79	0.62	0.01
B	24.40	1.40	0.03	12.54	0.72	0.01	15.33	0.88	0.01
Hg	17.46	0.26	0.00	0.15	0.00	0.00	0.00	0.00	0.00
Li	0.14	0.01	0.00	0.14	0.01	0.00	1.80	0.07	0.00
Mo	8.80	0.40	0.00	5.85	0.27	0.00	7.06	0.32	0.00
Sb	65.90	1.98	0.13	97.95	2.94	0.29	97.12	2.91	0.28
Se	8.36	6.69	0.06	6.00	4.80	0.03	5.46	4.37	0.02
Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	31.58	1.05	0.03	14.01	0.47	0.01	20.99	0.70	0.01
Tl	36.70	0.14	0.01	32.16	0.12	0.00	11.55	0.04	0.00

Table 85 Risk potential posed on drinking water by analysed major and minor elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) under acidic leach conditions

	Sample A			Sample B			Sample C		
	EFi	**EnFi**	**HPFi / 1000**	**EFi**	**EnFi**	**HPFi / 1000**	**EFi**	**EnFi**	**HPFi / 1000**
Major elements									
Si	125.29	0.00	0.00	92.47	0.00	0.00	111.45	0.00	0.00
Al	8994.71	0.01	0.10	21226.11	0.03	0.55	12033.15	0.01	0.18
Fe	29889.37	0.14	4.25	25251.99	0.12	3.04	15417.90	0.07	1.13
Ti	0.44	0.00	0.00	0.37	0.00	0.00	0.23	0.00	0.00
Ca	724.58	0.46	0.34	163.31	0.10	0.02	7.89	0.01	0.00
Mg	137.76	0.14	0.02	28.18	0.03	0.00	2.80	0.00	0.00
P	0.28	0.00	0.00	22.56	0.11	0.00	4.23	0.02	0.00
K	5.67	0.02	0.00	5.64	0.02	0.00	6.08	0.02	0.00
S	24.54	29.22	0.72	19.00	22.62	0.43	20.22	24.07	0.49
Minor elements									
Mn	11151.17	0.51	5.65	1976.14	0.09	0.18	437.53	0.02	0.01
Ba	240.24	0.71	0.17	126.53	0.37	0.05	55.60	0.16	0.01
Sr	14.06	0.27	0.00	4.07	0.08	0.00	1.50	0.03	0.00
Na	0.92	0.01	0.00	1.36	0.01	0.00	5.96	0.05	0.00

Table 86 Risk potential posed on drinking water by analysed trace elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) under acidic leach conditions

Element	Sample A			Sample B			Sample C		
	EFi	EnFi	HPFi / 1000	EFi	EnFi	HPFi / 1000	EFi	EnFi	HPFi / 1000
As	241.14	1.15	0.28	153.19	0.73	0.11	113.97	0.54	0.06
Be	0.00	0.00	0.00	0.00	0.00		3.09	0.10	0.00
Co	75.05	0.25	0.02	61.05	0.20	0.01	33.37	0.11	0.00
Cr	79.52	0.03	0.00	79.55	0.03	0.00	680.59	0.24	0.17
Cu	7.73	0.11	0.00	7.04	0.10	0.00	8.93	0.13	0.00
Ni	636.27	0.14	0.09	563.17	0.13	0.07	490.81	0.11	0.05
Pb	2000.28	2.00	4.00	1279.34	1.28	1.64	2061.28	2.06	4.25
Th	1.73	0.07	0.00	0.41	0.02	0.00	3.23	0.12	0.00
U	49.07	0.41	0.02	27.38	0.23	0.01	34.54	0.29	0.01
V	87.37	0.05	0.00	53.70	0.03	0.00	47.01	0.02	0.00
Zn	7.31	0.46	0.00	4.04	0.26	0.00	10.70	0.68	0.01
B	33.29	1.91	0.06	19.16	1.10	0.02	19.87	1.14	0.02
Hg	40.67	0.61	0.02	38.57	0.58	0.02	38.09	0.57	0.02
Li	0.96	0.04	0.00	5.79	0.24	0.00	6.87	0.28	0.00
Mo	23.97	1.09	0.03	14.71	0.67	0.01	61.52	2.80	0.17
Sb	152.08	4.56	0.69	177.57	5.33	0.95	174.04	5.22	0.91
Se	14.21	11.37	0.16	9.39	7.51	0.07	7.94	6.35	0.05
Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	42.57	1.42	0.06	30.75	1.02	0.03	26.11	0.87	0.02
Tl	88.00	0.33	0.03	67.92	0.26	0.02	63.28	0.24	0.02

Table 87 Risk potential posed on drinking water by major and minor elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) under oxidising leach conditions

	Sample A			Sample B			Sample C		
	EFi	**EnFi**	**HPFi / 1000**	**EFi**	**EnFi**	**HPFi / 1000**	**EFi**	**EnFi**	**HPFi / 1000**
Major elements									
Si	270.19	0.01	0.00	232.12	0.00	0.00	227.30	0.00	0.00
Al	18784.71	0.02	0.43	40136.11	0.05	1.96	23110.65	0.03	0.65
Fe	102481.03	0.49	50.01	43060.33	0.21	8.83	49951.24	0.24	11.88
Ti	53.88	0.04	0.00	14.15	0.01	0.00	5.13	0.00	0.00
Ca	724.58	0.46	0.34	163.31	0.10	0.02	7.89	0.01	0.00
Mg	144.23	0.15	0.02	28.18	0.03	0.00	2.80	0.00	0.00
P	0.28	0.00	0.00	78.12	0.39	0.03	15.63	0.08	0.00
K	5.67	0.02	0.00	5.64	0.02	0.00	6.08	0.02	0.00
S	84.69	100.83	8.54	46.29	55.10	2.55	89.28	106.29	9.49
Minor elements									
Mn	12156.11	0.55	6.72	2123.68	0.10	0.20	460.76	0.02	0.01
Ba	344.69	1.01	0.35	385.69	1.13	0.44	110.68	0.33	0.04
Sr	14.54	0.28	0.00	22.43	0.44	0.01	5.59	0.11	0.00
Na	1.32	0.01	0.00	1.79	0.02	0.00	6.40	0.06	0.00

Table 88 Risk potential posed on drinking water by trace elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) under oxidising leach conditions

Element	Sample A			Sample B			Sample C		
	EFi	EnFi	HPFi / 1000	EFi	EnFi	HPFi / 1000	EFi	EnFi	HPFi /1000
As	763.92	3.64	2.78	412.64	1.96	0.81	401.74	1.91	0.77
Be	0.00	0.00	0.00	0.00	0.00		3.09	0.10	0.00
Co	140.09	0.47	0.07	76.78	0.26	0.02	45.16	0.15	0.01
Cr	274.11	0.10	0.03	297.52	0.11	0.03	874.54	0.31	0.27
Cu	29.92	0.44	0.01	27.21	0.40	0.01	22.39	0.33	0.01
Ni	1222.29	0.27	0.33	835.12	0.19	0.15	744.77	0.17	0.12
Pb	2517.38	2.52	6.34	2550.99	2.55	6.51	2470.22	2.47	6.10
Th	20.11	0.76	0.02	34.01	1.29	0.04	37.35	1.42	0.05
U	122.13	1.02	0.12	135.03	1.13	0.15	86.97	0.72	0.06
V	451.30	0.24	0.11	225.31	0.12	0.03	149.49	0.08	0.01
Zn	14.37	0.91	0.01	6.48	0.41	0.00	12.09	0.77	0.01
B	54.21	3.12	0.17	35.73	2.05	0.07	28.78	1.65	0.05
Hg	212.40	3.17	0.67	354.42	5.29	1.87	242.54	3.62	0.88
Li	3.37	0.14	0.00	5.79	0.24	0.00	11.88	0.49	0.01
Mo	72.30	3.29	0.24	45.64	2.07	0.09	123.82	5.63	0.70
Sb	329.23	9.88	3.25	274.04	8.22	2.25	213.20	6.40	1.36
Se	30.32	24.26	0.74	30.24	24.19	0.73	20.15	16.12	0.32
Sn	0.46	1.04	0.00	0.20	0.44	0.00	0.14	0.31	0.00
Cd	54.20	1.81	0.10	38.77	1.29	0.05	35.68	1.19	0.04
Tl	139.10	0.52	0.07	80.34	0.30	0.02	92.72	0.35	0.03
Ce	8.19	0.14	0.00	36.53	0.61	0.02	33.64	0.56	0.02
La	2.67	0.08	0.00	15.88	0.47	0.01	14.35	0.42	0.01
Sc	10.14	0.39	0.00	7.05	0.27	0.00	3.84	0.15	0.00
Sm	3.91	0.65	0.00	3.82	0.64	0.00	3.13	0.52	0.00
Eu	0.62	0.34	0.00	0.62	0.34	0.00	0.51	0.28	0.00
Tb	0.62	0.66	0.00	0.36	0.39	0.00	0.31	0.33	0.00
Y	18.70	0.64	0.01	15.44	0.53	0.01	8.73	0.30	0.00
Yb	1.02	0.36	0.00	0.00	0.00	0.00	0.66	0.23	0.00
Pr	1.22	0.14	0.00	3.72	0.43	0.00	3.70	0.43	0.00

'Table 16 Continued' 1

Element	Sample A			Sample B			Sample C		
	EFi	EnFi	HPFi / 1000	EFi	EnFi	HPFi / 1000	EFi	EnFi	HPFi /1000
Nd	9.08	0.28	0.00	17.52	0.53	0.01	15.25	0.46	0.01
Gd	4.09	0.79	0.00	3.11	0.60	0.00	2.53	0.49	0.00
Dy	3.93	0.63	0.00	2.89	0.47	0.00	1.81	0.29	0.00
Ho	0.59	0.49	0.00	0.53	0.44	0.00	0.28	0.23	0.00
Er	1.60	0.53	0.00	1.37	0.46	0.00	0.88	0.29	0.00
Tm	0.14	0.31	0.00	0.12	0.26	0.00	0.05	0.12	0.00
Lu	0.16	0.00	0.00	0.11	0.00	0.00	0.04	0.00	0.00
Te	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 89 Risk potential posed on soil by analysed major, minor and trace elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) under neutral leach conditions

	Sample A			Sample B			Sample C		
	EFi	EnFi	HPFi / 1000	EFi	EnFi	HPFi / 1000	EFi	EnFi	HPFi / 1000
Major elements									
S	2.70	25.76	0.07	1.89	17.98	0.03	1.64	15.61	0.03
Minor elements									
Mn	0.34	0.23	0.00	0.08	0.05	0.00	0.02	0.02	0.00
Trace elements									
As	0.06	0.15	0.00	0.04	0.11	0.00	0.08	0.21	0.00
Co	0.01	0.10	0.00	0.00	0.02	0.00	0.01	0.09	0.00
Cr	0.09	0.00	0.00	0.10	0.00	0.00	0.55	0.03	0.00
Cu	0.01	0.00	0.00	0.00	0.00	0.00	0.19	0.04	0.00
Ni	0.03	0.03	0.00	0.02	0.02	0.00	0.07	0.07	0.00
Pb	0.17	0.35	0.00	0.04	0.09	0.00	0.07	0.14	0.00
V	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.07	0.23	0.00	0.01	0.04	0.00	0.20	0.62	0.00
Hg	0.02	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	0.02	1.05	0.00	0.01	0.47	0.00	0.01	0.70	0.00

Table 90 Risk potential posed on soil by analysed major, minor and trace elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) under acid leach conditions

	Sample A			Sample B			Sample C		
	EFi	**EnFi**	**HPFi / 1000**	**EFi**	**EnFi**	**HPFi / 1000**	**EFi**	**EnFi**	**HPFi / 1000**
Major elements									
S	3.07	29.22	0.09	2.37	22.62	0.05	2.53	24.07	0.06
Minor elements									
Mn	0.75	0.51	0.00	0.14	0.10	0.00	0.03	0.02	0.00
Trace elements									
As	0.42	1.15	0.00	0.71	1.96	0.00	0.69	1.91	0.00
Co	0.03	0.25	0.00	0.03	0.26	0.00	0.02	0.15	0.00
Cr	0.61	0.03	0.00	2.29	0.11	0.00	6.73	0.31	0.00
Cu	0.48	0.11	0.00	1.70	0.40	0.00	1.40	0.33	0.00
Ni	0.14	0.14	0.00	0.18	0.19	0.00	0.16	0.17	0.00
Pb	1.00	2.00	0.00	1.28	2.55	0.00	1.24	2.47	0.00
V	0.06	0.05	0.00	0.15	0.12	0.00	0.10	0.08	0.00
Zn	0.15	0.46	0.00	0.13	0.41	0.00	0.25	0.77	0.00
Hg	0.04	0.61	0.00	0.38	5.29	0.00	0.26	3.62	0.00
Cd	0.03	1.42	0.00	0.03	1.29	0.00	0.02	1.19	0.00

Table 91 Risk potential posed on soil by analysed major, minor and trace elements in coal waste samples A (Waterberg coal slurry), B (Witbank coal slurry) and C (Witbank coal discards) under oxidising leach conditions

	Sample A			Sample B			Sample C		
	EFi	**EnFi**	**HPFi / 1000**	**EFi**	**EnFi**	**HPFi / 1000**	**EFi**	**EnFi**	**HPFi / 1000**
Major elements									
S	10.59	100.83	1.07	5.79	55.10	0.32	11.16	106.29	1.19
Minor elements									
Mn	0.82	0.55	0.00	0.14	0.10	0.00	0.03	0.02	0.00
Trace elements									
As	1.32	3.64	0.00	0.71	1.96	0.00	0.69	1.91	0.00
Co	0.05	0.47	0.00	0.03	0.26	0.00	0.02	0.15	0.00
Cr	2.11	0.10	0.00	2.29	0.11	0.00	6.73	0.31	0.00
Cu	1.87	0.44	0.00	1.70	0.40	0.00	1.40	0.33	0.00
Ni	0.27	0.27	0.00	0.18	0.19	0.00	0.16	0.17	0.00
Pb	1.26	2.52	0.00	1.28	2.55	0.00	1.24	2.47	0.00
V	0.30	0.24	0.00	0.15	0.12	0.00	0.10	0.08	0.00
Zn	0.30	0.91	0.00	0.13	0.41	0.00	0.25	0.77	0.00
Hg	0.23	3.17	0.00	0.38	5.29	0.00	0.26	3.62	0.00
Cd	0.04	1.81	0.00	0.03	1.29	0.00	0.02	1.19	0.00