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Determination of hazardous trace elements in select Hwange, Zimbabwe coal samples with a comparison to select South African coal samples.

Nonhlanhla Gugu Mguni

A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Engineering

Johannesburg, 2015

Declaration

I declare that this dissertation is my own, unaided work. It is being submitted to the degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

……

(Signature of Candidate)

9th day of March 2015

Abstract

In southern Africa, coal is a relatively abundant and cheap fossil fuel which is a major source of energy and a huge income generator. Although coal has found a lot of use, it is an anthropogenic source of trace element emissions and although these trace elements (TEs) may occur in parts per million, mass consumption of coal during utilisation results in the release of large quantities of potentially harmful TEs to the environment. With reported diseases like arsenism, minamata disease and selenosis (Zheng et al., 1999) from coal combustion emissions, it is important to regulate TE emissions. Due to global perception, the following TEs were chosen for consideration: As, B, Be, Co, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se and V (which were analysed by ICP-MS) and Hg (which was analysed using an automatic Hydride Generation-Flow Injection Mercury System).

There is limited data on TEs in African coals and whilst no TE control legislation exists, Pb in petrol is currently being regulated in South Africa. Important factors such as the mode of occurrence of TEs and their associations with other minerals in coal influence, or affect, the fate of TEs release during coal utilisation.

Three run-of-mine (ROM) belt cut coal samples were supplied by Hwange Colliery and two South African samples were used for comparison. The coal samples were subjected to density fractionation and sequential leaching. Mineral matter was determined using XRD and coal petrography was used to consider the organic components. Comparisons of the ROM coals with average global and mean South African values were carried out. Generally, TEs like Cd, Sb and Se in ROM samples of both coalfields appear consistent with published SA data and global average values, whilst values of Hg and Mn in all the coal samples are above the global and SA average values.

Density fractionation data show most TEs are concentrated in higher density fractions, hence showing an association with minerals over organic matter. Most TEs in Zimbabwean coals seem to show a strong correlation with mineral matter

which should be able to be removed prior to coal utilisation during efficient beneficiation practises.

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List of Abbreviations

ACCCE	American Coalition for Clean Coal Electricity
CRM	Certified Reference Material
DOE	US Department of Energy
EXAFS	Extended X-Ray Absorption Fine Structure
FI-MH-AAS	Flow injection mercury hydride atomic absorption spectrometer
HAPs	Hazardous Air Pollutants
IARC	International Agency for Research on Cancer
ICCP	International Committee for Coal and Organic Petrology
ICP-MS	Inductively coupled plasma mass spectrometer
IEA	International Energy Agency
LA-ICP-MS	Laser ablation inductively coupled plasma mass spectrometer
MATS	Mercury and Air Toxic standards
MOE	Ministry of the Environment programs and initiatives
RE	Relative Enrichment
ROM	Run-off Mine
TEs	Trace Elements
USEPA	US Environmental Protection Agency
WHO	World Health Organisation
XAFS	X-ray Absorption Fine Structure spectroscopy
XRD	X-ray diffraction

Chapter 1

Introduction

Coal still remains a versatile fossil fuel, finding use in a variety of domestic and industrial applications. About 25% of the world's primary energy is thermal energy (IEA, 2012); America's coal use accounts for 39% of its electricity (ACCCE, 2013). Following the Fukushima nuclear disaster in Japan, countries like Germany have passed legislation to stop using nuclear energy and build more thermal power stations as well as opting for renewable means to provide electricity for their huge economy (Carrasco, 2011). In southern Africa coal is relatively abundant, and in Zimbabwe it is being produced for both local and global markets. In South Africa, coal is a major abundant indigenous resource accounting for more than 70% of coal resources in Africa and generating over 94% of electricity used around the country (World Coal Association, 2013). It is the back bone of South Africa's industry, finding use both in the energy sector as well as the metallurgical industry where it is used to reduce iron and steel (Snyman and Botha, 1993). South Africa is also expanding its energy supplies to assist its growing economy by building two new thermal power stations, namely Medupi in the Limpopo province and Kusile in the Mpumalanga province.

Due to large quantities of coal burnt, coal combustion is an anthropogenic (man-made) way of releasing large quantities of trace elements (TEs) into the environment, creating environmental and health risks (Wagner and Hlatshwayo, 2005). Release of these TEs has become an area of great concern due to their detrimental effects to health and environment. Important factors like their mode of occurrence and their associations with other minerals in coal influence or affect the fate of TEs during coal combustion (Spears et al., 2007). The mode of occurrence of TEs in coal refers to the organic and inorganic affinity of that element in coal. Selective mining and/or coal washing could be applied effectively to reduce the emission of these TEs after understanding the distribution of these TEs in coal.

Trace elements in coal are elements which occur at concentrations less than 1000 ppm. Although they occur at low concentrations (even parts per billion, ppb, or

parts per trillion, ppt, in coal), due to the high quantities of coal which are utilised, their quantities emitted to the environment are potentially high. Though some TEs are essential for normal growth in plants and human beings, when concentrations exceed their nutritional needs, they become toxic. Gupta (1999) listed 25 TEs including Al, Sb, Hg, Cd, Ge, V, Si, Rb, Ag, Pb, Bi, and Ti, which are not needed for human growth, development, and reproduction, but still occur more or less constantly in living tissues. These TEs are usually acquired by the body through environmental contaminants. Trace elements usually find their way into the human body either by direct absorption through the skin, by inhalation or ingestion. The extent to which these TEs may have hazardous impact is dependent on the period of exposure, concentration and quantity of material used (Gupta, 1999). Zheng et al. (1999) attributed diseases like arsenism and endemic selenium intoxication in southern China to the use of high As and Se coals in unvented ovens.

Literature reveals that there is great variation in concentration of TEs in coals from different parts of the globe (Swaine, 1990; Ketris and Yudovich, 2009). These differences exist due to differences in the factors controlling the dispersion and accumulation of chemical elements in coal forming basins. This project aimed to determine TEs in selected Zimbabwe Hwange coals (no previous data available in literature) and two selected South African coals, and to compare the TE fingerprints of these two Karoo-aged coal sample sets from different coal basins with each other and with global values.

Hwange Colliery is located in Hwange town, in the Matabeleland North Province in Zimbabwe. During early lower Permian age at the end of glaciatial period, a large inland sea was formed between Zambia and Zimbabwe, forming the mid Zambezi valley basin (Duguid, 1980). The mid Zambezi Valley basin contains approximately 92.5% of Zimbabwe's coal reserves, which contain immense amounts of steam coal and relatively very little coking coal (Moyo, 2012).

1.1 Research problem

Trace elements have become a major concern due to their detrimental effects on the environment as a result of large quantities emitted during coal utilisation;

hence there is a need to study and understand their occurrence and determine mitigation options. Whilst there is limited South African data on TEs (Willis, 1983; Waitling and Waitling, 1982; Cairncross, 1990; Wagner and Hlatshwayo, 2005; Dabrowski et al., 2008; Bunt and Waanders 2009; Wagner and Tlotleng, 2012), there is no published data on TE in Zimbabwean coals.

1.2 Aim

To determine TEs in selected Zimbabwean coals and hence compare with TEs in selected South African coals.

1.3 Objectives

- To compare the TE values obtained for the selected southern African coals with average global values and mean South Africa (SA) values.
- To compare the data from both coalfields and find correlations between them.
- To infer the modes of occurrence of trace elements in these coal samples by using density fractionation and leaching sample preparation techniques.
- To compare the density fractionation and leaching sample preparation methods.

1.4 Scope of the dissertation

This document outlines the work which was covered during the research project to achieve a MScEng in Chemical Engineering. Chapter 2 presents the Literature Review. Chapter 3 outlines the methodology undertaken to fulfill the work of this project, first discussing the coal characterization techniques, followed by the density fractionation and leaching experiments. Chapter 4 concerns the Results and Discussion section of this document, laid out in the same format as the methodology section. The conclusions of this work are outlined in Chapter 5, followed by recommendations.

Chapter 2

Literature Review

In this chapter a theoretical framework for the research is provided. Coal origin and formation in both Zimbabwean and South African coalfields are outlined. The structure and constituents of coal are discussed. Previous work on TEs is discussed, as well as methods of identifying TEs in coal. Health and environmental effects of TEs in coal are outlined in this chapter.

Understanding the origin of coal and the factors influencing coal formation are important to locate coal resources, their extent, and quality, as well as utilising them in an environmentally friendly manner (Malvadkar et al, 2004). This project seeks to address TEs in coal and their modes of occurrence as a means of utilising the information to reduce emissions of hazardous air pollutants.

2.1 The Origin of Coal

Coal is a combustible sedimentary rock composed of lithified plant debris which was originally deposited in a swampy depositional environment to form soft, spongy sediment called peat (Ward and Suárez-Ruiz, 2008). Coal contains varying amounts of C, H, N, O, S, as well as trace amounts of other elements and mineral matter. It is a heterogeneous and extremely complex material which exhibits a wide range of physical properties and varies in colour from brown to black due to rank changes. There are two sequential processes of coal formation, peatification and coalification.

2.1.1 Peatification

Peatification is the biochemical process of converting plant material into peat by anaerobic bacteria (Malvadkar et al., 2004).

2.1.2 Coalification

Coalification is the conversion of buried peat to increasingly higher ranking coal by geological processes. Physical and chemical processes brought about by compaction and elevated temperatures with prolonged burial at depths of up to several kilometers and over periods of up to several hundred million years lead to the coalification process (Ward and Suárez-Ruiz, 2008). Coalification is a

continuing process involving increases in both temperature and pressure resulting from burial in the Earth, and as it proceeds coal of increasing hardness, calorific value and reduced tar, oil and gas content is produced (Schweinfurth and Finkelman, 2003). Organic matter, which is relatively rich in water, oxygen, and hydrogen gradually loses these constituents, becoming highly enriched in fixed carbon as coalification proceeds. Some of the carbon and hydrogen are converted to methane gas (CH_4) in this process. Coalification of the less massive parts of trees and small plants resulted in the formation of open structure deposits, fusain (mineral charcoal) and durain (dull coal) which enabled enrichment by mineral matter both by chemical reactions and by simple admixture (Schweinfurth and Finkelman, 2003).

Increasing temperature is considered more important than increasing pressure in promoting coalification, as higher temperatures eliminate moisture and volatile elements therefore producing coals of higher rank and higher calorific value (Schweinfurth and Finkelman, 2003).

Different geological ages have led to the formation of coal in the northern and southern hemispheres. The Carboniferous Period in the northern hemisphere (Europe and North America), which consisted of warm periodic flooding or drought conditions, led to the formation of vitrinite rich deposits varying in rank from brown coal to anthracite coal (Malvadkar et al., 2004). In the southern hemisphere, which is also known as Gondwanaland (Africa, Australia, South America and the Antarctic), Permian swamps existed under cold to cool temperature conditions associated with the decline of a massive cold ice age (Falcon, 1986) resulting in thinner inertinite-rich deposits. The main differences in northern and southern Hemisphere coals are shown in Table 2.1.

Table 2. 1: Main Features distinguishing Northern and Southern Hemisphere coals (Falcon, 1986)

Feature	Northern hemisphere	Southern Hemisphere
Climate	Hot, humid, equatorial	Cold-cool-warm temperature; wet and dry
Plant growth	Rapid, long continuous growing Seasons	Moderate, short growing seasons
Rate of plant degradation	Relatively rapid	Slow to moderately rapid
Geological setting and coal-bearing basins	Uncompacted deep, rapidly subsiding geosynclines	Relatively stable continental (cratonic and intercratonic) regions
Depositional conditions	Wide coastal lowlands	Fluviatile, lacustrine, deltaic, coastal back swamps
Geochemical conditions	Predominately marine	Fresh water, brackish to marine
Plants	Lycopod flora	Glossopterid flora
Factors inducing rank	Geothermal heat from deep burial and pressure (regional)	Geothermal heat from crustal fractures and local igneous intrusions (regional and local)

2.2 Coal formation in southern Africa

Gondwana coal deposits in southern Africa are found in two major tectonic settings: cratonic platforms and rifted fault-bounded basins (Snyman and Botha, 1993). The major coal-bearing strata in southern Africa occur in the Karoo Sequence and these coals range from Early Permian through to Early Triassic, and are predominately bituminous to anthracite in rank (Falcon, 1989). Trace elements may be concentrated in specific coal beds and have different affinities for either the organic compounds or the mineral matter of the coal. The coals are characterised by high inertinite, variable semifusinite, vitrinite, and low sulphur content (Cadle et al., 2000). South African coal basins occur in intracratonic rifts whilst the Hwange (Zimbabwe) coal basins occur in the craton of the Zambezi basin.

2.2.1 Coal Formation in Zimbabwe

In Zimbabwe, coal deposits occur in the lower part of the thick succession in the Lower Karoo and are all of the Permian age. The main areas of coal deposition are the mid-Zambezi basin in the north and north-west (where Hwange coalfields are), the Mazunga basin in the south (which constitutes the eastern part of the Tuli basin), and the Sabi-Limpopo in the south and the south-east which are the Save and Tuli basin put together (Johnson et al., 1996), as shown in Figure 2.1. The Hwange (formerly Wankie) coalfields are shown in Figure 2.2

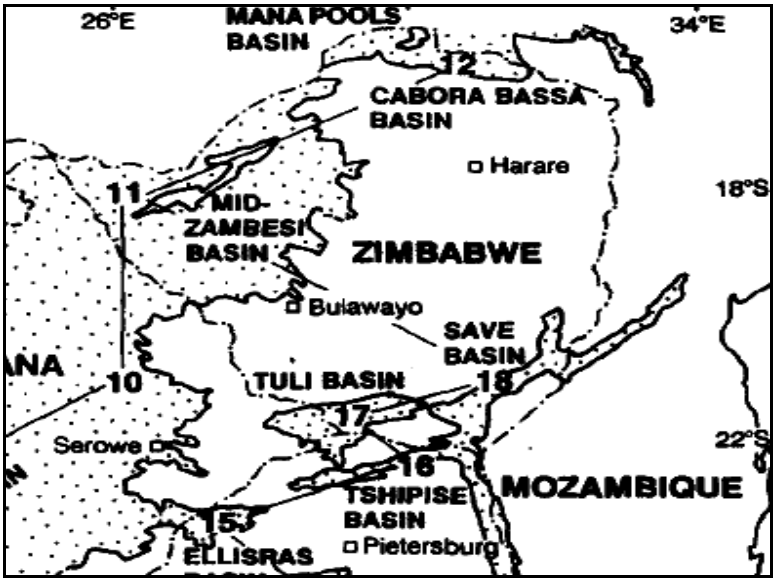

Figure 2.1: Karoo basins in Zimbabwe (Johnson et al.,1996)

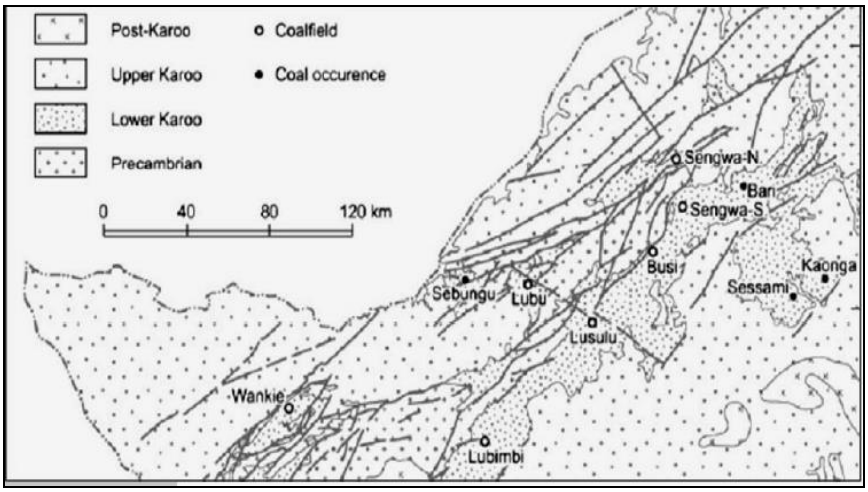

Figure 2.2: Hwange (Wankie) coalfield in the Mid Zambezi basin (Moyo, 2012)

Hwange Colliery is the only commercial coal mine in the Hwange coalfield and it is located in Hwange town (Matabeleland North Province), Zimbabwe. Duguid (1986) explained the Hwange coal measures using a facies model as shown in Figure 2.3. The model shows the transgression of a freshwater lake (post-glacial) over a shoreline plain.

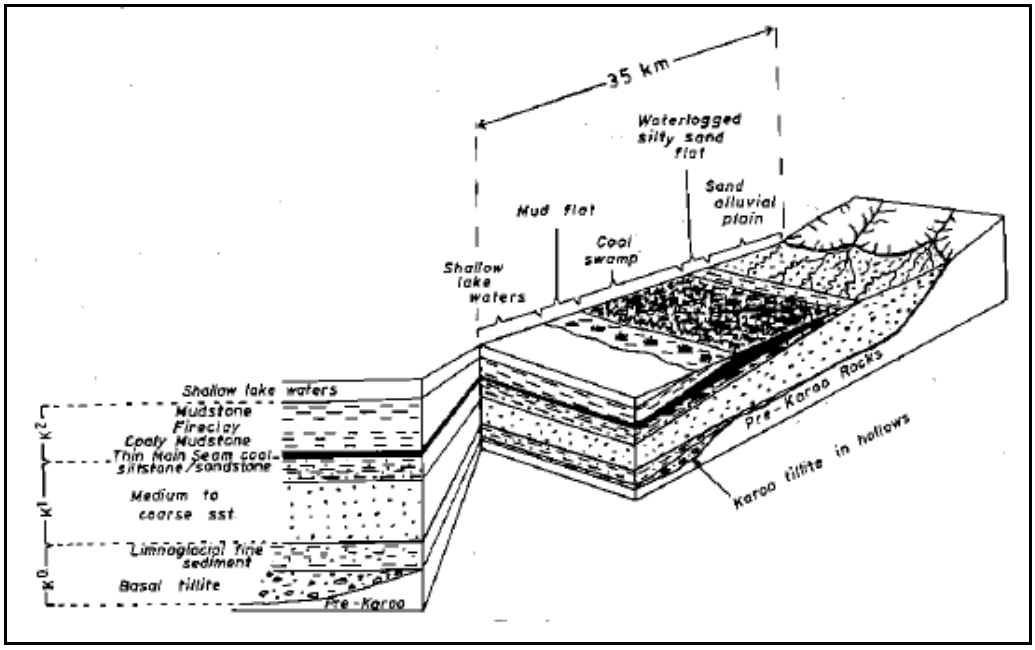

Figure 2.3: The generalized facies model of the Hwange coal measures, during peat swamp times, based on borehole and field evidence (Duguid, 1986)

The coals in Zimbabwe are palaeoshoreline deposits, and peatification took place on the gently-shelving paleoplain (Duguid, 1980). Though deposition started on metamorphosed rocks, the coal bearing strata are unmetamorphosed. Coal-bearing strata were laid down on belts of crustal weakness which probably sagged as a result of high heat flow of the mantle. The Mid-Zambezi Basin was largely stripped by erosion, whilst the Mazunga Basin in the south and the Sabi-Limpopo Basin in the south and south-east were mostly covered by flood basalts, which terminated Karoo sedimentation (Duguid, 1980). A general stratigraphy of the Hwange main seam is shown in Figure 2.4.

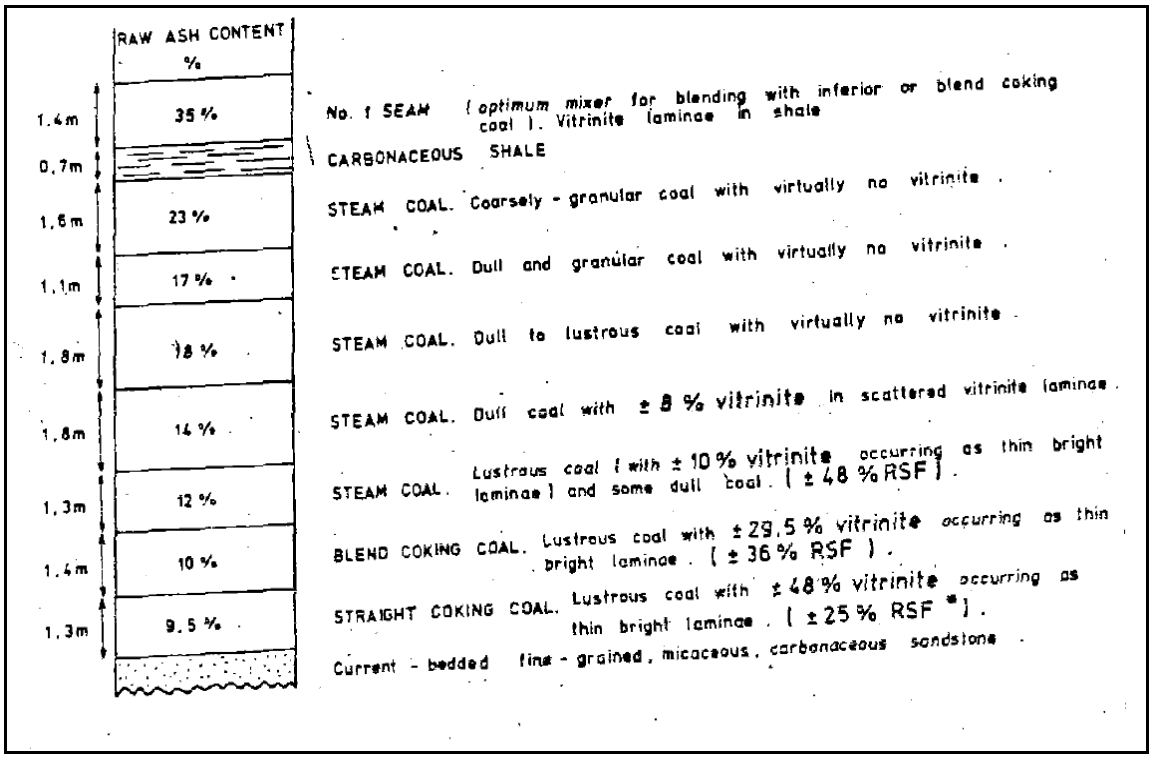

Figure 2.4: The general stratigraphy of the Hwange Main Seam coal and the position of the No. 1 Seam around Hwange (Duguid, 1980)

2.2.2 Coal Formation in South Africa

South African coal deposits are hosted in the Karoo sequence of Carboniferous to Jurassic age (Snyman and Botha, 1993) primarily in the Permian as shown in Figure 2.5. The stratigraphy of the Karoo basin comprises Dwyka, Ecca, Beaufort and Stormberg groups, which represent sediments deposited in glacial, marine, fluviodeltaic, fluviolacustrine, dry and wet environments (Cadle et al., 2000). In South Africa, coal is found in 19 coal fields which contain coal ranging from low rank bituminous in the Free State to anthracite in Kwazulu Natal (KZN). Though these coalfields occur in the Karoo basin, coal formation in the KZN, Limpopo, Springbok Flats, and Waterberg coalfields have different stratigraphic terminologies (Cairncross, 2001). With the commercially exploited Witbank and Highveld coalfields nearing depletion, the Waterberg seems a likely replacement as it has the potential to contain the vast majority of the country's remaining in situ virgin coal resources (Jeffrey, 2005).

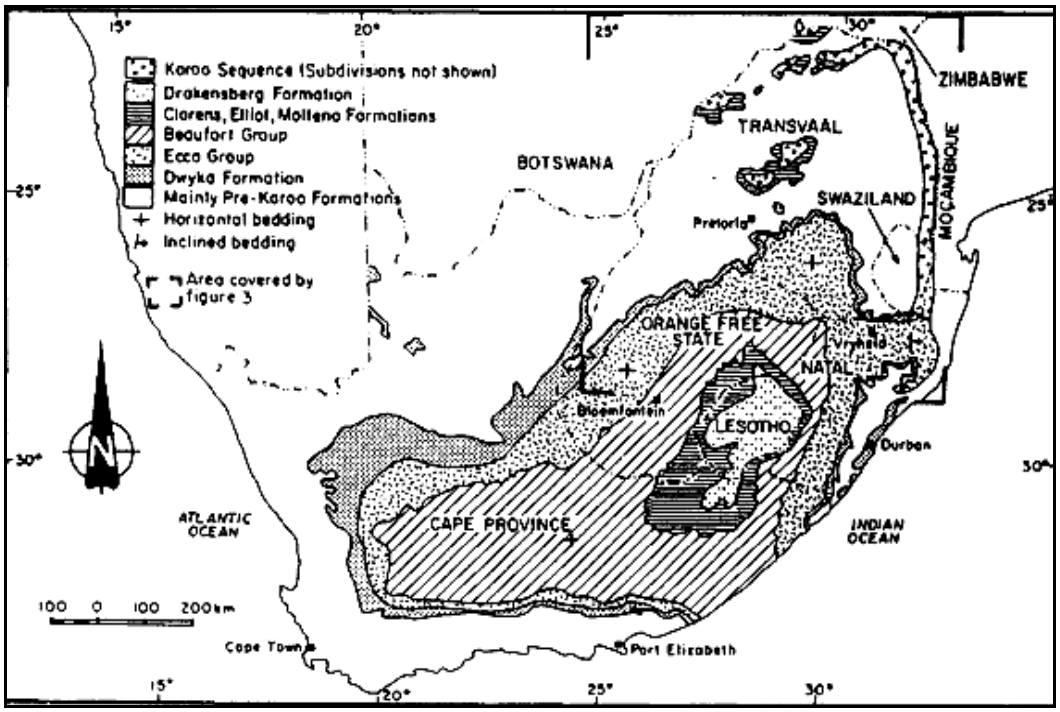

Figure 2.5: The distribution of rocks of the Karoo sequence in South Africa and the subdivision of the Sequence within the main basin (Snyman and Botha, 1993).

The Witbank-Highveld coals are hosted in the sedimentary succession of the Vryheid Formation of the mid-Permian Ecca Group of the Karoo Supergroup (Wagner and Hlatshwayo, 2005). These coals which formed in a cool to warm environment are low rank bituminous coals with high ash content of 20-30% (Wagner and Hlatshwayo, 2005).

Waterberg coals occur in two basins, the Warmbaths and the Middleburg basins which have sedimentary rocks up to 5 000 m thick (Callaghan, 1993) and typically contain high vitrinite, high ash coals in the Kungurian Grootegeluk formation and high inertinite, low ash coals in the Artinskian Vryheid Formation (Wagner and Tlotleng, 2012). These two basins are both fault bonded grabens.

2.3 Coal Classification

Coal can be classified or grouped into different types, rank, carbon-hydrogen ratio, and volatile matter (Speight, 2005) according to certain properties.

2.3.1 Coal Rank

Coal rank refers to the degree of metamorphism or coalification undergone by a coal and is a measure of the maturity of coal. It is assessed in terms of the fixed carbon content (the combustible solid matter left in coal after lighter volatile hydrogen rich compounds are driven off during coalification), moisture, calorific value, volatile matter and vitrinite reflectance; hence coal quality is largely determined by coal rank.

As coal rank increases, the chemical composition of the vitrinite correspondingly changes; the vitrinite macerals become increasingly reflective as viewed under the petrographic microscope. The percentage reflection of a beam of normal incident white light from the surface of polished vitrinite is a function of the rank (maturity) of the maceral (Schweinfurth and Finkelman, 2003). Higher rank coals were buried more deeply and they were subjected to higher temperatures and pressures during and after burial; hence, older coals tend to be of a higher rank. Figure 2.6 shows the successive transformation of peat into different types of coal as geological processes apply pressure on the peat (Bowen and Irwin, 2008).

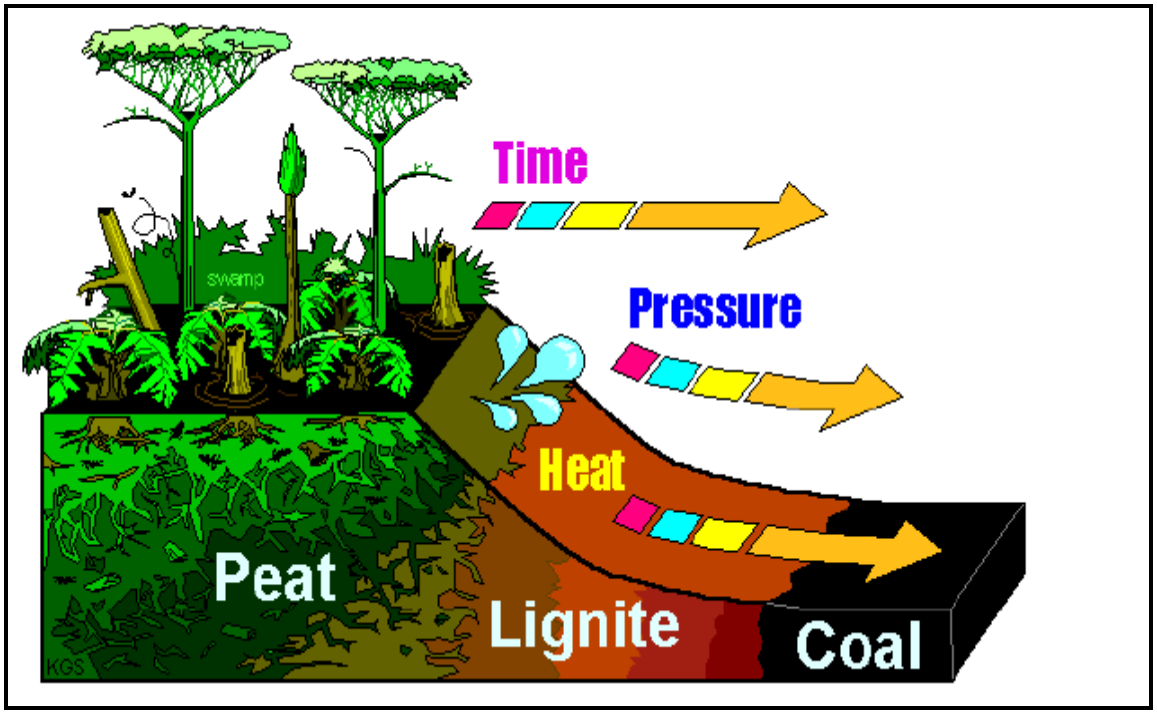

Figure 2.6: Coal Formation (Bowen and Irwin, 2008)

Coal is usually divided into four ranks, from highest to lowest rank: anthracite, bituminous, subbituminous to lignite (which is comparable to brown coal) (Bowen and Irwin, 2008). About 1% coal reserves in a few countries is anthracite, which is mostly used in the metallurgical industry. In South Africa, 2% of the coal reserves are anthracite (Eberhard, 2011), whilst in Zimbabwe there have not been reports on anthracite reserves, although there is coking coal.

Bituminous coal is used for electricity generation as well as for steel production. This category of coal dominates global coal with South Africa's reserves constituting 90% bituminous coal found in South Africa and 100% of coal reserves found in Zimbabwe are bituminous. Brown coal is a third rank coal which is found in South Africa in very low amounts.

2.3.2 Coal Type

Coal type refers to the kind of plant material, which is the nature of the organic components of the coal. This is based on the relative amounts of constituent macerals (vitrinite, liptinite and inertinite) (Snyman, 1989; Moore and Shearer, 2003). Coal type differences show most clearly in differences of volatile matter and hydrogen, which progressively diminish at higher ranks (Suggate and Dickinson, 2004).

In hand specimens, coal usually shows more or less pronounced banded appearance due to accumulation of duller and brighter coal laminae (Van Krevelen and Schuyer, 1957). According to Van Krevelen and Schuyer (1957), Stopes in 1919 classified bright coal into vitrain and clarain and dull coal into durain and fusain on a macroscopic level. Microscopically coal is identified via macerals.

2.3.2.1 Macerals

Macerals are entities evolved from different organs and tissues of the original plant material during primary accumulation, peatification and the early stages of coalification (Falcon and Snyman, 1986). These are the particles of the organic matter. Identification of the plant materials of an individual coal maceral is important for determining the quality of the coal and hence its use.

The Heerlen nomenclature distinguishes between lithotypes (types of coal with the nature dependent on the original plant structure) and macerals, which are the homogenous microscopic organic constituents of coal (Van Krevelen and Schuyer, 1957). Formation of macerals is dependent on a number of factors like type of plant community, climatic controls, ecological conditions, acidity value and the redox values. There are three maceral groups which occur in coal: liptinite, vitrinite, and inertinite. Each maceral group exhibits a distribution of densities; liptinite distributions do not overlap with other macerals (vitrinite and inertinite) whilst vitrinite density distributions overlap significantly with inertinite distributions (Dyrkacz et al., 1984).

Liptinite

Liptinite are finely ground macerated remains originally formed by spores, pollen, dinoflagellate cysts, leaf cuticles, plant resins and waxes (Padley, 1995). The liptinite group contains several subgroups based on these original plant parts namely alginite, reinite and sporinite. Liptinite macerals are more enriched in hydrogen than either vitrinite or inertinite, producing larger amounts and higher grades of liquid fuel when subjected to destructive distillation (Schweinfurth and Finkelman, 2003). Liptinite reflectance is the lowest among the maceral groups due to their dark colour in reflected light (Suárez-Ruiz and Ward, 2008).

Vitrinite

Vitrinite is one of the primary components of coal which results from the coalification of amorphous humic plant material. It is derived from cell-wall material and the woody tissue of plants. Vitrinite has a shiny appearance resembling that of glass. Chemically vitrinite is composed of polymers, cellulose and lignin. Vitrinite is highly sensitive to heat and it becomes more vitreous, denser and tougher as it is subjected to higher heat levels. Coal scientists use an index of vitrinite reflectance to determine the level of heat or maturity to which coals have been subjected (Schweinfurth and Finkelman, 2003). Vitrinite dominates in northern hemisphere coals.

Inertinite

Inertinite is a common maceral in most southern African coals. These are formed from barks, stem, leaves and roots that have been strongly altered and degraded under oxidising conditions before deposition, or by redox, biochemical, and chemical processes at the peat stage (Suárez-Ruiz and Ward, 2008). These macerals exhibit high degrees of aromatization and condensation with high levels of cross-linking (Suárez-Ruiz and Ward, 2008). A representative of inertinite is fusinite, or mineral charcoal, which formed when occasionally or seasonally peat swamps dried out and the surface peat either slowly got oxidised or caught fire, or growing plants were partially charred (Schweinfurth and Finkelman, 2003). Sub categories of inertinite include semifusinite and inertodetrinite. Compared to other macerals, inertinite is more inert and hence less reactive in carbonisation.

2.3.3 Coal Grade

Coal grade refers to the range of impurities in the coal, which is the extent of dilution by mineral matter. Coal grade reflects the extent to which accumulation of plant debris has been kept free of contamination by mineral matter including the periods before burial (i.e., during peat accumulation), after burial, and during rank advance (Ward and Suárez-Ruiz, 2008). Coal grade is based on the quantity of inorganic material (ash) left after complete combustion. Typically southern African coals have a low grade, that is they are rich in mineral matter.

2.3.3.1 Mineral matter in coal

The inorganic constituents of coal are all compounds that are not part of the organic coal. These are referred to as the mineral matter in coal (Speight, 2005). These minerals are made up of common elements including O, Al, Si, Fe, S and Ca. In coal, minerals normally occur as single crystals or clusters of crystals intermixed with the organic matter or fill void spaces in coal (Schweinfurth and Finkelman, 2003; Schweinfurth , 2009). Ash is formed from mineral matter in coal which is burnt in oxygen or air. The amount of mineral matter in coal varies from seam to seam and even within seams. Mineral matter in coal may be

classified as inherent mineral matter or adventitious mineral matter. Inherent mineral matter cannot be readily separated from the coal substance as it is closely associated with it. Adventitious mineral matter is inorganic material which is less loosely associated with coal and can be readily separated. Syngenetic minerals were initially present in the original plant tissue or they were introduced into the swamp from waterborne or windborne sediments. Epigenetic minerals followed the initial stages of coalification and were produced by water .precipitation.

Trace elements associated with syngenetic minerals are finely disseminated in the coal matrix, hence they are difficult to fully separate from the organic substrate, whilst TEs associated with epigenetic or extraneous minerals may be liberated through coal washing (Bergh et al., 2011).

Minerals can be subdivided into major, minor and trace elements. Trace elements and the main mineral groups are discussed further. Although 120 different minerals have been identified in coal, out of 33 common minerals only 8 are abundant enough to be termed major constituents of coal. Common minerals found in coal are shown in Table 2.2. Minerals mainly fall into five main groups: silicates, sulphide and sulphate minerals, carbonates and other minerals that include elements that may occur in trace amounts (Speight, 2005). Minerals contribute very little, if anything to coal utilisation (Ward, 2002) but can cause slagging, fouling, clinker formation or high ash formation. Coal ash can be used for various applications such as brick making or road building. After fully understanding the minerals in coarse and fine ash particles from the Sasol gasification process, anorthite/mullite is used in the refractory industry, whilst coarse ash size fractions are used as aggregates in road construction and bricks manufacture (Matjie and Van Alphen, 2008). The -38+ 20µm ash size fraction which is characterised by high proportions of aluminosilicates enhances pozzolanic reactivity which makes it suitable for the cement/concrete industry (Matjie and Van Alphen, 2008). The main mineral groups are discussed further below: (silicates, sulphides, sulphates and carbonates).

Table 2.2: Common minerals found in coal and their elemental composition (Schweinfurth and Finkelman, 2003; Nalbandian, 2012)

Mineral matter	Chemical Composition	Remarks
	Major Mineral Constituents	
Quartz	SiO_2	
Clay Minerals		
Kaolinite	$Al_2Si_2O_5(OH)_4$	
Illite	$KAl_4(AlSi_7O_{20})(OH)_4$	
Montmorilinite	$(1/2Ca.Na)_{0.7}(Al,Mg,Fe)_4[(Si,Al)_4O_{10}]_2(OH)_4.nH_2O$	
Chlorite	$(Mg,Al,Fe)_{12}[(Si,Al)_8O_{20}](OH)_{16}$	May contain Mn, Be,Cr,Ni and other TEs
Pyrite	FeS_2	May contain As, Cd, Co, Hg, Ni, Sb and Se
Calcite	$CaCO_3$	
Siderite	$FeCO_3$	May contain Mn.
	Minor Mineral Constituents	
Analcime	$NaAlSi_2O_6.H_2O$	
Apatite	$Ca_s(PO_4)_3(OH,F,Cl)$	
Barite	$BaSO_4$	
Chalcopyrite	$CuFeS_2$	
Clausthalite	PbSe	
Crandalilite Group		
Crandallite	$CaAl_3(PO_4)_2(OH)_5.H_20$	
Florencite	$CeAl_3(PO_4)_2(OH)_6$	
Gorceixite	$BaAl_3(PO_4)_2(OH)_5.H_20$	
Goyazite	$SrAl_3(PO_4)_2(OH)_5.H_20$	
Dolomite	$CaMg(CO_3)_2$	
Feldspars	$(Ca,K,Na)AlSi_3O_8$	
Galena	PbS	
Marcasite	FeS_2	May contain same elements as pyrite
Monazite	$(Ce,La,Y,Th,Nd)PO_4$	
Rutile/Anatase	TiO_2	
Sphalerite	ZnS	May contain Cd
Xenotime	YPO_4	
Zircon	$Zi[SiO_4]$	
	Trace Mineral Constituents	
Chromite	$FeCr_2O_4$	
Gibbsite	$Al(OH)_3$	
Gold	Au	
Gypsum	$CaSO_4.2H_2O$	
Halite	NaCl	
Magnetite	Fe_3O_4	
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	

Silicate Minerals

Silicate minerals occur in coal chiefly as aluminosilicates (clays) and quartz and constitute between 60-90% of the total mineral matter in most bituminous coals (Raask, 1985). The presence of clays results in a loss in calorific value, and an additional economic penalty associated with ash handling and disposal (Spears, 2000). Some TEs such as Cr and V are associated with clay. The most common clay mineral is kaolinite which is usually found within and associated with coals in most of the coal basins in the world (Speight, 2005). Clays may be of either syngenetic or epigenetic or detritus origin (Xiuyi, 2009). The second most abundant silicate is quartz, with up to 20 weight percent being common (Renton, 1986). Ruppert et al. (1985) interpreted quartz to be dominantly authigenic with an association with vitrain and mineral-rich bands from petrographic data. About 20% quartz is of detrital origin with an association with mineral-rich bands and clay-parting material.

Sulphide Minerals

The most common sulphides associated with coal are pyrite (FeS_2) and marcasite (FeS_2). Though pyrite and marcasite have the same chemical formula they have different crystal structures: pyrite is isometric whilst marcasite is orthorhombic. These two minerals contribute significantly to the total sulphur content which causes boiler tube fouling, corrosion and pollution (Speight, 2005). Pyrite and marcasite break down upon combustion into individual elements Fe and S which combine with O_2 to become iron oxide, a heavy solid which becomes part of the ash and a gas SO_x , which is emitted as part of flue gas (Schweinfurth and Finkelman, 2003). Certain trace elements like Cd, Co, Ni are associated with sulphides.

Sulphate Minerals

Sulphate minerals are not that significant in unoxidised coal. They result mostly from oxidation (weathering) of pyrite to form hydrated states of ferrous and ferric sulphates ($FeSO_4.xH_2O$). The sulphates gypsum ($CaSO_4.2H_2O$) and barite (Ba_2SO_4) are found in fresh coal (Speight, 2005). According to Silva et al. (2012), Cr, Mn, Mo and Ni may be associated with sulphate minerals.

Carbonate Minerals

Calcium, iron and magnesium are the major cations found in carbonate minerals in coal. Calcite ($CaCO_3$) and ankerite (mixed crystal of Ca, Mg, and Fe carbonates) are abundant in some coals, whilst siderite ($FeCO_3$) is dominant in other coals (Speight, 2005). These minerals make up about 10 weight percent of each group of minerals in coal (Renton, 1986), with calcite being the most common carbonate mineral, frequently occurring in veins or cleat infillings as well as in cell cavities of macerals. These minerals are all from authigenic origin which may be either syngenetic or epigenetic.

2.4 Trace Elements in coal

Many geological factors and coal forming periods influence the enrichment of TEs in coal (Dai et al., 2003). Coal contains approximately 120 inorganic compounds which were either derived directly from the vegetation or were introduced by either waterborne or windborne sediments (Schweinfurth and Finkelman, 2003). Coal may contain 76 of the 92 naturally occurring elements in the periodic table and some tend to be detrimental and hazardous to humans and the environment (Schweinfurth and Finkelman, 2003). Trace elements are emitted during coal combustion or utilisation, and the quantities emitted are dependent on the physical and chemical properties of the element, its concentration in coal, combustion conditions as well as the particulate control devices used (Nalbandian, 2012). Organically bound TEs are difficult to remove using precombustion cleaning processes as they are released only upon combustion. They can be released by deep chemical leaching processes, but this technology is expensive.

Table 2.3 shows the average global (Ketris and Yudovich, 2009) and mean SA (Wagner and Hlatshwayo, 2005) values of selected TEs in coal.

Table 2.3: Average global (Ketris and Yudovich, 2009) and mean SA (Wagner and Hlatshwayo, 2005) trace elements values in coal.

Element(ppm)	Avg global values	Mean SA values
As	9.0±0.8	2.7±1.0
Cd	0.2±0.03	0.24±0.17
Co	6±2.0	6.9±1.6
Cr	17.0±1.0	43.2±12.0
Cu	17.0±1.0	12.6±1.6
Hg	0.1±0.01	0.15±0.05
Mo	2±0.1.0	2.09±1.06
Mn	76.0±6.0	99.1±8.4
Ni	16.0±1.0	16.6±3.4
Pb	9.0±0.9	7.0±2.6
Sb	1.0±0.09	<0.136±0.06
Se	1.4±0.1	0.99±0.24
V	29.0±1.0	31.2±3.9

Recently concerns have been raised about reducing the emissions of certain TEs (specifically As, Be, Cd, Cl, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se, and U) following coal combustion. According to Schweinfurth and Finkelman (2003), the U.S. Environmental Protection Agency (EPA) in 1996 indicated that TE emissions from coal-burning power plants that use coal with relatively low to moderate TE concentrations, or that have efficient pollution control devices, may not present a significant health risk.

In other countries, TE emissions from coal burning power plants have been shown to cause severe health problems: for example, Bencko et al. (1977) found that in Czechoslovakia, children living in the vicinity of a power plant suffered hearing loss which resulted from As poisoning from the power plant emission. These lignite coals contained high levels of As (1000 ppm). The most widespread health effect of trace elements emissions has been experienced in domestic coal use in developing countries such as China. Zheng et al. (1999) discussed diseases like arsenism and endemic selenium intoxication due to the use of high As and Se coals in unvented ovens in southern China.

Finkelman (1999) argued that the widespread health problems associated with emission of TEs is caused by domestic coal combustion in developing countries where thousands suffer from arsenism.

The effects of the TEs to humans and the environment have led to the introduction of emission standards for some TEs. Many countries like Canada, China and the USA have implemented legislation to control trace element emissions from thermal power stations (Sloss, 2012). China's Hg emission limit is 30 $\mu m/m^3$ and the Canadian and USA standards are shown in the Tables 2.4 and 2.5. In southern Africa there is no legislation concerning TEs emissions from combustion: the National Environment Management: Air Quality Bill (2003) in South Africa only regulates emission control for Pb which basically results from petrol based sources.

Table 2.4: Canadian Hg standards (Sloss, 2012)

Coal type	Required Capture, %	Emission Rate, kg/TWh
Bituminous	85	3
Subbituminous	75	8
Lignite	75	15
Blends	85	3

Table 2.5: USA Hg and Air Toxics Standards (MATS) (Sloss, 2012)

Input-based emission limits for existing facilities	
Coal-fired unit(any coal other than lignite)	1.8 g/GWh
Coal-fired unit(lignite units)	6.2 g/GWh
IGCC unit (any fuel-coal or petcoke)	3.8 g/GWh
Petcoke fired unit	1.3 g/GWh
Alternative output-based emission limits for existing facilities	
Coal-fired unit(any coal other than lignite)	5 g/GWh
Coal-fired unit(lignite units)	17 g/GWh
IGCC unit (any fuel-coal or petcoke)	13 g/GWh
Petcoke fired unit	0.8 g/GWh
Output-based emission limits for new facilities	
Coal-fired unit(any coal other than lignite)	0.08 g/GWh
Coal-fired unit(lignite units)	17 g/GWh
IGCC unit (any fuel-coal or petcoke)	1.3 g/GWh
Petcoke fired unit	0.8 g/GWh

2.4.1 Classification of trace elements

Coal undergoes complex changes during combustion and gasification, which include thermal decomposition, fusion, disintegration, agglomeration, formation of char, and volatisation of volatile elements. Minerals in coal also undergo the same processes, where non-combustible minerals form either slag or fly ash or bottom ash. The classification of TEs is related to their enrichment where the relative enrichment, RE of an element in ash is defined as:

$$\mathrm{RE} = \frac{\text{element concentration in ash}}{\text{element concentration in fuel}} \times \frac{\%\ \text{ash in fuel}}{100} \qquad 2.1$$

According to the way TEs behave upon combustion and gasification they can be classified into 3 classes (Clarke, 1993):

- **Class 1** elements concentrate in coarse residues or become equally partitioned between coarse residues and finer particles. They therefore become enriched in the bottom and fly ash (Nalbandian, 2012). The release of these elements is directly related to efficient control of total particulate emissions. Examples include Mn, Be, Co and Cr.
- **Class 2** elements are volatilised in the combustor or gasifier but condense downstream. They become concentrated in the finer particles (fly ash) which may escape particulate control systems. Many studies have shown the enrichment of Group 2 elements with decreasing particle size because volatile elements condense preferentially on the surface of smaller particles in the flue gases as cooling occurs. Smaller particles have a greater ratio of surface area to volume (Clarke, 1993). These elements are enriched in the fly ash and the control of these elements is dependent on the collection of fine particles. These elements include As, Cd, Pb and Sb.
- **Class 3** elements are the most volatile elements and are not enriched in solid phases like in the bottom and fly ash (Nalbandian, 2012); they are all emitted in the vapour phase. In both combustion and gasification systems the most volatile elements like Hg may remain in the gas phase during passage through the plant, and particulate controls may have a limited

impact on the emission of these elements. However, it has been shown that highly efficient flue gas detail and particulate control devices can reduce oxidised Hg emissions by flue gas desulphurisation (FGD) (Sloss and House, 1995; Davidson et al., 2003; Sloss, 2012), though FGD cannot guarantee elemental Hg reductions.

The overlap between the classes of certain elements shows volatile behaviour in some studies but partitioning into solid residues in others, due to wide variations in the operating conditions, especially temperature, that control element volatility (Clarke, 1993). Figure 2.7 shows the categorisation of TEs behaviour during combustion and gasification.

From a computer based thermodynamic model (Fact-Sage), Bunt and Waanders (2010) successfully predicted the elemental ash phase partitioning behaviour of Class I non-volatile elements: Ba, Co, Cr, Mn and V. Bunt and Waanders (2008) found As and Se to be highly volatile, partitioning into the gas phase whilst Hg was found to be the most volatile. In fixed bed gasification, Hg was found present in the gas phase in the form of elemental $Hg_{(g)}$. The volatilities of these elements vary in the order: Hg > Se > Cd > Pb > As (Bunt and Waanders, 2008). Class II elements like Zn showed limited de volatilization behaviour in the drying and pyrolysis zone of the fixed-bed gasifier (Bunt and Waanders, 2009).

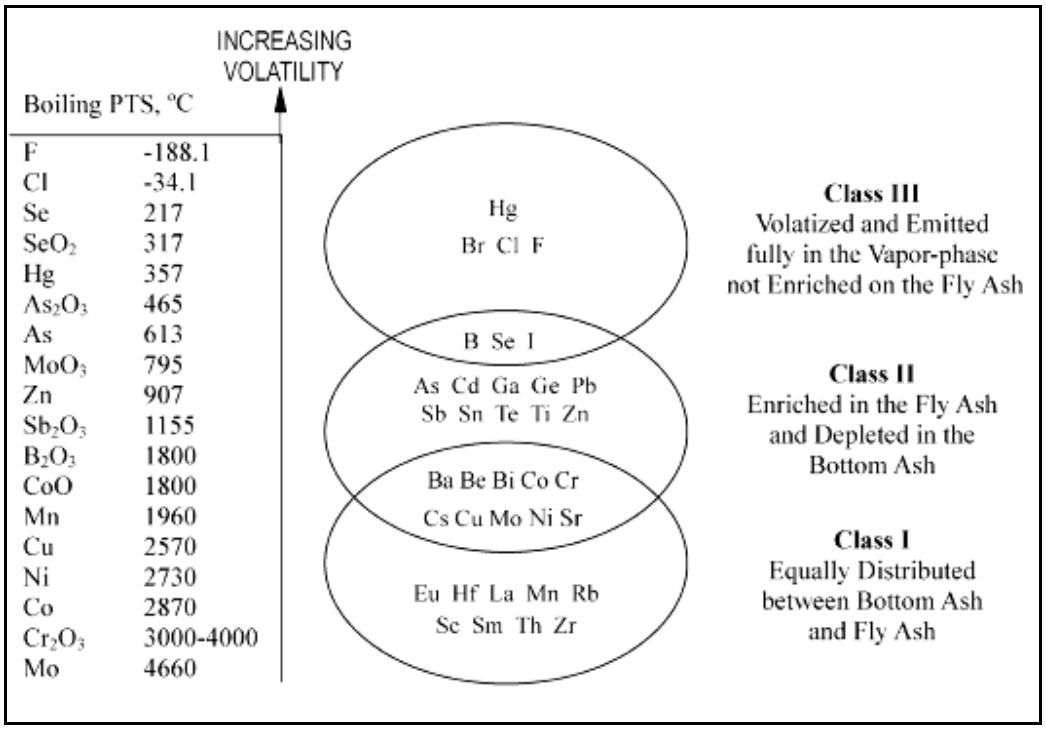

Figure 2.7: Classification of TEs based on their volatility behaviour

(Xu et al., 2003)

2.5 Modes of occurrence or speciation of trace elements in coal

The mode of occurrence refers to the organic or inorganic affinity of the element, and how an element is chemically bound and physically distributed in coal (Finkelman, 1994). Modes of occurrence of TEs determine the behaviour of the element during cleaning, combustion, conversion, or leaching of the coal, or during the weathering of the coal or its products upon disposal (Finkelman, 1980). Understanding this helps in determining which measures can be undertaken to reduce the emissions of these TEs from coal combustion.

Raask (1985) stated that the distribution and mode of occurrence of TEs in the coal substance and mineral matter depends on the chemical characteristics of the elements and also on the age, i.e. rank of coal deposits. Trace elements may be associated with either organic or inorganic matter, or both, with proportions varying with coals globally. There are certain groups of organic matter in which TEs may be associated, either free or embedded, namely: carboxylic acid

(-COOH), imino (-NH), marcapto (-SH) and phenolic hydroxyl (-OH) (Swaine and Goodarzi, 1995). Many TEs are associated with mineral matter as discrete minerals, as replacement ions in minerals, or absorbed on minerals as shown in Figure 2.8.

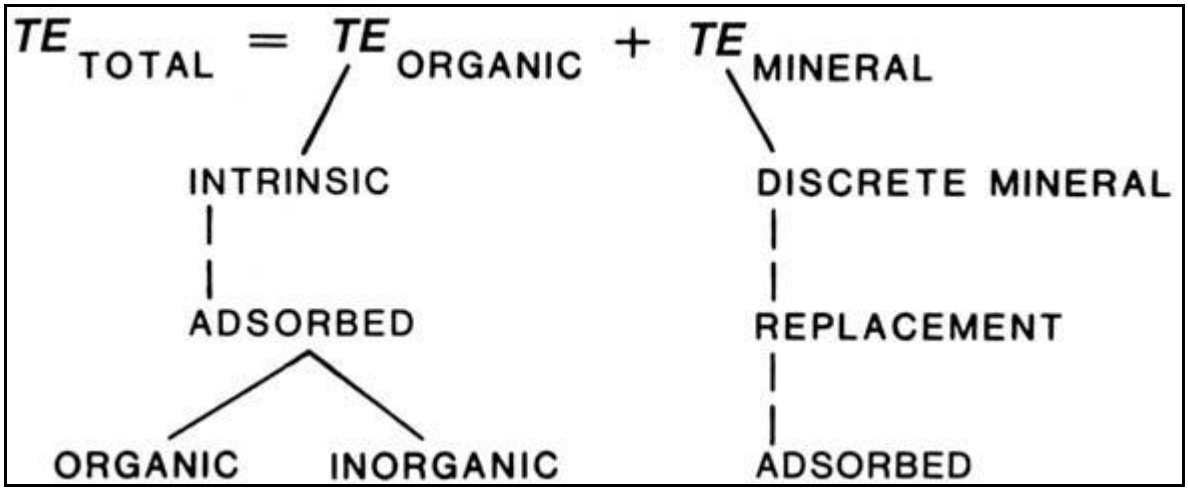

Figure 2.8: Modes of occurrence of TEs in coal (Swaine, 1990).

2.5.1 Determination of Modes of occurrence

There is limited literature which gives general rules or trends which can be used to predict elemental modes of occurrence for coal. Due to a wide variation of elemental modes of occurrence it is difficult to determine how specific elements occur in coal when their concentrations are less than 100 ppm. Literature portrays various direct and indirect methods being used to determine elemental modes of occurrence with various degrees of success. Information on modes of occurrence should include the textural relationships of the minerals and the chemical form of the elements (i.e. organic/inorganic associations). This will enable prediction regarding how the inorganic constituents will behave upon cleaning, combustion, conversion, or leaching of the coal.

Huffman et al. (1994) demonstrated the capability of X-ray absorption fine structure spectroscopy (XAFS) to provide speciation information about most TEs in coal at realistic concentration levels of 10-100 ppm provided a solid-state

multielement germanium detector is used. Huggins and Huffman (1996) found the XAFS efficient for determination of elements greater than 5ppm.

Finkelman (1994) showed that using scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) is another effective method of detecting and analysing TEs in coal as small as one micron in diameter. Micron sized minerals can be detected in situ in polished blocks (Finkelman, 1980). Swaine and Goodarzi (1995) suggested that the most effective method for determining the mode of occurrence of TEs is SEM-EDX, as it also provides textural relationships of the minerals.

Kolker et al. (2000) used selective leaching, XAFS spectroscopy and electron microbe analysis to determine the mode of occurrence of As in US coals. Arsenic was shown to be largely found in pyrite in bituminous coals from XAFS spectroscopy data. Huggins et al. (2000) examined the mode of occurrence of Cr using XAFS spectroscopy and a selective leaching protocol supplemented by scanning electron microscopy (SEM) and electron microprobe measurements. These techniques provide a basic model of predicting the fate of trace elements during combustion.

Riley et al. (2012) used sequential extraction which they compared with XAFS and near edge structure (XANES) spectroscopy. They concluded that chemical extraction gives a good indication of the speciation of TEs, if data is generated and interpreted with care. One limitation is that TEs detected in the residue may be assumed to be associated only with the organic matter of coal which may not be completely so, as some mineral matter may be shielded by organic matter or trace elements may occur in acid resistant minerals.

Li et al. (2005) felt it better to understand TE partitioning in combustion ash and determine the association of TEs with mineral matter or organic matter by using float–sink and sequential leaching experiments. Instrumental Neutron Activation Analysis (INAA) was employed to determine TE content in float and sink fractions of fly ash as well as in three major phases in the bottom ash.

Density fractionation to infer modes of occurrence

Density fractionation, or float-sink analysis, is an effective technique for the study of TE in high mineral matter coals (Davidson, 2000), and in determining their mode of occurrence. Van Krevelen and Schuyer (1957) suggested density fractionation as an indirect method of determining modes of occurrence. Querol et al. (2001) obtained seven density fractions between < 1.3 and > 2.8 g/cm^3 using heavy liquid mixtures of bromoform, tetrachloroethylene, and xylene, and combined density fraction with mathematical deconvolution of chemical analyses of whole coals and their density fraction to determine modes of occurrences of TEs in coal. Intercorrelation of TE contents with ash contents, major elements and mineral phases can be applied to study distributions of TEs (Querol et al., 2001) in density fractions. Wagner and Tlotleng (2012) used density fractionation for sample preparation in the determination of TEs and their affinities in coal, following Huggins et al. (2000), followed by ICP-MS analysis. Several other authors who have used density fractionation include Finkelman (1980), Feng and Hong (1999), Wagner and Hlatshwayo (2005), Huggins et al. (2009) and Bergh et al. (2011).

Various techniques, including XRD, can be used to analyse and identify various minerals in each float and sink fraction. Feng and Hong (1999) and Querol et al. (2001) have used XRD to determine mineral contents in the coals in an effort to infer modes of occurrence in density fractions.Wagner and Tlotleng (2012) used scanning electron microscopy with energy dispersive spectroscopy to determine pyrite and other minerals. In this project XRD will be used to determine minerals in coals.

Conaway (2001) and Wagner and Tlotleng (2012) performed washability tests on float and sink fractions. Finkelman (1980) calculated correlation coefficients of float and sink fractions of coal to investigate common modes of occurrence for TEs. Gluskoter et al. (1977) performed statistical analysis on washed coals which were separated by specific gravity methods.

Sequential Leaching to infer Modes of occurrence

Sequential chemical leaching, a long established method for determining the mineral fractions in which TEs occur (Spears, 2012), is another way of indirectly determining modes of occurrence of TEs. Different TEs are removed by different chemicals. Palmer et al. (1996) used sequential selective leaching with slight modification to Finkelman et al. (1990). Coal samples were sequentially leached with 35 ml each of 1N CH_3COONH_3, 3N HCl, concentrated HF (48%) and 2N HNO_3 and the leachate was analysed using ICP (inductively coupled plasma) analysis while the residue was analysed using instrumental neutron activation analysis (INAA). Various authors who have used sequential leaching include Wang et al. (2004b), Wang et al. (2008), Dutta el al. (2009), Norris et al. (2010), Spears (2012), and Neupane and Donahoe (2013).

Various chemicals are used in sequential leaching to destroy certain minerals and organic matter, and liberate TEs which are associated with these minerals. Extraction is carried out in stages were a chemical liberates certain elements and the residue is taken to the next stage. Wang et al. (2008) used a 10 mm diameter and 70 cm long column to leach 20 g of coal samples with 3 different acidic pH solutions of distilled water and HNO_3.

Distilled or deionised water (H_2O) can be the chemical solution used in the first stage to remove elements present in pore fluids and water soluble elements (Norris et al., 2010; Spears, 2012). Ammonium acetate (CH_3COONH_4) removes exchangeable cations and a portion of the carbonate-hosted cations. (Hlatshwayo, 2008). Hydrochloric acid (HCl) removes carbonates like calcite and exchangeable cations and monosulphides (Spears, 2012). Dilute nitric acid (HNO_3) can be used to remove TEs associate with pyrite and carbonates mainly dolomite and ankerite (Spears, 2012). Spears (2012) used concentrated HNO_3 to destroy organic matter and liberate TEs associated with organic matter. Hydrofluoric acid (HF) is used to liberate silicate bound TEs.

Kolker et al. (2000) outlines the sequential leaching procedure depicted in Figure 2.9; various elements associated with different minerals are removed by specific chemicals. Elements which are not removed by the leaching process may be

present in the organic matrix, or occur in insoluble phases such as zircon or titanium dioxide (Kolker at al., 2000). In this project distilled water was used first to remove water soluble TEs, by the sequence of steps described by Kolker et al. (2000).

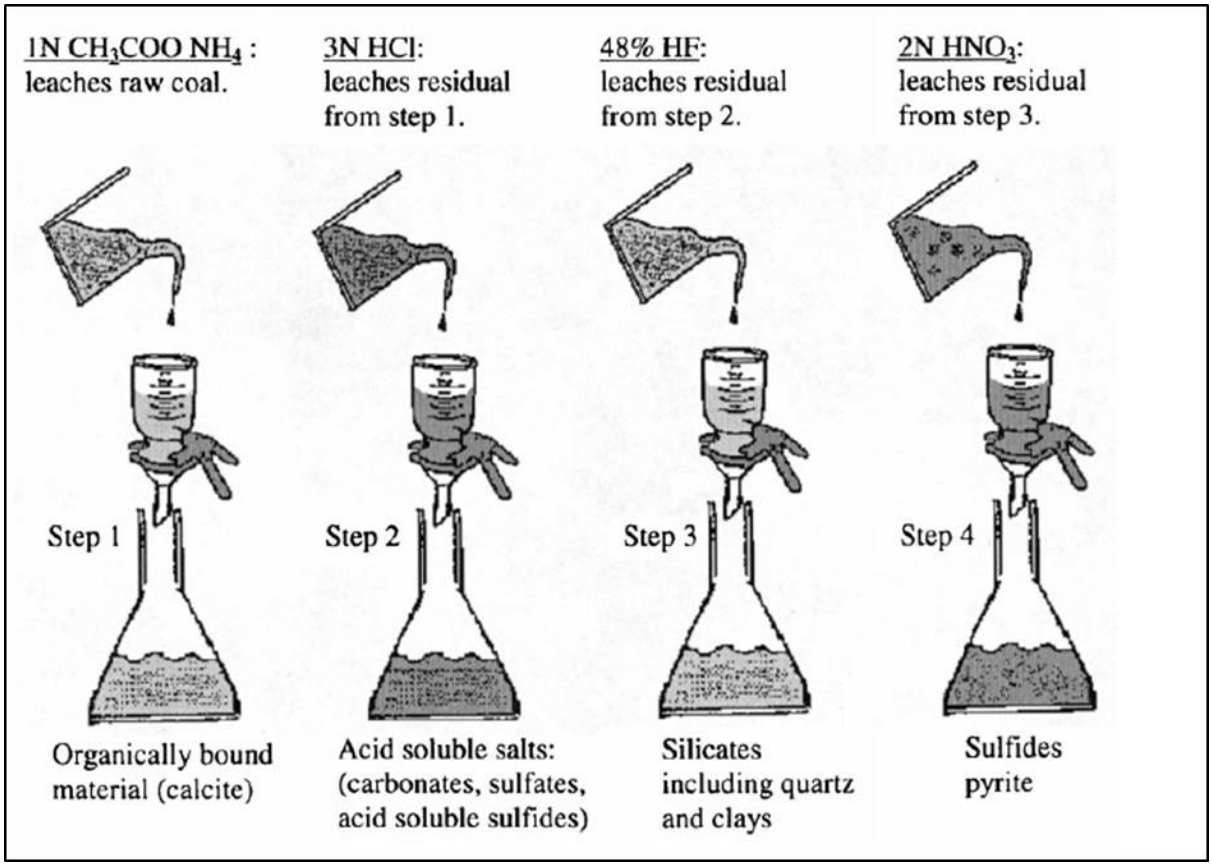

Figure 2.9: Sequential steps used in selective procedure leaching of coal samples (Kolker at al., 2000)

2.6 Trace elements considered in this study

Trace elements considered to be hazardous air pollutants (HAPs) will be discussed in this section. Their health and environmental effects will be outlined as well as their modes of occurrence. The elements which are of health and environmental concern include As, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Hg, Mn, Mo, Ni, Sb, Se, U and V. Table 2.6 shows the likely modes of occurrence of some of the TEs as determined by Finkelman (1995). A higher level of confidence, for

example 8, shows that there is a greater correlation of the TE with the mineral or organic matter, whilst a low level of confidence for example 2, shows a lower level of confidence of the suggested possible associations.

Table 2.6: Likely mode of occurrence of trace elements in coal (Finkelman, 1995)

Element	Mode of occurrence	Level of confidence
Antimony	Pyrite and accessory sulphides	4
Arsenic	Pyrite	8
Beryllium	Organic association	4
Boron	Organic association	6
Cadmium	Sphalerite	8
Chromium	Organic or clay association	2
Cobalt	Pyrite, some in accessory sulphides	4
Copper	Chalcopyrite	8
Lead	Galena	8
Mercury	Pyrite	6
Manganese	Carbonates, especially siderite and ankerite	8
Molybdenum	Probably sulphides	2
Nickel	Unclear	2
Selenium	Organic association, pyrite and accessory sulphides, selenides	8
Uranium	Organic and some in Zircon	7
Vanadium	Clays and organic association	3

Antimony (Sb)

According to Cooper and Harrison (2009), chronic exposure to Sb results in eye, skin and lung irritations with pneumoconiosis, altered electrocardiograms and stomach ulcers resulting from long-term exposure. Limited information is available on the modes of occurrence of Sb in coals. From float-sink data, Finkelman (1995) suggested that ambiguous results are obtained for the modes of occurrence of some Sb as it showed organic association, while others concluded it was inorganically bound. According to Finkelman (1980), Goldschmidt (1954) suggested that Sb is a chalcophile element with a high association with sulphides and hence it is found in sink fractions from density fractionation separation. Gluskoter et al. (1977) indicated that Sb is associated with organic matter in coal.

Finkelman (1995) concluded that the most likely modes of occurrence of Sb are with pyrites and minute accessory sulphides dispersed throughout the organic matrix, whilst some may be organically bound. According to Zeng et al. (2001), previous research showed that Sb is associated with pyrites.

Arsenic (As)

The International Agency for Research on Cancer (IARC) (1987) classified As and the As compounds as Group I carcinogens. Arsenic is a chronic poison which never leaves the body once it enters (Hatt, 2008), hence it is a major health concern. Zheng et al. (1999) discusses diseases like arsenism intoxication in southern China, due to the use of high As coals in unvented ovens. It is estimated that 252 tonnes of As have been emitted from coal-fired plants every year in China (Kang et al., 2011). Arsenic concentration varies with coal-forming age (rank) and the accumulation of As in coal is controlled by many geological factors during coal-forming processes, including plant decomposition, sedimentary environments, and epigenetic hydrothermal activity (Kang et al., 2011). Arsenic is not as big an environmental concern as Hg, because it does not leave the stack as a vapour, but it vaporises in the flame and condenses out in the boiler causing a build-up of As in the boiler (Hatt, 2008). Arsenic also poisons the catalyst used in selective reduction of NO_x.

Arsenic has several modes of occurrence, but from literature it appears that As is mainly associated with mineral matter such as pyrites as well as other sulphide minerals, and also organic matter (Kang et al., 2011). The distribution of As varies with each geological basin. Arsenic is a chalcophilic element with an affinity for organic and inorganic matter (Finkelman, 1980).

Beryllium, Be

Beryllium has adverse health effects associated with its exposure. It affects the respiratory system, the lymph nodes, the skin, and other target organs (Brisson, 2009). The US Department of Energy (DOE) (1999) passed a final rule implementing the chronic beryllium disease prevention program (CBDPP) to reduce the exposure of humans to Be. There is no data on mean global values of

Be since Be presents difficulties in determining its modes of occurrence because of its low atomic number (4). According to Finkelman (1994), Be has a high affinity for the organic components of coal and may be associated with clays.

Boron, B

Crop yields become poor due to high B soils (Nalbandian, 2012). The American Environmental Protection Agency (US EPA) and the Australian National Pollution Inventory consider B in coal utilisation to be a great concern due to its toxic effects on land plants (Boyd, 2002). Swaine (1990) indicated that B may be associated with the organic matter in coal though Boyd (2002) also found it to be associated with clays (illite) as well as bound to the crystal lattice of tourmaline. Boron associated with the organic matter is found to have a greater environmental impact than B associated with tourmaline (Boyd, 2002), as it can be released during combustion with fly ash unlike B associated with tourmaline which can be removed through coal washing.

Cadmium, Cd

Cadmium accumulates in the kidneys and the liver and its carcinogenic properties result in emphysema and fibrosis of the lung (Nalbandian, 2012). The US EPA in 2012 classified Cd as one of the HAPs of major concern which is highly toxic to biological systems at values above critical levels (Nalbandian, 2012). According to Finkelman (1994), Cd in coal occurs in sphalerite though there may be minor amounts of Cd associated with other minerals, generally in sulphides.

Chromium, Cr

Chromium in its hexavalent state, Cr (VI), is highly carcinogenic and very toxic. Compared to Cr (III), which is less toxic and is an essential element for metabolic processes, Cr (VI) is very mobile in the environment. The valence of Cr in coal and coal ash was determined as Cr (III) using XAFS (Huffman et al., 1994; Huggins and Huffman, 1996). Finkelman (1994) suggested that there was insufficient data to specify the modes of occurrence of Cr in coal. According to Huggins et al. (2000), most of the Cr is associated with macerals whilst some Cr seems to be associated with clays as most of the Cr was removed by HF. It is very

important to understand Cr's modes of occurrence and the form it occurs in as it is emitted during combustion.

Data from sequential leaching led to the conclusion that Cr is mostly associated with silicates with minor associations with carbonates or monosulphides and the residual organic matter (Riley et al., 2012).

Cobalt, Co

Cobalt is essential to humans in the form of vitamin B12, as it supports important synthetic reactions in metabolic processes and is essential for the production of red blood cells (Facts, 2006). Compared to other metals, Co's level of toxicity is quite low and high levels of exposure have effects on the respiratory organs like the lungs (MOE, 2001). The level of Co's toxicity increases at any concentration in more acidic soils (MOE, 2001).

Finkelman (1994) suggested that there is a degree of uncertainty of the modes of occurrence of Co in coal. Although it has a high association with sulphides especially pyrites, most of it reported in floats from float and sink experiments also indicating an organic association (Finkelman, 1994).

Lead, Pb

Lead is a poisonous heavy metal to both animals and humans and is highly detrimental to the neurological development of children (US EPA, 1991). It causes damage to the brain, red blood cells and kidneys of young children and pregnant women.

Lead occurs as sulphides or is associated with sulphides and it can occur as galena, PbS (Finkelman, 1994). Although Pb seems to have a high inorganic association, in coal cleaning less than 50% of it is removed, hence showing that it occurs as micron-size crystals of galena or PbSe in the organic matrix. From studies carried out using secondary ion mass spectrometry (SIMS), synchrotron radiation induced X-ray fluorescence (SXRF) and laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS), Pb shows a great association with pyrite (Kolker and Finkelman, 1998).

Manganese, Mn

Manganese is an essential nutrient in human and animal health which serves as a cofactor for various enzymes (Jankovic, 2005; WHO, 2011). High Mn exposure leads to neurotoxicity in both humans and animals (WHO, 2011). In coals Mn is generally present in greater concentrations than any of the HAPs. From float-sink experiments and leaching experiments, Finkelman (1994) suggests an association with carbonates though small amounts may be associated with clays, pyrites or organic components of coal.

Mercury, Hg

Mercury is viewed as a very dangerous pollutant due to its tendency to bioaccumulate in the food chain (Speight, 2005). The large amounts of coal consumed during coal combustion account for huge anthropogenic emissions of Hg into the atmosphere (Yudovich and Ketris, 2005a). US EPA (1990) proposed rules to reduce Hg emissions from coal-fired power plants. There are no laws in South Africa which regulate the emission controls of TEs except for Pb (National Environment Management: Air Quality Bill, 2003); Hg is a HAP which should be included in the New Air Quality Bill. In order to apply proper Hg emission control strategies it is very important to understand the modes of occurrence of Hg in coals used for thermal energy power stations.

Mercury's greatest adverse impact occurs in the aquatic ecosystem where after a series of chemical reactions it is converted by bacteria in the sediments to methylmercury. This state of Hg is very toxic to humans and wildlife. Fish absorb methylmercury from the water through their gills and as they feed on other organisms. Bioaccumulation of Hg occurs as methylmercury concentrations increase in the bigger fish as they feed on the smaller fish. Consequently, larger predator fish usually have higher concentrations of methylmercury from eating contaminated prey. Humans, birds and other wildlife that eat fish are exposed to methylmercury in this way. Methylmercury poisoning leads to minamata disease which is characterised by neurological paralysis (Ekino et al., 2007).

In the atmosphere, Hg vapour is present mainly as Hg^0 (elemental Hg, which comprises about 90%) and the rest is most likely Hg^{2+} (probably $HgCl_2$ and methylmercury) (Yudovich and Ketris, 2005a; Gibb et al., 2000). Mercury and its compounds are highly toxic and mutagenic (Yudovich and Ketris, 2005b). The primary cause of Hg poisoning in humans is mostly due to eating poisoned fish. Mercury is a neurotoxin that harms the brain, heart, central nervous system, kidneys, lungs, and immune system (Risher and Amler, 2005). Young children and developing foetuses are most at risk, and can suffer developmental problems from mercury poisoning.

Mercury is generally present in low concentrations (ppt) but it is highly volatile and hence offers challenges in determining its modes of occurrence. Generally Hg is an authigenic chalcophile element which has a strong affinity for organic and inorganic coal matter (Yudovich and Ketris, 2005a).

In coal there are no fewer than three Hg forms which may be present, which are: clays (Hg_{clay}), organic matter (Hg_{org}), and sulphides (Hg_{sulf}). Finkelman (1994) concluded that most of the Hg is present in pyrites. Diehl et al. (2004) showed a pyritic association of Hg using LA-ICP-MS. Kolker (2012) showed the presence of Hg in Fe disulphides in coal at concentrations below detection by electron beam instruments through the use of LA-ICP-MS, selective leaching studies of bulk coal, and by correlation with Fe disulphide proxies such as total Fe and pyritic sulphur. High sulphur coals tend to contain most of the Hg found in the coals and this has been proven by Feng and Hong (1999) who used sequential leaching experiments where most of the Hg was removed by HNO_3. From sequential leaching extraction, Lusialo-Makiese et al. (2012) found a substantial proportion of Hg associated with organic constituents and pyrite. Density fractionation experiments also showed a correlation of mineral sulphides and Hg, and also managed to show a correlation between Hg and total sulphur (Wagner and Hlatshwayo, 2005; Wagner and Tlotleng, 2012).

Maceral concentrates may be used to indicate the Hg_{org} form in parent coals; however these results should be interpreted cautiously because an apparent organic Hg enrichment of a maceral concentrate may result from micro-sulphide

inclusions (Yudovich and Ketris, 2005b). The anticipated removal of Hg by conventional coal cleaning procedures can be great for coals with Hg associated with minerals.

Molybdenum, Mo

High levels of Mo in pastures cause diseases in cattle and sheep which results in poor growth and anemia (Nalbandian, 2012). Molybdenum affects the lactation of cows and it also affects absorption and metabolism of Cu, an essential element for growth. Ambiguous results have been reported for the modes of occurrence of Mo, especially in float sink data (Finkelman, 1994). According to Goldschmidt (1954), Mo is a chalcophile element with a high affinity for sulphides. Finkelman (1994) suggested perhaps an association with pyrites and sulphides.

Nickel, Ni

Nickel's adverse effects depend on the route of exposure which can be through inhalation, oral or dermal means (Das et al., 2008). In both humans and animals, Ni exposure causes formation of free radicals in various tissues which leads to various modifications to DNA (Deoxyribonucleic acid) bases, enhanced lipid peroxidation, and altered calcium and sulphhydryl homeostasis (Das et al., 2008).

According to Finkelman (1994) there is insufficient direct evidence to show the modes of occurrence as the indirect evidence appeared contradictory. According to Swaine and Goodarzi (1995), Swaine in 1980 concluded that much evidence pointed to Ni's association with organic constituents of coal. Inorganically bound Ni seems to be largely associated with sulphides. Kolker and Finkelman (1998) suggested a pyritic association from XAFS data though this is not a dominant mode of occurrence of Ni.

Selenium, Se

Selenium is a non-metal with intermediate properties between S and Te. Selenium has photoelectric and semiconductor properties which make it useful in solar cells, rectifiers, photographic exposure meters and xerography (Dhanjal and Cameotra, 2010). Selenium exists naturally in the environment and can be released from both natural and manufacturing processes.

Selenium is a biophilic element (Liu et al., 2007) which, although in trace amounts is necessary for cellular function, in large amounts it becomes very toxic to both animals and plants. At elevated levels, Se causes anemia, gastrointestinal disturbance, liver and spleen damage (Nalbandian, 2012). According to Goldschmidt (1937), Se is a coalphile element. Finkelman (1994) suggested sufficient evidence to suggest the bulk association of Se with the organic components of coal. Data also suggest minor associations with pyrite and other small associations with other minerals such as chausthalite and galena.

Uranium, U

Uranium is a naturally radioactive element hence radioactivity from U in coal has been cited as a potential health problem (Finkelman and Repetski, 1999). Although there is no evidence to date that radioactivity from coal or coal-combustion products has caused any human health problems (Finkelman and Repetski, 1999), it is important to regulate U emissions. In the body, U, which is a heavy metal, acts similarly to other heavy metals like Hg, Mo or Pb (Kathren and Burklin, 2008).

During coal combustion most of the U is released from the original coal matrix and distributed between the gas phase and solid combustion products. Since U is less volatile it is almost entirely retained in solid combustion wastes and in modern power plants in USA 99.5% of U is retained in the solid combustion wastes (Zielinski and Finkelman, 1997). Uranium is found in both the organic and mineral matter of coal and some U may have been slowly added through organic matter extracting it from ground water over geological time (Zielinski and Finkelman, 1997). Finkelman (1995) suggested that U may be organically associated with some being found in Zircon.

Vanadium, V

Vanadium is a toxic non-volatile metal which may be emitted as oxides in coal combustion (Gummow, 2011). Carbonaceous deposits have unusually high V concentrations (Finkelman, 1980). From density fractionation studies, Gluskoter

et al. (1977), V generally showed an organic association. According to Finkelman (1995), V may be found in clays or the organic matter of coal.

2.7 Sample Preparation methods for trace element determination

With most of the analytical methods, the decomposition of solid samples is of utmost importance. X-ray fluorescence (XRF) analysis can analyse solid samples (Vandecasteele and Block, 1993) without dissolution procedures (Chand et al., 2009). However, other analysis techniques, like inductively couple plasma (ICP) techniques, require dissolution of solid samples for analysis. Ashing or digestion are usually done at elevated temperatures to decompose solid samples for analysis. During ashing or digestion, volatile elements like Hg may escape; hence elemental preconcentration and chemical separation is also required to improve the quality of measurements. Several authors have discussed various sample preparation methods, and they still continue to improve sample preparation time and liberation of all elements for analysis. Lachas et. al. (1999) evaluated two digestion methods to extract 17 elements from coal and coal ash. Acid digestion which uses H_2SO_4, HF, $HClO_4$ and HNO_3 in open vessels was compared to sealed microwave digestion using HNO_3 only. The microwave digestion method using HNO_3 only may not break down silicates which harbour many TEs, but can extract As and Se (which are highly volatile) quantitatively (Lachas et al., 1999). Wagner and Hlatshwayo (2005) used microwave digestion as a preparation technique to determine 14 TEs using ICP-AES (discussed further in Section 2.7.1).

The volatility of Hg causes errors during quantification when methods based on acid digestion are used. Richaud et al. (1998) determined Hg using an atomic absorption spectrometry. Jongwana and Crouch (2012) used an automatic mercury analyser (AMA-254) and a capillary electrophoresis (CE) coupled with a photodiode array (PDA) detector for determining the mode of occurrence of Hg in coal. Automatic analysers for mercury are now possible instruments to use for analysis.

2.7.1 Microwave Coal Digestion

Microwave digestion is a high-pressure dissolution in a sealed vessel/system, where the elevated temperatures attained lead to faster sample breakdown and analyte dissolution. Microwave pressure digestion has been shown to provide considerable time savings, reduce sample contamination risks and reduce risks of sample loss as there is no need of dry ashing to eliminate organic carbon compared to ashing and other dissolution techniques (Alvarado et al.,1990; Watkins et al.,1995). Different methods have been used for digestion of coal samples. Alvarado et al. (1990) placed a known amount of coal sample (0.1-l.5 g) inside glass test-tubes, to which 5 ml of concentrated HNO_3 and 2 ml of concentrated HF were added. Each test-tube was closed and submitted to microwave heating at high pressures to test the convenience of total extraction of V (Alvarado et al.,1990).

Rodushkin et al. (2000) evaluated four microwave assisted digestion methods using different dissolution mixtures of HNO_3 and HF acids, aqua regia and H_2O_2. They found that the dissolution mixture which provided the best agreement of results with certified, recommended, literature-compiled or consensus values was a mixture of HNO_3, HF and H_2O_2, though fusion was necessary to obtain quantitative recoveries for Si, Cr and Zr.

Sun and Hoffman (1996) used concentrated H_2SO_4 which they found to be a highly effective solvent for destroying all organic compounds, concentrated HNO_3 to liberate many TEs associated with most of the matrices, and concentrated HF acid for coal dissolution and preserving Hg. Though several authors found the need to use HF to destroy and liberate TEs associated with silicates and sulphides, trials that Sun and Hoffman (1996) carried out after digestion with the former described acids showed no difference in analysis results.

Antes et al. (2010) and Picoloto et al. (2011) applied microwave induced combustion (MIC) and used ICP-MS for determining TEs, as well as for the determination of Hg. Microwave induced combustion promises to be an even more efficient method compared to microwave assisted digestion as it uses no chemicals, has a shorter digestion time and liberates more TEs for analysis.

Microwave induced combustion is based on sample ignition by microwave radiation using closed quartz vessels pressurized with O_2 and the use of NH_4NO_3 as an ignition aid (Mello et al., 2008). Antes et al. (2010) combusted 500 mg pellets of coal in a Multiwave 3000 (Anton Paar, Graz, Austria) equipped with up to eight high-pressure quartz vessels using 20 bar of O_2 and NH_4NO_3.

In this current research HNO_3, HCl and HF were used in the Department of Chemistry at University of the Witwatersrand and HNO_3, HF, and H_2O_2 were used at the UIS analytical services for microwave digestion.

2.8 Analytical techniques for trace element analysis

Several ISO, ASTM (ASTM D6357–11) and SABS (SANS406:2006 trace elements) methods can be used to determine TEs in coal. Several analytical techniques are destructive (as the sample may require ashing and dissolution), whilst others are nondestructive (Nalbandian, 2012) such as X-ray absorption fine structure (XAFS) spectroscopy. Since TEs occur in minute quantities, it is important to pick sensitive techniques which give very reliable results.

SANS 411:2006 is a standard for determining As, Sb and Se in higher rank coals using the hydride generation method. A known mass of coal sample is ignited in intimate contact with the Eschka mixture in an oxidizing atmosphere at 800°C to decompose the organic matter. Hydrochloric acid is used to extract the residue and the analytes are determined by atomic absorption or atomic fluorescence spectrometry after conversion to their volatile hydrides.

SANS 412:2006 is also used for determining B after ashing the coal sample in the presence of Eschka mixture. A known mass of the coal sample is ignited in intimate contact with Eschka mixture in an oxidising atmosphere at 800 °C to decompose the organic matter. Hydrochloric acid is used to extract the residue and boron is determined by ICP-AES.

Huggins (2002) reviewed analytical methods for determining the inorganic constituents of coal in three fronts as shown in Figure 2.10. In this work XRD was used to determine minerals in coal.

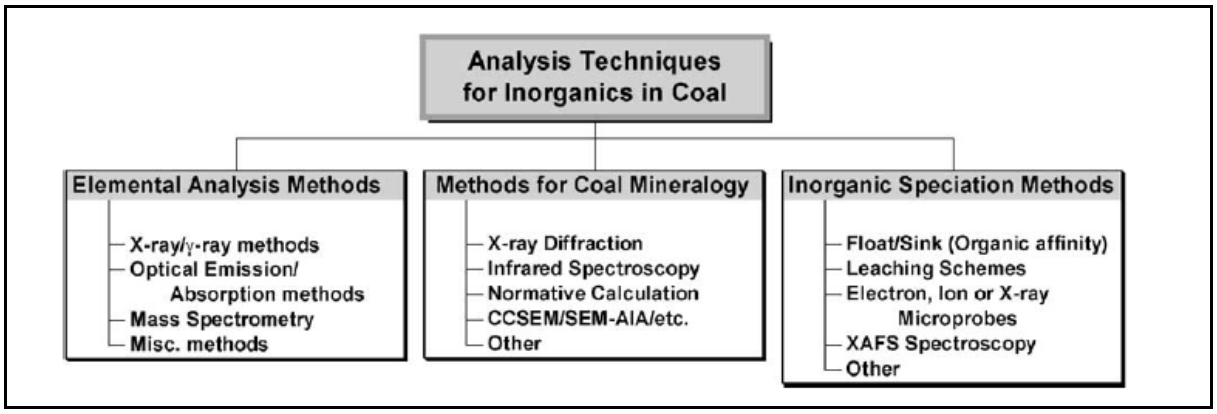

Figure 2.10: A subdivision of analytical methods for determining inorganics in coal (Huggins, 2002).

Many authors have used different analytical methods to determine the concentration of TEs in coal (Sun and Hoffman, 1996 ; Lachas et al., 1999; Rodushkin et al., 2000; Querol et al., 2001; Wang et al., 2004a; Wagner and Hlatshwayo, 2005; Antes et al.,2010; Picoloto et al., 2011; Wagner and Tlotleng, 2012). Huggins (2002) separated methods of elemental concentrations into four broad groups:

a) Instrumental X-ray/-γ techniques

b) Optical absorption/emission techniques

c) Mass spectrometric techniques

d) Miscellaneous techniques.

a. Instrumental X-ray/- γ ray techniques

These techniques are usually capable of determining many elements simultaneously and depend on the generation, detection and measurement of characteristic X-rays and/or γ-rays for element determination. X-ray fluorescence analysis (XRF) is the use of an automated instrument that has been extended to determine TEs in coal (Kuhn et al., 1975). It is a fully automated instrument, although it has low sensitivity to TEs and needs matrix corrections for best precision (Huggins, 2002).

Several authors have used XRF and XRD analysis for their analysis (Ward et al., 1999; Bergh et al., 2011). XRD is used for identifying and quantifying mineral species in coal, and it was used in this project to aid in identifying modes of occurrence in density fractionation samples. X-ray absorption fine structure (XAFS) spectroscopy provides details of how X-rays are absorbed by an atom at energies near and above the core-level binding energies of that atom (Newville, 2004). XAFS is the modulation of an atom's X-ray absorption probability due to the chemical and physical state of the atom, hence it provides practical and simple ways to determine the chemical state and local atomic structure for a selected atomic species (Newville, 2004).

b. Optical absorption/emission techniques

Optical emission spectroscopy (OES), also known as atomic emission spectroscopy (AES) (Swaine, 1990), depends on the generation, detection and measurement of characteristic atomic transitions in the visible and near-visible regions of the electromagnetic spectrum for elemental determination (Huggins, 2002). In ICP-OES, the sample is introduced to the core of the inductively coupled argon plasma which generates temperature of approximately 8000ºC where elements become thermally excited and emit light of their characteristic wavelengths. The light is collected in the spectrometer and passes through a diffraction grazing which resolves the light into a spectrum of its constituent wavelengths. The diffracted light within the spectrometer is collected by wavelength and amplified to yield intensity measurements which are converted to elemental concentrations by comparison with calibration standards. The ICP-OES has very good detection power with medium to low detection limits of ~0.2-100 ppm and it offers efficient conditions for determining analytes concentrations reliably and rapidly (Eschnauer et al., 1990). This technique requires sample digestion before analysis.

Suzuki (2006) used ICP-OES to determine the bulk elemental content to determine trace metals in his aim to characterise airborne particulates and associated trace metals deposited on tree bark. Mujuru et al. (2009) applied ICP-OES for elemental analysis of bituminous coal. In this project this technique was

used in both the School of Chemistry at the University of the Witwatersrand and an external laboratory, UIS analytical services.

c. Mass spectrometric methods

Mass spectrometric techniques are highly sensitive techniques capable of determining most elements in the periodic table simultaneously including metals at concentrations below one part per billion (ppb). Mass spectrometric methods depend on total volatilization of the sample and its introduction in such form into a mass spectrometer so that the atomic mass can be used to discriminate quantitatively among the different elements (and isotopes) (Huggins, 2002). Inductively coupled plasma mass spectroscopy (ICP-MS) is finding great use in determining trace elements in coal (Antes et al., 2010; Picoloto et al., 2011). Wang et al. (2004a) found that the ICP-MS showed an improvement in accurate and precise determination of some TEs when compared to ICP-OES.

The ICP-MS has a sample introduction system which consists of a torch, water cooled spray chamber and nebulizer as shown in Figure 2.11. The nebulizer converts the sample solution initially to an aerosol mist which is then carried to the plasma by argon gas. There is a spray chamber which acts as a filter and removes droplets that are too large and cannot be excited by the plasma. The plasma is the gas which contains a sufficient concentration of ions and electrons to make the gas electrically conductive which dries the aerosol, dissociates the molecules, removes an electron from the components rendering them single-charged ions which are then directed to the mass spectrometer which is a mass filtering device.

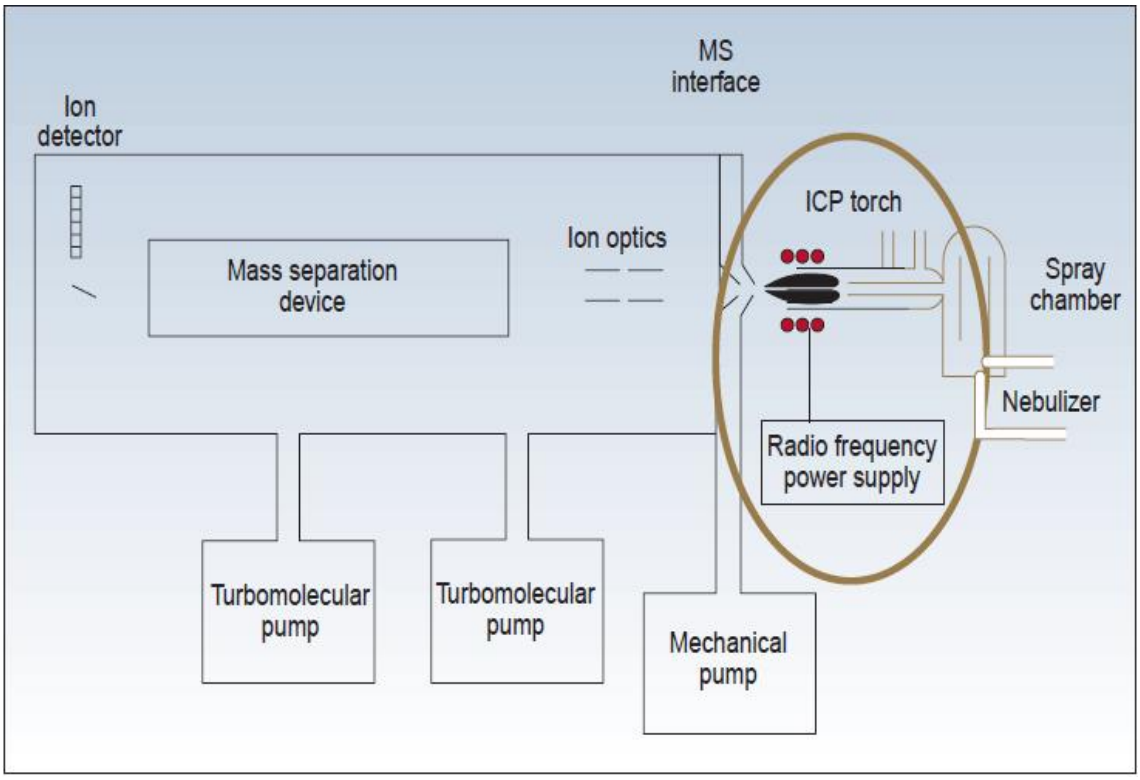

Figure 2.11: **A schematic of the ICP-MS showing the sample introduction system (Thomas, 2001)**

ICP-MS, unlike ICP-AES, is able to monitor isotopic speciation for the ions of choice with a superior detection limit as well. It is able to handle both simple and complex matrices with a minimum of matrix interferences due to the high-temperature of the ICP source (Thomas, 2001). Both ICP-MS and ICP-OES will be used for analysis of most TEs in this project.

d. Miscellaneous techniques

Miscellaneous techniques generally determine one or more elements that, for one reason or another, cannot be adequately determined by other more general methods such as ICP-MS. Miscellaneous techniques include wet chemical and various electroanalytical methods (Huggins, 2002). Examples of these methods include cold vapour atomic absorption spectrometry (CVAAS) and direct mercury analysers. Wagner and Hlatshwayo (2005) used CVAAS to determine Hg in coal. In this project a direct Hg analyser was used. CVAAS reduces ionic Hg in the digested solution to elemental state and transfers it into the absorption cell of the

atomic absorption spectrometer (Nguyen et al., 1998). Standard solutions ranging from 0.2 to 10 ppb can be used to calibrate the machine (Nguyen et al., 1998).

Another technique showing much potential is LA-ICP-MS which can be applied directly to analyse the TEs in coal using polished sections or blocks (Spears et al., 2007). Trace element concentrations of minerals are measured with a high degree of accuracy and precision by firing a laser beam at a flat surface of a sample and introducing the ablated material into the ICP-MS for quantification (Sylvester and Ghaderi, 1997).

2.9 Chapter Summary

The geological coal formations of both the Zimbabwean and the South African basins have been compared. Trace elements have been discussed and according to literature, most of the TEs are associated with the mineral matter of the coal. The following TEs were considered in this project: As, B, Be, Co, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, U and V. Classification and modes of occurrence of TEs have been discussed, as well as the health and the environmental effects.

Density fractionation and sequential leaching are typically used to infer modes of occurrences of TEs in coal. Sample preparation techniques like microwave digestion are undertaken on solid samples which include ROM, density fractions and leach residues prior to analysis by various analytical techniques including ICP-OES, ICP-MS, and direct Hg analyser. Leach solutions may be analysed directly on the ICP-OES, ICP-MS and direct Hg analyser.

Chapter 3

Methodology

3.1 Introduction

This chapter outlines the methods carried out in order to achieve the objectives of this project. Sample acquisition and characterisation are detailed. All chemicals used in this project were pure analytical grade chemicals purchased from reputable chemical suppliers MERCK and SIGMA ALDRICH.

Characterisation analysis experiments including petrography, TGA, carbon / sulphur Leco analysis, and XRD analysis were carried out in order to determine coal composition.

Density fractionation and sequential leaching were sample preparation techniques used to determine the modes of occurrence of TEs. Microwave digestion was done on all solid samples before analysis on the ICP-MS and direct Hg analyser. Leach solutions were directly analysed on the ICP-MS and the direct Hg analyser. ICP-MS analysis was performed on all products from preparation techniques. Most of the techniques were carried out in the School of Chemical and Metallurgical Engineering at the University of the Witwatersrand, whilst XRD and ICP-MS were carried out at external laboratories. Direct Hg analysis was carried out in the School of Chemistry at the University of the Witwatersrand using an automated Perkin Elmer Flow Injection Analysis-Mercury Hydride System (FI-MH-AAS). A schematic of the experiments carried out is as shown in Figure 3.1.

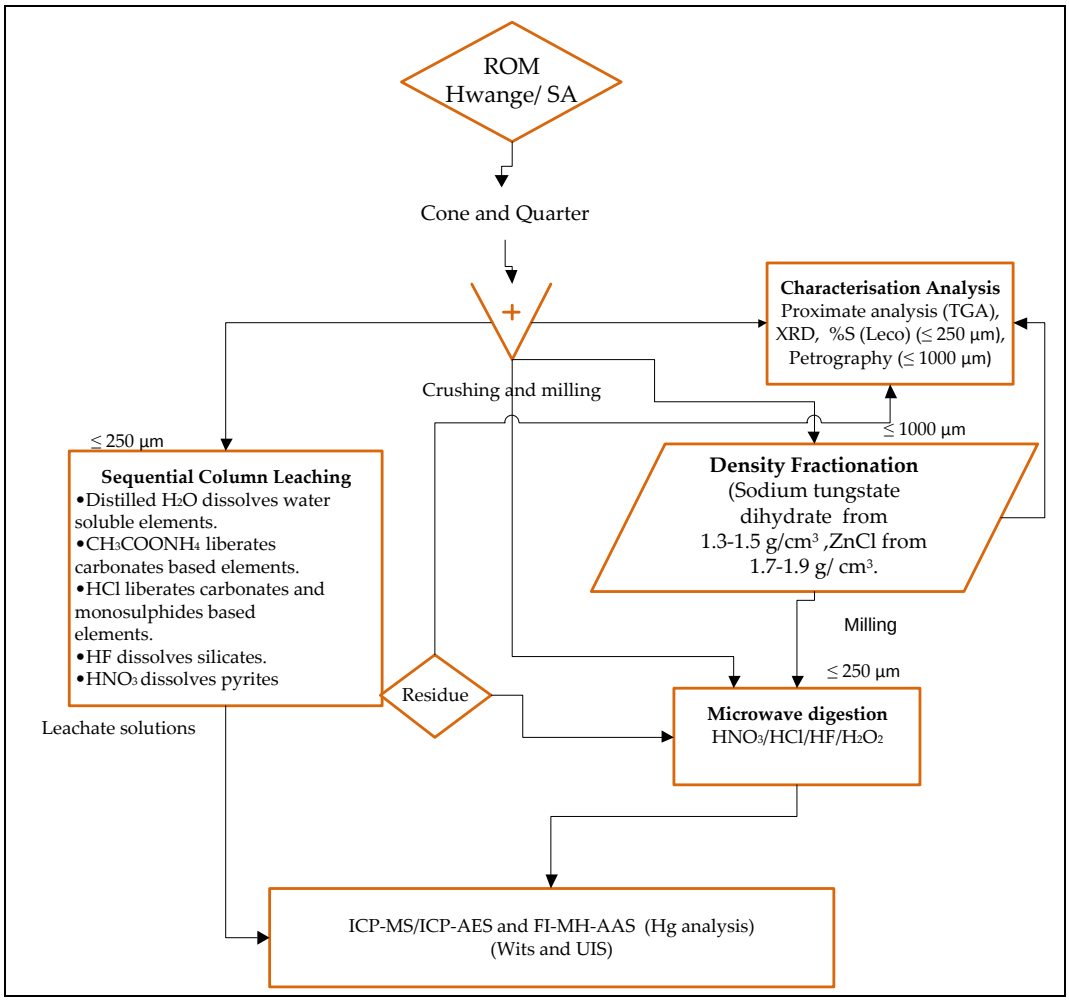

Figure 3.1: Schematic of Methodology

3.2 Sample acquisition and initial preparation

Three run of mine (ROM) coal samples, each 20 kg, of size passing through 4 mm (≤ 4 mm), were supplied by the Hwange Colliery in Zimbabwe. Two South African ROM samples also 20 kg each, were included in this project; these samples were cone and quartered and then crushed using jaw crushers to give size passing 4 mm. All samples were milled in the Retsch mill ZM200 in the School of Chemical and Metallurgical Engineering to sizes ≤ 1000 µm and ≤ 250 µm for relevant analysis.

3.3 Characterisation Analysis

Since coals are heterogeneous it is important to give detailed characterisation analysis which helps classify coal and hence predict its most appropriate use. Coal characterisation can be carried out on two levels:

i) empirical (chemical and physical properties) and

ii) fundamental (organic and inorganic constituents).

Empirical analysis includes proximate and ultimate analysis, whilst fundamental analysis includes petrographic analysis which is carried out using a microscope (Falcon and Ham, 1988).

3.3.1 Proximate Analysis

Proximate analysis of coal is the determination of the inherent moisture, volatile matter, ash and fixed carbon by a series of standard methods. Several test methods of proximate coal analysis including ASTM D3172, ISO 1171 (Speight, 2005), SANS 5925, SABS ISO 562. However, a rapid technique using a Perkin Elmer STA 6000 Thermogravimetric analyser (TGA) housed in the School of Chemical and Metallurgical Engineering was used for proximate analysis in this research. All ROM, density fractions, and leached residues were analysed using this technique.

The TGA measures the mass loss a coal sample undergoes when heated to 900°C under a N_2 atmosphere, followed by a switch to O_2 combustion. Between 10 and 15 mg samples of size ≤ 250 µm were placed in the TGA crucible. Please refer to Appendix A for a curve depicting TGA proximate analysis determination.

The inherent moisture content is the water which may be physically or chemically bound in coal, and is determined by the mass loss that a coal sample undergoes when it is heated to 110°C under a N_2 atmosphere. This is the water which is retained within the pores and tissues of coal after all superficial surface moisture has been removed. The percentage of water present in coal varies with the rank of the coal. Anthracite has the lowest moisture, then bituminous coal, followed by subbituminous coal, and lignite has the most.

Volatile matter, which is derived from both the organic and the mineral matter in coal, varies with rank of coal, with anthracite coal having the least volatile matter (typically 2-12%) (Donahue and Rais, 2009). Volatile matter is slowly removed during the coalification process (Schweinfurth and Finkelman, 2003). The volatile products evolved between 110–900°C under N_2 using a TGA result from thermal decomposition and correspond to the volatile matter content of coal.

The fixed carbon content in coal is the solid combustible material that remains after the volatile matter has been removed. The combustion of the fixed carbon occurs when the sample is held at 900°C and the atmosphere is switched from N_2 to O_2 using the TGA. Anthracite has the highest fixed carbon content (75–85%), bituminous coal 50-70%, subbituminous coal 30-57%, and lignite 25-30% (Speight, 2005).

The residue that remains after coal has lost its moisture, volatile matter, and fixed carbon during combustion in O_2 is called the ash. Ash is therefore a product of mineral matter that has undergone thermal decomposition. Ash is composed of the major oxides of Al, Ca, Fe, Mg and Si.

3.3.2 The Leco Carbon Sulphur analyser

The Leco SC 632 analyser is used to determine the amount of C and S in a coal sample. This is an ASTM approved method for carbon and sulphur determination. A sample of weight between 0.25-0.35 g, of size $\leq$ 250 µm is combusted in pure O_2 to produce CO_2 and SO_2, which are then detected and quantified by infrared detection.

Standards CRM 502-383, CRM 502-435, CRM 502-385 and CRM 502-388 with C and S content comparable to the anticipated level in the samples were used to calibrate the instrument. The samples certifications are shown in Appendix B.

3.3.3 Coal Petrography

According to Van Krevelen and Schuyer (1957), Hutton in 1830 laid the basis of coal petrography. He developed a technique of examining thin coal sections by transmitted light under a microscope. It was observed that bright coals are composed of translucent and homogeneous materials which cause reflectance and hence vegetation structures could be recognized. According to Van Krevelen and Schuyer (1957), Winter in 1913 then developed the examination of polished surfaces by reflected light under a metallurgical microscope. As years passed coal petrography has been further improved and oil immersion techniques are used to enhance the refractive index of the image.

Various authors have used coal petrography as a tool in their projects to characterise coal including Hower et al. (2008), Hower and Robertson (2003), O'Brien et al. (2003), Wagner and Tlotleng (2012). Falcon and Snyman (1986) characterised the petrographic constituents of bituminous coals in Southern Africa, which is an invaluable reference source.

ROM and float and sink fraction coal samples were crushed to -1 mm and epoxy-bound particulate pellets of each coal sample were prepared using epoxy resin. Polishing was done on these blocks using a Struers Tegraforce polisher to achieve highly reflective surfaces with a final stage of using MD Chem with a 0.05 µm alumina oxide solution following SAB ISO 7404-2. Microscopic examination was carried out using reflected light and an oil immersion objective on a Leica DM4500P petrographic microscope. A detailed maceral analysis including subdivisions of mineral matter was conducted following SAB ISO 7404-4; 500 points were determined per sample. Vitrinite reflectance (mean random) was conducted using a J and M spectrolytic system attached to the Leica microscope following SABS ISO 7404-3. Petrographic analyses were undertaken by Professor Nicola Wagner in the School of Chemical and Metallurgical Engineering. Micrographs were taken using a Zeiss Universal microscope with an Axiocam digital camera and software.

3.3.4 X-ray Diffraction (XRD)

X-ray diffraction is a non-destructive technique which uses the technique of scattering (diffracting) X-rays from an ordered crystal, giving the crystalline structure of minerals, and both qualitative and quantitative chemical analysis of both natural and synthetic materials (Sharma, 2012). XRD compares the Bragg intensity data of unknown spectra to known spectra generated by standard samples to evaluate the concentration of mineral components in multicomponent mixtures of minerals, like coal (Renton, 1986). Each mineral has its own set of spacing which allows for its qualitative determination (Studer, 2008). Each crystal has its distinct diffraction pattern, where positions of the lines are determined by the spacing of corresponding planes (Hull, 1917) based on Bragg's equation:

$$n\lambda = 2d\sin\theta \qquad 3.1$$

where θ is the angle between the incident ray and the plane (hence 2θ is the angular deviation), d is the distance between consecutive planes, λ is the wavelength of incident rays and n is the order of the reflection. Mineralogical analysis of coal and the density fractions help determine the modes of occurrence of TEs in coal. All ROM, density fractionated and leach residue samples were analysed using XRD.

Samples were run by Dr Sabine Verryn of XRD Analytical and Consulting. Samples of size passing 250 µm were mounted and pressed onto a sample holder and then exposed to X-rays for a given amount of time. The samples were prepared for XRD analysis using a back loading preparation method and were analysed with a PANalytical Empyrean diffractometer with PIXcel detector and fixed slits with Fe filtered Co-Kα radiation. The phases were identified using X'Pert Highscore plus software. The relative phase amounts (weight %) of coal were estimated using the Rietveld method (Autoquan Program).

3.4. Methods for Inferring Modes of Occurrence of Trace Elements in Coal

3.4.1 Density Fractionation

Float and sink analysis, or density fractionation, is a laboratory method used to determine the specific gravity of coal which assesses its quality and washability. Commercially, heavy medium density separation (HMS) is used in the coal industry to pre-concentrate minerals (coal washing) to produce a commercially graded end product (Wills and Napier-Munn, 2006). Viscosities of liquids determine the speed of separation of solid particles during the float and sink procedure. Stoke's law states that velocity of separation is inversely proportional to viscosity (Rhodes and Miles, 1991).

Several authors have used density fractionation as a means of sample preparation to determine TEs and their affinities in coal (Hower et al., 1994; Aktas et al., 1998; Davidson, 2000; Querol et al., 2001; Wagner and Hlatshwayo, 2005; Bergh et al., 2011; Wagner and Tlotleng, 2012). Various dense liquids have been used at different densities to affect separation; for example, Aktas et al. (1998) used a mixture of isopropyl alcohol (IPA)-carbon tetrachloride mixture and zinc chloride solution to effect separation.

Although many researchers have concluded that organic liquids are the most suitable heavy liquids due to their high densities and relatively low viscosities (Browning, 1961; O'Connell, 1963), bromoform is very toxic both to human health and the environment (Munsterman and Kerstholt, 1996). Zinc chloride, which is used as an alternative to bromoform, is noxious (physically harmful) and has high viscosities (Wills and Napier-Munn, 2006). Sodium polytungstate (SPT) has very low viscosity in aqueous salt solutions at densities from 1.0 to 3.1 g cm^{-3}, and can be used for float and sink analysis of coal. Float and sink samples have to be washed thoroughly with distilled/ deionised water because sodium polytungstate contains TEs which may interfere with analysis (Callahan, 1987). In this project, sodium tungstate dihydrate ($Na_2WO_4.2H_2O$) was used in solution with warm deionised water and $ZnCl_2$ for higher densities.

The method undertaken in this project followed Querol et al. (2001), Bergh et al. (2011) and Wagner and Tlotleng (2012), and involved the following:

1. 100 g of coal sample of size ≤ 1000 μm was climatised to the laboratory temperature of 23.5°C in a fume cupboard before float and sink analysis.

2. Solutions of sodium tungstate dihydrate of densities 1.3 ($\rho_{1.3}$) and 1.5 g cm^{-3} were prepared in warm deionised water. Density solutions of 1.7 and 1.9 g cm^{-3} were prepared with $ZnCl_2$ with deionised water and measured with a hydrometer. For the density of 1.9 g cm^{-3} a centrifuge was used to separate the sink product from solution.

3. The coal sample was placed in a beaker containing 1.3 g cm^{-3} density solution and allowed to separate completely overnight into float and sink fractions, as shown in Figure 3.2.

4. Floats were removed and filtered in a Buchner funnel and dried in an oven at 35°C for 6 hours. The sink fraction was placed into the next density separating vessel. The mass of the floats and sink were measured for each density fraction and cumulative yield determined.

5. All fractions were analysed using petrography, as discussed in Section 3.3.3. The material was then further milled to ≤ 250 μm and analysed using XRD (refer to section 3.3.4), ICP-MS, FI-MH-AAS (Flow Injection Analysis Mercury Hydride System Atomic Absorption Spectrometry), TGA (Thermogravimetric analysis, section 3.3.1) and Leco SC 632 (refer to section 3.3.2).

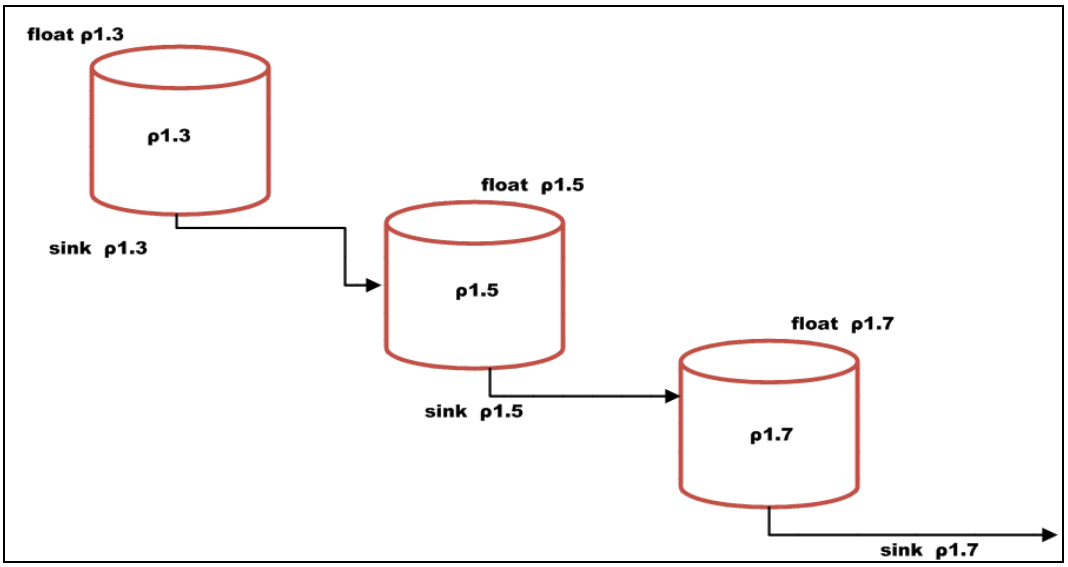

Figure 3. 2: Density fractionation of coal samples (ρ/ g cm^{-3})

3.4.2 Sequential Leaching

Column leaching experiments were carried out to determine the elements removed by certain chemicals so as to investigate their association with certain minerals.

All leaching apparatus was soaked in HNO_3, washed and rinsed with distilled water. Samples were crushed and milled to a particle size ≤ 250 µm (refer to section 3.2). 5 g of sample was loaded into the column leaching tube. Cotton wool was fitted at both ends of the bed as shown in Figure 3.3.

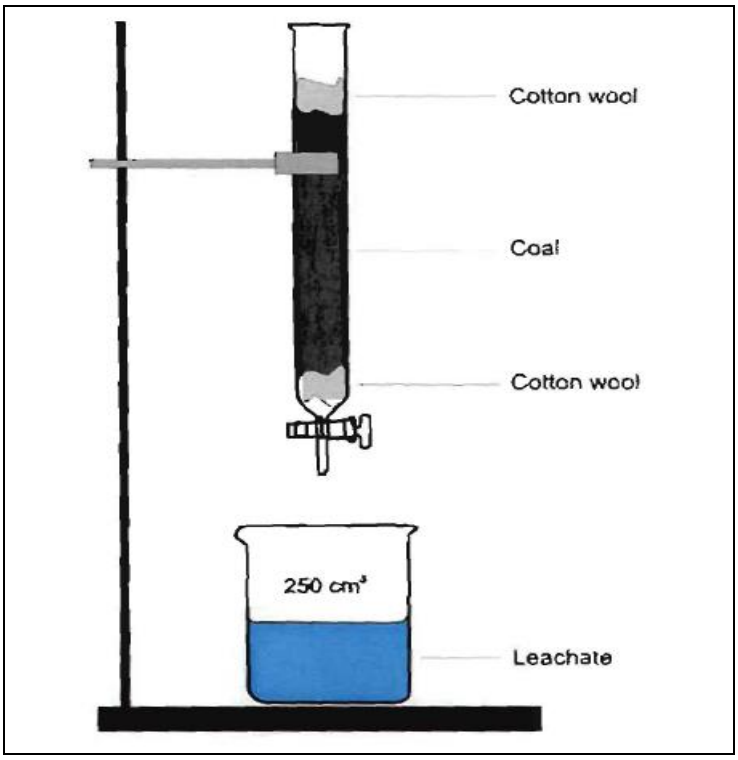

Figure 3.3: Column leaching apparatus (Hlatshwayo, 2008)

The 5 g samples were sequentially leached with 35 ml of the following solutions based on the methods of Palmer et al. (1996), Hlatshwayo (2008) and Wang et al. (2008):

Stage 1: 5 g of coal was leached with 35 ml distilled water (H_2O) for an hour to remove elements associated with soluble minerals like sulphates and sparingly soluble calcite.

Stage 2: To the residue remaining from stage 1, 35 ml 1 M ammonium acetate (CH_3COONH_4) was added over an hour to remove elements associated with exchangeable cations and a portion of carbonate-hosted cations (Palmer et al., 1996).

Stage 3: 35 ml 3 M hydrochloric acid (HCl) was added to the residue remaining from stage 2 to remove cations associated with carbonates and monosulphides (sphalerite, galena and chalcopyrite) (Spears, 2012).

Stage 4: 35 ml concentrated hydrofluoric acid (i.e. 48 % HF) was added to the residue remaining from stage 3 to dissolve silicates and liberate elements present in silicates, including those associated with clays, illite and kaolinite (Palmer et al., 1996; Hlatshwayo, 2008).

Stage 5: 35 ml 2 M nitric acid (1:7) (i.e. HNO_3) was added to the remaining residue from stage 4 to remove insoluble fluoride compounds that form during the leaching process and also dissolve pyrites and marcasites (disulphides) (Jorjani et al., 2011).

Residence time allowed for each reaction was 1 hour and 70 ml of distilled water was used in between each step to thoroughly wash the previous solution; this leachate was added to the previous solution. The remaining residue was weighed. The leachates and remaining residue were analysed using ICP-MS, ICP-OES and the direct Hg analyser.

3.5 Sample preparation for Trace elements determination

Two laboratories were used for TE determination: the School of Chemistry at the University of the Witwatersrand and UIS Analytical services (an external commercial laboratory). Some problems were encountered with equipment at both laboratories during the project.

3.5.1 Microwave Digestion: School of Chemistry

Microwave digestion was carried out in the School of Chemistry on solid samples i.e. ROM, leach residues and density fractions, prior to Hg analysis and IC-AES analysis of TEs. Known amounts of coal (250 mg) were digested using acid solutions of 6 ml HNO_3 (55%), 2 ml HCl (32%) and 1 ml HF (40%) for 45 minutes at 240ºC, 800 W in a closed microwave assisted extraction (MAE) system. The microwave digester the Multiwave 3000 was equipped with PTFE-TFM liners, as shown in Figure 3.4 using the program conditions shown in Table 3.1.

6.0 ml of boric acid was then added to each microwave digested sample to neutralise the damaging effects of HF for glass made materials such as the ICP torch.

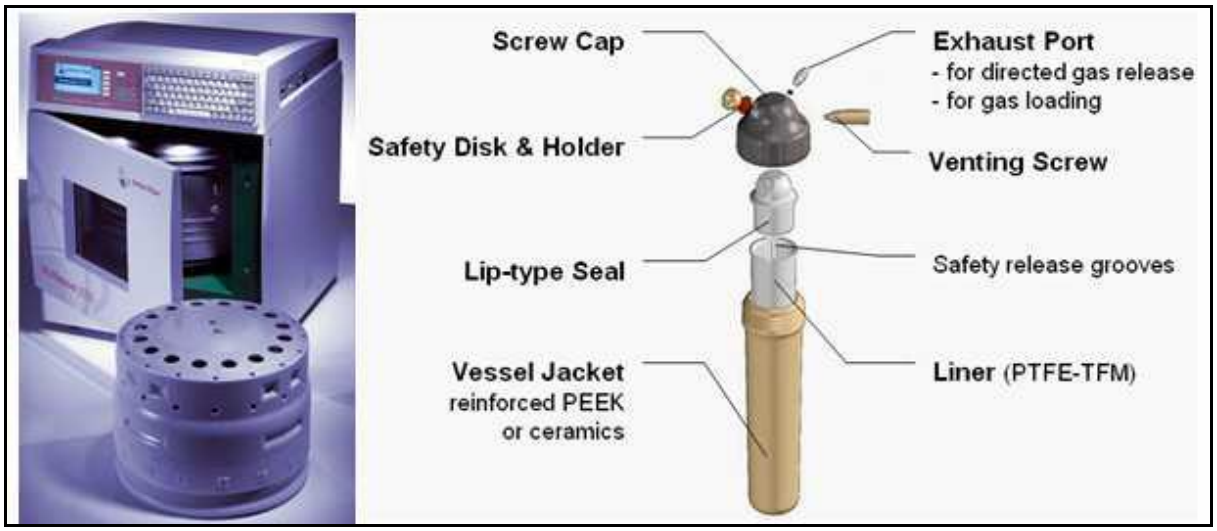

Figure 3.4: Multiwave 3000 MAE system and the vessel design (Lusilao-Makiese, 2012)

Table 3.1: Microwave programme for sample preparation (School of Chemistry)

Phase	Power (W)	Ramp (min)	Hold (min)	Fan
1	800	5	15	1
2	600	5	10	1
3	0	5	5	3

3.5.2 Microwave digestion: UIS

Due to equipment breakdowns at the School of Chemistry, samples were sent to an external laboratory, namely UIS Analytical Services, which is a SABS accredited laboratory. Microwave digestion was carried out on solid samples prior to ICP-MS analysis on ROM, leach residue and density fractionation samples. 200 mg samples were digested using a Microwave High Pressure labstation (Milestone

Ethos). The reagents used for digestion for each coal sample were 10 ml 65% HNO_3, 3 ml 40% HF, and 1 ml 30% H_2O_2. The Guaranteed-Reagent (GR Grade) HNO_3 and HF for sample digestion were further purified by sub-boiling distillation. The maximum pressure reached was 30 bars whilst the highest temperature was set at 220°C for 30 minutes.

3.6 Trace element analysis techniques

After dissolution of organic and mineral matrices using microwave digestion these liquid solutions were submitted for direct analysis using ICP-OES and ICP-MS techniques. Leached solutions were analysed directly using the ICP. The ICP is able to identify and quantify a number of elements in a very short space of time whilst requiring fairly little solution of sample (Savic, 2008), as discussed in Section 2.8. Though several methods exist, the ICP technique is best for the analysis of the TEs: Ba, Be, Cr, Mn, Ni, P, Sr, Ni, V and Zn, as its detection limit is better or may be comparable to other atomic spectral procedures.

In this work the ICP techniques were used at UIS and the School of Chemistry; and Hg was determined at the School of Chemistry using the FI-MH-AAS. The combined use of ICP-OES and –MS enables more accurate determinations of the TEs at UIS analytical laboratory. The procedures are described in the sections that follow.

3.6.1 Inductively coupled plasma (ICP) techniques at UIS

The ICP-MS (Perkin Elmer Elan 6100 DRC) an automatic pulse/analogue counting mode using 15 sweeps per reading and 3 replicates per analysis was used to determine TEs in coal samples.

For As and Se, the dynamic reaction cell technology (DRC) was used in order to avoid disturbance of polyatomic ions. Arsenic was measured at mass 75 and Se was measured at mass 78. Methane gas was used for the DRC cell to minimize the interferences of ArCl (mass 40 + mass 35 = mass 75) on As and Ar_2 (mass 38 + mass 40 = 78) on Se.

The inductively coupled plasma optical emission spectrometer (ICP-OES) (Perkin Elmer Optima 5300 DV) at UIS was used to determine other TEs like Mn. The oxides of major elements like MnO were determined. The coal ash samples were prepared by lithium tetraborate fusion in a platinum crucible and leached in diluted HCl to get the sample into solution. The solutions were then analysed by ICP-OES to determine the percentage of the total oxides in the ash.

All coal solid samples analysed using the ICP-MS and ICP-OES were microwave digested, whilst leach solutions were analysed directly using the ICP-MS and the ICP-OES.

NIST traceable Multi-element standards were used for calibration of TE concentrations whilst coal certified reference materials SARM (South African Reference material) 18, 19 and 20 were used as quality check standards for TEs determination.

3.6.2 Inductively coupled plasma atomic emission spectroscopy (ICP-AES) at the School of Chemistry

A Genesis Spectro ICP-AES machine was calibrated using multi element standards prepared from SARM standards of concentrations 0.1, 0.5, 1 and 2 ppm. The elements to be analysed were selected from the Spectro Genesis software. The liquid solution samples were analysed.

3.6.3 Mercury Analysis at the School of Chemistry

Mercury in coal occurs at very low concentrations, and some techniques are not able to detect these low concentrations. Coal leachate samples were analysed for total Hg using a Perkin Elmer automated FI-MH-AAS after preconcentration. The basic principle of the instrument consists of reducing the different mercury species into the elemental form (Hg^0) prior to analysis using a mixture of aqueous solutions of sodium borohydride ($NaBH_4$) and HCl. The reduced Hg is then transferred via a carrier gas (Argon) to the electrodeless discharge lamp (EDL) for detection. The calibration of the instrument was performed at the limit of $\mu g\ L^{-1}$ (ppb) and the obtained calibration line is presented in Figure 3.5. The method

detection limit which was calculated as three times the standard deviation of six blank measurements was 0.056 µg L^{-1}.

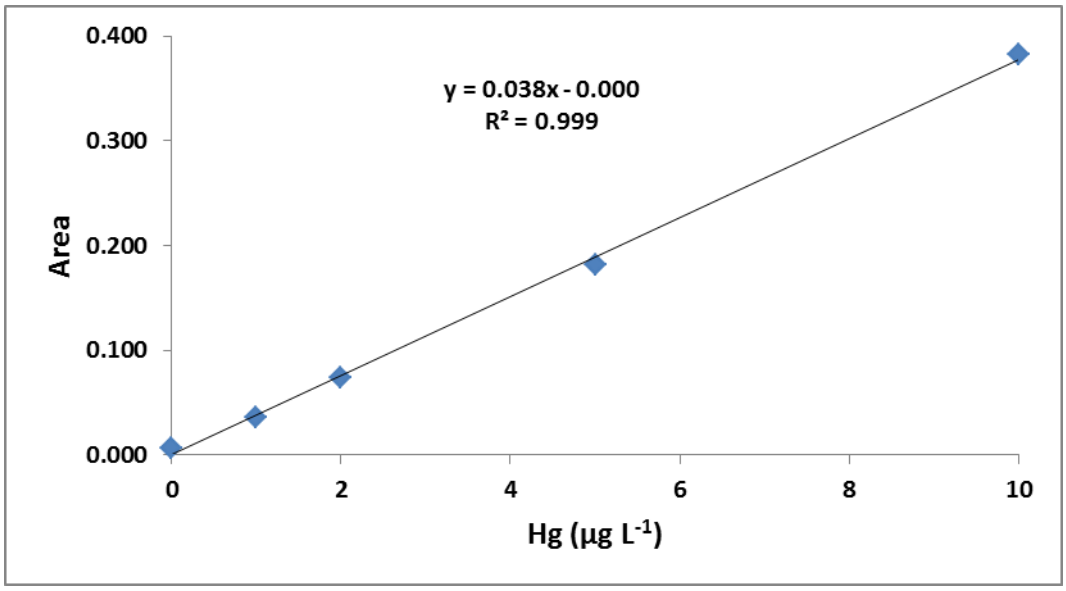

Figure 3.5: Standards calibration line obtained for the coal leachate samples analysis

3.7 Washability Data Analysis

Washability curves were constructed according to Gluskoter et al. (1977) and England et al. (2002). Washability curves are graphical presentations of the density fractionation test results (Meyers et al., 2002). The cumulative grade of the TE's is plotted against cumulative mass yield. Washability curves are types of cumulative curves from which the expected concentration of an element at any given recovery rate of a coal can be read, assuming the separation was based on specific gravity differences (Gluskoter et al., 1977). Uniformly distributed elements in all or most of the various fractions of washed coal will be characterised by flat washability curves (with a zero gradient). A negative slope on the other hand indicates the element's concentration with the organic matter of the coal whilst a positive slope indicates the element's concentration in the inorganic portion of the coal (Gluskoter et al., 1977).

3.8 Chapter Summary

Two sample preparation techniques, density fractionation and sequential leaching, to infer the modes of occurrence have been outlined. All solid samples were characterised using petrography, TGA, C/S Leco analysis and XRD. Trace element determination was conducted using ICP-MS and ICP-OES at UIS analytical laboratories, whilst Hg analyses were done using FI-MH-AAS. Trace elements were determined in the School of Chemistry. The data will be assessed by the production of washability curves. Certified reference materials certificates are shown in the appendices.

Chapter 4

Results and Discussion

4.1 Introduction

In this chapter, the results from the two different sample preparation techniques (density fractionation and sequential leaching), and the analytical techniques used for coal characterisation are presented and then discussed. Results from the three samples (HS1, HS2 and HS3) from Zimbabwe and two South African samples (A and B) are provided.

4.2 Characterisation analysis of ROM samples

Characterisation analysis data, which includes proximate analysis, petrographic data and total sulphur, is shown in Table 4.1.a, whilst Table 4.1.b shows XRD data. The full petrographic results are shown in Appendix C. Petrographic pictures show the different constituents in coal which include the macerals, and minerals like pyrite and clays (Figures 4.1a-c). From Figure 4.1.c semifusinite and fusinite, subcategories of inertinite are shown.

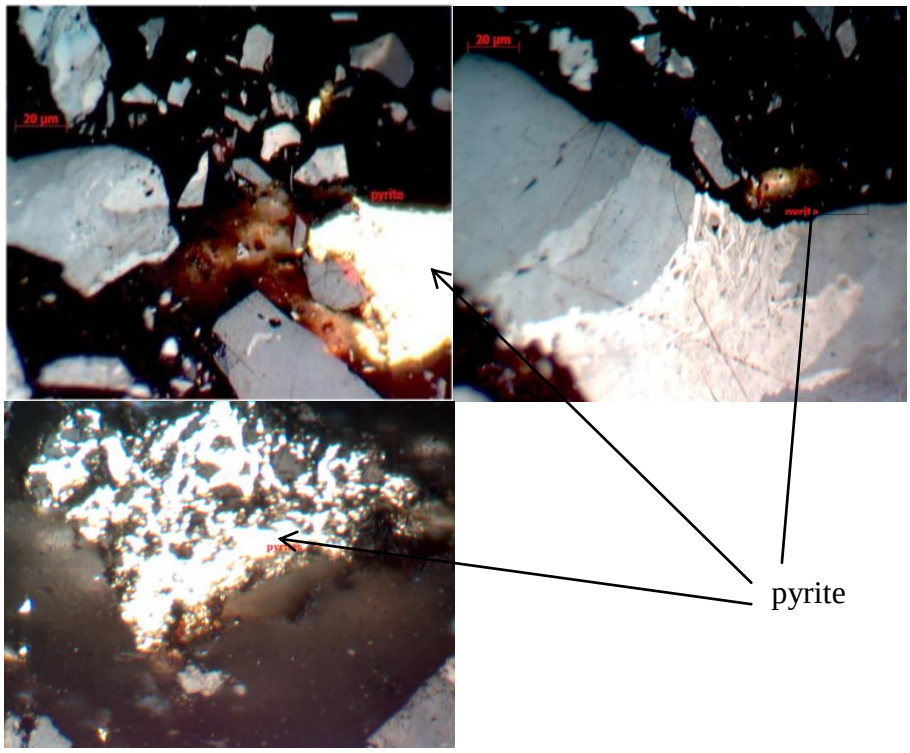

Figure 4.1.a: Petrographic images of pyrite minerals in coal *(*taken using an oil immersion lens, x500 magnification; scale bar shown).

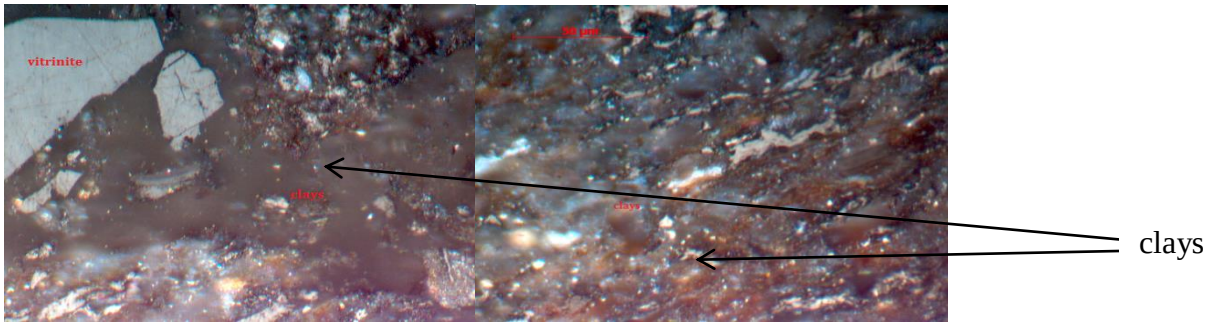

Figure 4.1.b: Petrographic images of clays *(*taken using an oil immersion lens, x500 magnification).

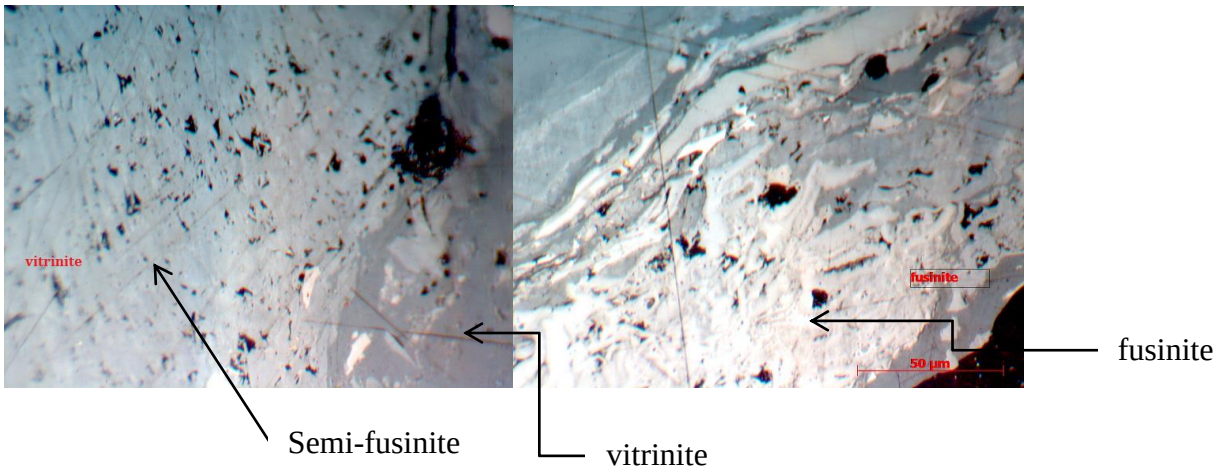

Figure 4.1.c: Petrographic images of different macerals *(*taken using an oil immersion lens, x500 magnification).

The proximate data (Table 4.1.a) shows higher fixed carbon and lower ash content in the Zimbabwe coal samples compared to South African coal samples. HS1 and Coal B have sulphur contents more than 2%.

Sample HS2 seems to have the highest reflectance readings, hence making it a better coking coal due to the slightly higher rank. The macerals which dominate in almost all of the coals is inertinite, which is typical for southern African coals. The coal samples have relatively low vitrinite content ranging from 14-37.6%. Coal A has a relatively high mineral content and the lowest rank.

According to the XRD data (Table 4.b), the most dominant mineral in all the samples is kaolinite; it comprises about 10% in HS1 and 35% in Coal A. Pyrite is the second dominant mineral in all coal samples, and may be a major host of TEs in coal (Diehl, 2004). The Zimbabwean coal samples seem not to have anatase (a mineral of TiO_2) and dolomite minerals compared to the South African coal samples.

Table 4.1.c shows the mineral matter content in vol % from petrographic analysis. It can be seen that Coal A has the highest quartz and mineral content.

Table 4.1.a: Characterisation data of ROM samples

Sample	Proximate Analysis (wt%)				Petrographic data (vol %)				Rank	Total
	H_2O	Ash	Volatile Matter	Fixed Carbon	Vitrinite	Liptinite	Inertinite	Mineral Matter	RoVmr%	Sulphur (wt%)
HS1	0.91	8.45	26.20	64.68	37.60	1.00	58.00	3.40	0.82	2.22
HS2	0.86	13.00	22.40	64.04	27.40	1.00	63.60	8.00	1.01	1.88
HS3	1.27	14.44	20.69	64.05	14.00	3.40	74.60	8.00	0.90	1.78
Coal A	2.72	55.77	18.18	24.29	14.10	6.30	26.40	53.30	0.73	0.77
Coal B	1.77	19.05	22.65	56.19	14.80	2.00	74.50	9.10	0.81	2.48

Table 4.1.b: XRD Data on ROM (all values in wt %)

	Graphite	Anatase	Calcite	Dolomite	Kaolinite	Muscovite	Pyrite	Quartz
HS1	85.78	0.00	0.46	0.00	9.20	1.65	2.90	0.00
HS2	78.76	0.00	0.88	0.00	10.60	1.77	2.12	5.87
HS3	81.92	0.00	0.00	0.00	11.50	3.17	2.46	0.94
Coal A	39.50	0.83	0.23	0.33	34.14	3.25	0.26	21.44
Coal B	68.32	0.09	0.05	1.53	21.24	0.75	3.93	4.10

Table 4.1.c : Mineral matter as determined by petrographic analysis (all values in vol %)

	Clays	Quartz	Pyrite	Carbonate	Other	% Total Mineral
HS1	0.20	1.00	1.60	0.60	0.00	3.40
HS2	1.00	1.60	4.40	1.00	0.00	8.00
HS3	0.20	2.80	4.80	0.00	0.20	8.00
Coal A	4.50	46.50	1.80	0.50	0.00	53.30
Coal B	0.30	4.00	1.50	3.00	0.30	9.10

4.3 Trace Elements in ROM samples

The as-received results obtained from the ICP-MS are shown in Appendices D and E. ICP-MS results of TEs in ROM coals are shown in Table 4.2.a. Most of the TEs in the Zimbabwean coal samples seem to fall in the range of average global and mean South Africa values, as indicated in Figures 4.2 a-d. The values of Cu, Cr, Pb, and V in South African coal sample A are greater than both the average global and mean South Africa values. The values of Cr and Ni in South African coal sample B exceed the average global and mean South Africa values.

No results from the ICP-AES used in the School of Chemistry are given in this section, as the machine could not detect most of the TEs (as shown in Appendix F).

Table 4.2.a: ICP-MS data on TEs in ROM samples

Element(ppm)	HS1	HS2	HS3	A	B	Average global (Ketris and Yudovich,2009)	Mean SA (Wagner and Hlatshwayo,2005)
As	3.45	3.17	8.15	7.66	3.58	9.0±0.7	2.7±1.0
Cd	0.029	0.028	0.053	0.239	0.219	0.2±0.04	0.24±0.17
Co	5.03	7.54	5.00	8.76	10.9	6.0±0.2	6.9±1.6
Cr	25.5	57.7	42.9	116	117	17.0±1	43.2±12.0
Cu	10.7	12.0	13.8	54.5	21	16.0±1	12.6±1.6
Mn	90.4	123	57.9	106	95	71.0±5	99.1±8.4
Mo	1.77	4.46	2.1	4.66	6.63	2.1±0.1	2.09±1.06
Ni	35.4	35.2	25.0	35.5	83.7	16.0±1	16.6±3.4
Pb	4.16	5.17	10.2	33.7	15.1	9.0±0.7	7.0±2.6
Sb	<0.1	<0.1	0.31	0.51	0.17	1.0±0.09	<0.136±0.06
Se	0.20	0.38	0.35	0.91	0.36	1.6±0.1	0.99±0.24
V	9.71	11.70	17.1	96.7	22.3	28.0±1	31.2±3.9

Cd, Sb and Se values (Figure 4.2.a) are lower in the Zimbabwe coal samples compared to the two SA coal samples, as well as the average global and mean SA values. The Sb value is greater in HS3 than in coal B. The South African coal samples seem to have higher TEs compared to the Zimbabwean coal samples although the values of Cd and Se are still within the mean SA and average global elements limit as shown in Figure 4.2.a.

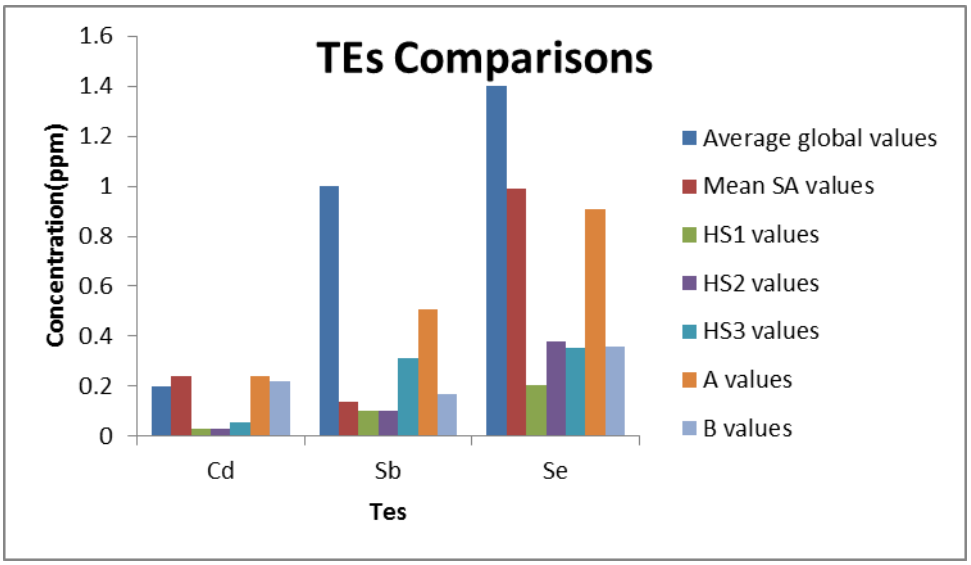

Figure 4.2.a: **Comparison of Cd, Sb, and Se with average global and mean SA values.**

Arsenic in all coal samples seems to be within the average global values (Figure 4.2.b). Cobalt values show some variance especially with Zimbabwean coals. Cobalt values in HS1 and HS3 are almost the same whilst the Co value of HS2 is the highest of all 3 selected Zimbabwean samples. The Co values in the selected South African coal samples analysed in this project are slightly above the average global and mean SA ranges. South African coal samples analysed here seem to have greater Cu and Pb values than the average global and mean SA values. South African coal sample A seems to have highest values of TEs as shown by the comparisons of Cu and Pb.

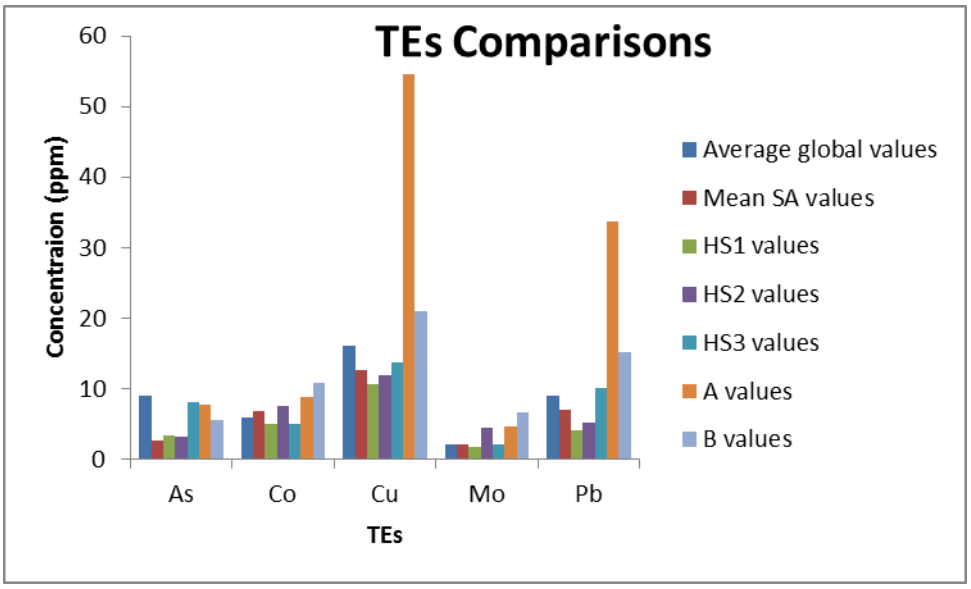

Figure 4.2.b: Comparison of As, Co, Cu, Mo, Pb with average global and mean SA values.

Figure 4.2.c shows comparison of Cr, Mn, Ni, and V in the Zimbabwean and South African samples with average global and mean SA values. The values for Cr, 116 ppm for coal A and 117 ppm for coal B (see Table 4.5) are high, but comparable to other values obtained for SA coals (see Wagner and Tlotleng, 2012). Certain sample analyses were repeated, and comparable values were obtained. Vanadium in the Zimbabwean coal samples and coal B is less than the average global and mean SA values. Coal A, on the other hand, shows the highest value of V and Ni compared to other coal samples; these values are higher than the average global and mean SA values.

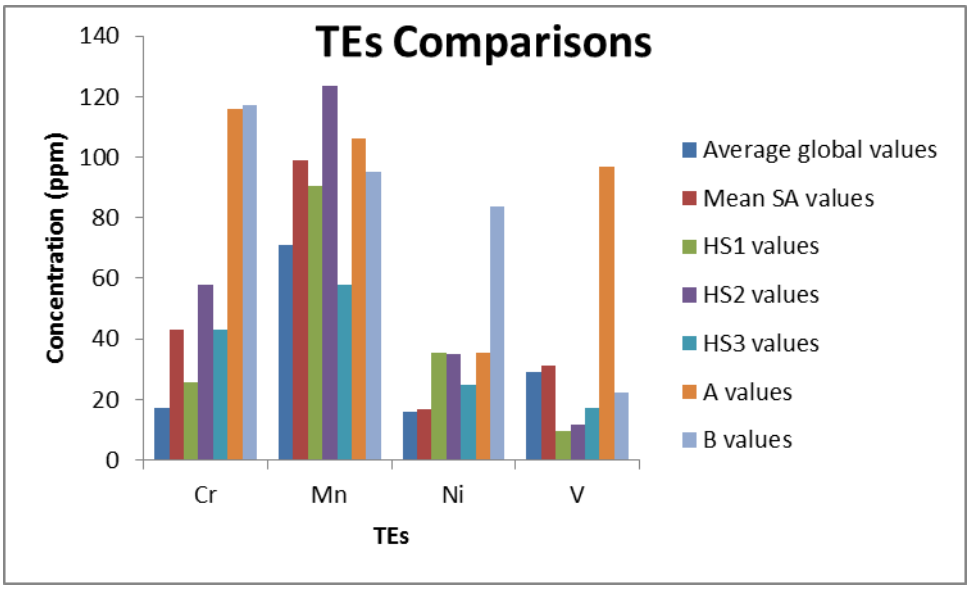

Figure 4.2.c: Comparison of Cr, Mn, Ni, and V with average global and mean SA values.

The Hg data, which was analysed using the FI-MH-AAS, is shown in Table 4.2.b and comparisons with the global mean and South African average values are as shown in Figure 4.2.d.

Table 4.2.b: FI-MH-AAS Mercury data on Average global and mean SA and ROM values

Sample	Hg (ppm)
Average global	0.1000±0.01
Mean SA	0.1500±0.05
HS1	0.1497
HS2	0.5343
HS3	0.6397
Coal A	0.4069
Coal B	0.4609

The sample HS1 seems to be comparable to the average global and mean SA values if a deviation of ± 30% is allowed (Richaud et al., 1998). The other samples seem to have Hg values much higher than the average global and mean SA values. High Hg concentrations could be due to the geology of both the Zimbabwean and SA sampling areas, with two of the Zimbabwean coal samples

reporting values far higher than the two SA coal samples. High Hg values could also be attributed to equipment error or Hg build up in the system. Some concern is noted regarding these analyses. The Zimbabwean coal samples generally report low TE contents compared to global average and mean SA values, apart from Hg. Wagner and Tlotleng also obtained high values of Hg in the South African coal samples from Waterberg coalfield.

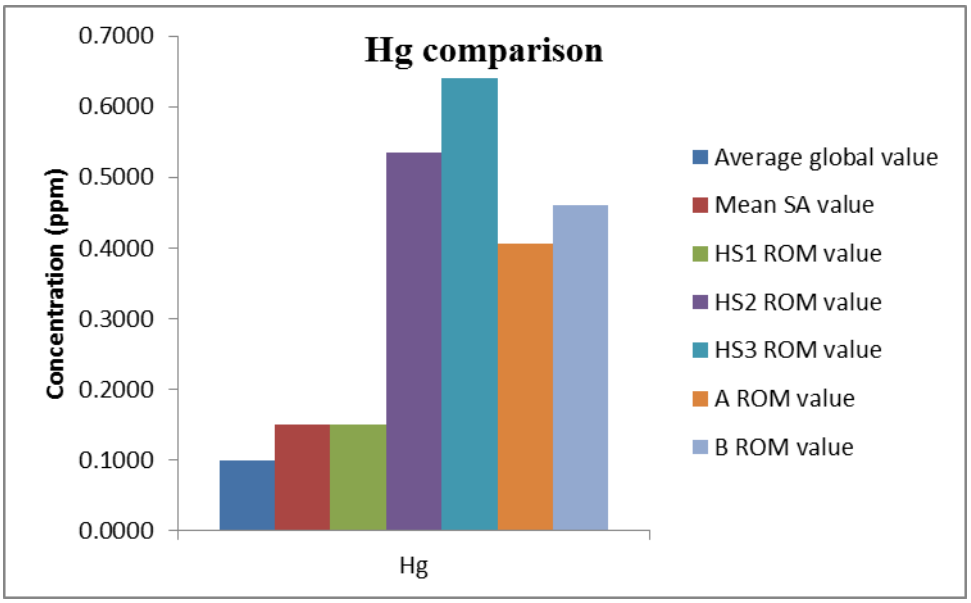

Figure 4.2.d: Comparison of Hg with average global values and mean SA values.

4.4 Density fractionated samples

ROM samples were density fractionated (Section 3.3.1) to obtain different fractions that would allow modes of occurrence to be inferred. HS1 ROM was not density fractionated due to the low ash content. From Table 4.3, which shows the results of proximate, %S, and petrographic analysis on ROM and density fractionated samples, S may be seen to increase with increasing density and is highly concentrated in the sink fractions, as expected if S occurs primarily as pyrite. Mineral matter and ash are highly concentrated in the sink fractions, again as expected. Minerals have a higher density compared to the organic component of coal, hence they concentrate in sink fractions. HS2, HS3 and B are inertinite-

rich coals, and this maceral is highly dominant in the float fractions. Vitrinite content decreases with increasing density, since it has a lower density.

Tables 4.4 and 4.5 show XRD and ICP-MS data for ROM and density fractionated samples. Yield data from density fractionation is shown in Table 4.5. The yield data shows that HS2 has over 50% of coal reporting to the $\rho_{1.3}$ float fraction. Samples HS3 and B have an almost equal proportion of coal reporting to all density fractions. In coal A about 17% is reporting to the $\rho_{1.5}$ fraction whilst most of the coal reports to the sink fraction due to its high mineral matter. Coal A has a high proportion of vitrinite to inertinite compared to other coal samples. About 2% each of coal reported to the float fractions of densities $\rho_{1.7}$ and $\rho_{1.9}$. Kaolinite is the most dominant mineral in both the Zimbabwean and South African ROM samples; HS1 and Coal B have the highest pyrite and sulphur content values.

Minerals like anatase and dolomite were not detected in the Zimbabwean ROM coal samples, but anatase was determined in the 1.7 float and sink products. Scheelite was found only in HS2, concentrated in higher density fractions, but was not found in the HS2 ROM (Table 4.1.b). South African coal samples do not have the mineral scheelite.

Most of the TEs concentrate in the sink fractions (Table 4.5), showing an affinity for mineral matter. There are high values of some TEs like Cr, Mn and Pb in some ROM samples like HS2, A and B and in their density fractions. Wagner and Tlotleng (2012) also showed high concentrations of these elements in the Waterberg samples. Beryllium seems to show equal distributions in all float fractions for all samples which were density fractionated. For TEs like Co, Cr, Mn, Mo, Ni, Pb, Sb and V, the concentration in coal A decreases with increasing density fractions unlike the other coal samples. The Hg values are reported in Table 4.13.a below.

Table 4.3: Characterisation data on ROM and density fractions

Sample	Proximate Analysis (wt%)				Petrographic data (vol%)				Total Sulphur (wt%)
	H_2O	Ash	Volatile matter	Fixed carbon	Vitrinite	Liptinite	Inertinite	Mineral Matter	
HS1 ROM	0.91	8.45	26.2	64.68	37.6	1.00	58.00	3.40	2.22
HS2 ROM	0.86	13.00	22.4	64.04	27.40	1.00	63.60	8.00	1.88
HS2 ρ1.3 float	1.61	11.67	22.46	64.09	27.30	0.30	67.30	5.40	1.91
HS2 ρ1.5 float	1.00	13.55	22.82	62.63	33.50	1.30	56.70	8.80	2.52
HS2 ρ1.5 sink	0.86	33.15	23.33	42.65	20.10	0.00	34.10	45.90	5.09
HS3 ROM	1.27	14.4	20.69	64.05	14.00	3.40	74.60	8.00	1.78
HS3 ρ1.3 float	1.32	10.81	22.50	65.37	24.80	4.20	66.50	4.20	1.52
HS3 ρ1.5 float	1.48	9.61	21.83	67.09	21.50	3.30	73.00	2.60	1.06
HS3 ρ1.7 float	1.36	13.60	19.36	65.67	9.20	3.30	81.20	7.10	1.03
HS3 ρ1.7 sink	1.32	21.73	18.97	57.98	10.50	0.60	58.50	30.60	5.62
A ROM	2.72	55.8	18.18	24.29	14.10	6.30	26.40	53.30	0.77
A ρ1.5 float	2.52	28.36	26.35	44.77	65.90	4.80	15.70	13.60	0.71
A ρ1.7 float	2.47	24.06	27.70	45.77	58.10	5.30	27.90	9.20	0.62
A ρ1.9 float	1.94	42.58	21.78	33.71	27.50	6.00	42.70	23.00	0.48
A ρ1.9 sink	1.17	63.18	15.92	19.74	12.00	9.00	22.50	56.50	0.67
B ROM	1.77	19.10	22.65	56.19	14.80	2.00	74.50	9.10	2.48
B ρ1.3 float	2.94	15.91	22.72	58.43	16.60	4.50	73.70	5.70	1.60
B ρ1.5 float	2.96	11.45	22.83	62.76	12.40	1.50	84.40	2.10	0.89
B ρ1.7 float	2.10	17.64	21.23	59.02	10.60	2.00	78.70	9.20	1.31
B ρ1.7 sink	1.97	28.79	19.85	28.79	6.10	3.50	64.20	26.70	4.81

Table 4.4: XRD Data on ROM and density fractions (all values in wt%)

Sample	Graphite	Anatase	Calcite	Dolomite	Kaolinite	Muscovite	Pyrite	Quartz	Scheelite
HS1 ROM	85.78	0.00	0.46	0.00	9.20	1.65	2.90	0.00	0.00
HS2 ROM	78.76	0.00	0.88	0.00	10.60	1.77	2.12	5.87	0.00
HS2 ρ1.3 float	82.28	0.00	0.60	0.00	8.41	1.27	1.95	5.36	0.14
HS2 ρ1.5 float	80.29	0.00	0.61	0.00	9.18	1.43	2.62	4.68	1.18
HS2 ρ1.5 sink	61.46	0.00	3.70	0.00	13.49	2.11	6.51	8.09	4.65
HS3 ROM	81.92	0.00	0.00	0.00	11.50	3.17	2.46	0.94	0.00
HS3 ρ1.3 float	86.26	0.00	0.00	0.00	8.92	2.68	1.95	0.19	0.00
HS3 ρ1.5 float	88.76	0.00	0.00	0.00	7.66	2.47	1.12	0.00	0.00
HS3 ρ1.7 float	85.96	0.19	0.00	0.00	9.43	2.10	1.22	1.10	0.00
HS3 ρ1.7 sink	77.14	0.14	0.00	0.00	11.29	2.37	7.28	1.79	0.00
A ROM	39.50	0.83	0.23	0.33	34.14	3.25	0.26	21.44	0.00
A ρ1.5 float	54.29	0.61	0.41	0.19	26.69	2.80	1.04	13.97	0.00
A ρ1.7 float	61.90	0.47	0.00	0.17	23.40	2.22	0.24	11.60	0.00
A ρ1.9 float	45.68	0.81	0.12	0.61	32.93	3.47	0.38	15.99	0.00
A ρ1.9 sink	35.70	0.84	0.26	0.72	37.81	4.81	0.65	19.25	0.00
B ROM	68.32	0.09	0.05	1.53	21.24	0.75	3.93	4.10	0.00
B ρ1.3 float	70.92	0.08	0.00	1.35	21.59	0.60	2.23	3.22	0.00
B ρ1.5 float	77.84	0.04	0.00	0.30	17.14	0.51	0.93	3.23	0.00
B ρ1.7 float	69.89	0.14	0.00	1.34	22.80	0.67	1.66	3.50	0.00
B ρ1.7 sink	59.13	0.07	0.22	2.27	23.80	0.79	7.99	5.72	0.00

Table 4.5: ICP-MS data on Trace Elements in ROM and density fractions (all values in ppm)

SAMPLE	Yield (%)	As	B	Be	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sb	Se	U	V
HS1 ROM		3.45	29.3	1.04	0.029	5.03	25.5	10.7	90.4	1.77	35.4	4.16	<0.10	0.2	0.06	9.71
HS2 ROM		3.17	20.90	3.52	0.03	7.54	57.7*	12.00	123.00*	4.46	35.20	5.17	<0.10	0.38	0.66	11.70
HS2ρ1.3 float	54.73	3.76	22.50	3.36	0.06	6.54	23.3	10.50	40.5	2.51	30.40	8.60	0.12	0.66	0.79	13.20
HS2ρ1.5 float	33.38	5.68	19.30	3.41	0.03	6.34	25.9	9.96	67.8	3.04	28.80	7.19	<0.10	0.29	0.84	15.30
HS2ρ1.5 sink	11.89	12.2	28.90	3.73	0.10	8.8	39.7	17.2	68.3	5.74	35.80	12.70	0.22	0.82	1.05	17.10
HS3 ROM		8.15	18.90	2.00	0.05	5.00	42.90	13.80	57.90	2.08	25.0	10.2	0.31	0.35	1.48	17.10
HS3ρ1.3 float	19.96	8.17	15.20	2.05	0.07	5.10	23.20	10.60	16.90	1.33	28.60	7.56	0.356	0.354	1.61	15.30
HS3ρ1.5 float	21.08	3.77	14.30	1.99	0.04	4.66	25.00	11.10	35.60	1.19	20.80	7.25	0.18	0.433	1.47	15.80
HS3ρ1.7float	33.94	4.73	25.10	2.04	0.22	3.18	32.40	11.50	32.00	1.06	42.00	13.80	0.29	0.113	1.84	15.40
HS3ρ1.7sink	25.02	34.30	29.50	2.30	0.30	5.97	45.70	23.70	113.50	4.04	40.90	20.90	1.43	0.85	2.32	17.70
A ROM		7.66	19.70*	3.34	0.24	8.76	116.00*	54.50	106.00*	4.66	35.50	33.70	0.51	0.91	3.71*	96.70
A ρ1.5float	17.33	3.65	27.38	3.12	1.01	9.59	91.23	55.02	42.33	5.63	43.30	37.00	1.07	0.5	5.06	110.00
A ρ1.7float	3.22	2.81	27.70	3.16	0.74	8.16	72.85	31.57	38.35	4.37	30.10	36.70	1.00	0.36	5.24	111.00
A ρ1.9float	2.73	5.56	28.54	3.37	0.62	5.83	77.67	30.16	33.83	3.65	33.10	43.70	0.73	0.29	5.53	92.00
A ρ1.9sink	76.72	6.45	29.44	2.96	0.95	3.58	73.95	28.30	34.14	3.94	34.60	27.80	0.63	0.26	5.09	68.30
B ROM		3.58	3.70*	2.37	0.22	10.90	117.00*	21.00*	95.00	6.63*	83.70	15.10*	0.17	0.36	1.39	22.30
B ρ1.3float	19.68	2.31	14.73	1.91	0.59	7.59	66.81	28.35	44.06	1.82	51.00	20.70	0.26	0.34	1.35	15.80
B ρ1.5float	21.39	1.83	12.23	2.82	0.44	8.99	56.28	24.39	31.34	1.47	63.10	16.50	0.23	0.08	1.59	21.90
B ρ1.7float	30.74	2.04	12.33	3.28	0.67	8.70	65.91	26.71	59.19	2.17	71.60	17.00	0.26	0.12	2.17	25.00
B ρ1.7sink	28.19	6.72	11.88	2.64	2.64	10.49	103.88	57.25	160.70	4.57	112.50	26.20	0.40	0.66	2.10	25.90

There are concerns with high TE values which are indicated by *. Wagner and Tlotleng (2012) also observed high values these TEs. At this point no values may be thought to be in error as the Hwange coalfield is of Permian age and the coalfield highlighted by Wagner and Tlotleng (2012) is also a Permian coalfield. Though the location of the South African coalfield remains anonymous it is still possible to assume that the values are reflective of the trace elements in the selected coal samples.

4.5 Washability Analysis

Washability curves were constructed according to Gluskoter et al. (1977) and England et al. (2002), to help draw possible conclusions on the modes of occurrence of the TEs in the coals. ICP-MS and XRD data (Tables 4.4 and 4.5) were used to draw the washability curves and correlations diagrams. The washability curves of the concentration of trace elements were plotted versus the cumulative mass yield. Whilst many correlations were tested, those of As, B, Be, Cd, Co, Cu, Cr, Hg, Mn, Mo, Ni, Pb, Sb, Se, U and V are discussed in this section.

To establish relationships between the different coal matrices and TEs in the coal samples, correlation coefficients were determined. The Pearson product moment correlation coefficient (r) is the statistical analysis which was performed on the data following Conaway (2001). Correlation coefficient, r, is a dimensionless index that reflects the extent of the linear relationship between two data sets and it ranges from –1 to +1.

4.4.1 Arsenic Washability Curves

In bituminous coals, As is believed to be associated with pyrite (Kolker et al., 2000). Correlation of pyritic sulphur and As showed an As association with pyrite in eastern Kentucky coals (Hower et al., 1997). In Figure 4.3 and Table 4.6, As generally seems to concentrate with increasing yield for samples HS2, HS3 and B, hence showing a possible association with pyrite. Coal A ROM has high As but the lowest pyrite content (reference to Table 4.4); hence not all pyrite in coal contain high amounts of As. The correlation coefficient of A, r = 0.0608 (Table 4.6) is too low to show a correlation of As with pyrite in coal A. The correlation coefficients of samples HS2, HS3 and B (Table 4.6, $r \approx +1$) show a strong correlation of As and pyrite, suggesting that As may be strongly associated with pyrite in these coal samples. Whilst As may be associated with pyrite, this is not always the case in coal sample A, as demonstrated here; As may also have an organic affinity.

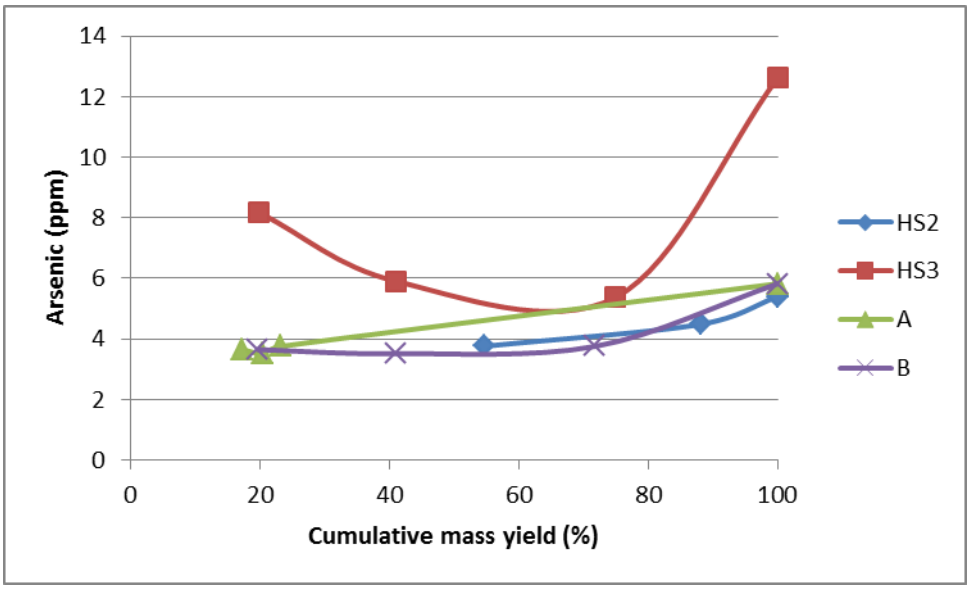

Figure 4.3: Arsenic washability curves for Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

Table 4.6: Correlation coefficient (r) of As: Pyrite in Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

As: Pyrite	R
HS2	0.9966
HS3	0.9999
A	0.0608
B	0.9966

4.4.2 Boron Washability Curves

Boron is typically associated with organic fractions (Finkelman, 1995). The washability curves of coal samples HS2 and A are almost linear, whilst the washability curve of HS3 shows a positive slope with boron increasing with increasing yield (Figure 4.4). Coal sample B shows a slight decrease of boron with increasing yield. From the correlation coefficients of coal samples HS2, HS3 and A (Table 4.7), B shows strong negative correlation coefficients with macerals, which are the inferred organic content in coal from petrographic analysis. Boron may not be associated with organic matter in Zimbabwean coal samples HS2 and

HS3 and South African coal sample A. The correlation coefficient of sample B may suggest an association of Boron with organic matter.

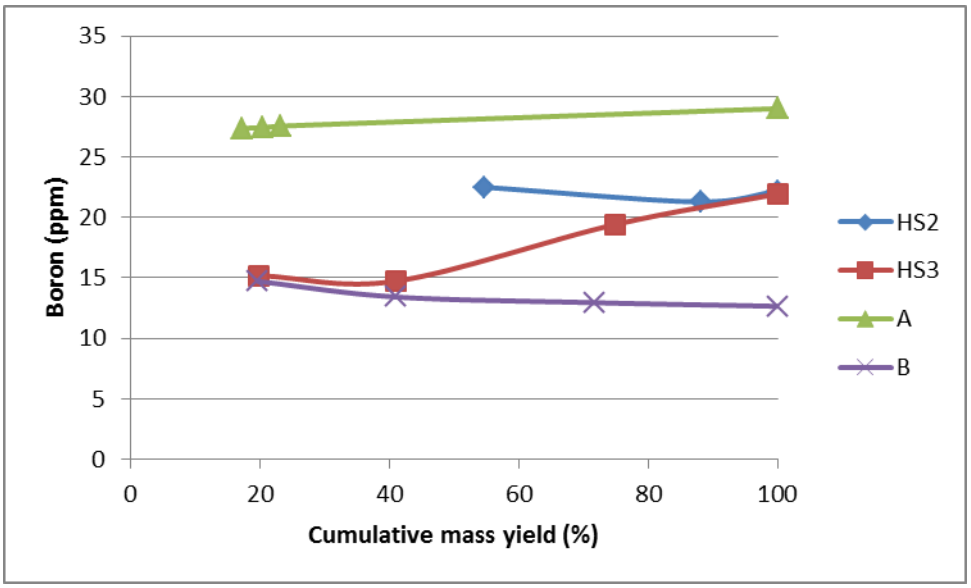

Figure 4.4: Boron washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B

Table 4.7: Correlation coefficient (r) of B: Macerals in Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

B:Macerals	r
HS2	-0.91761
HS3	-0.82189
A	-0.93413
B	0.44238

4.4.3 Be Washability Curves

According to Finkelman (1995), Be has an organic association. The washability curves (Figure 4.5) seem linear for coal samples HS2, HS3 and A. Beryllium increases with increasing density in coal sample B as seen in Table 4.5. The strong negative correlation coefficients (Table 4.8) of samples HS2 and HS3 show that there is no linear relationship of Be with macerals, hence suggesting that Be is not associated with organic matter in these Zimbabwean coal samples, but rather with mineral matter.

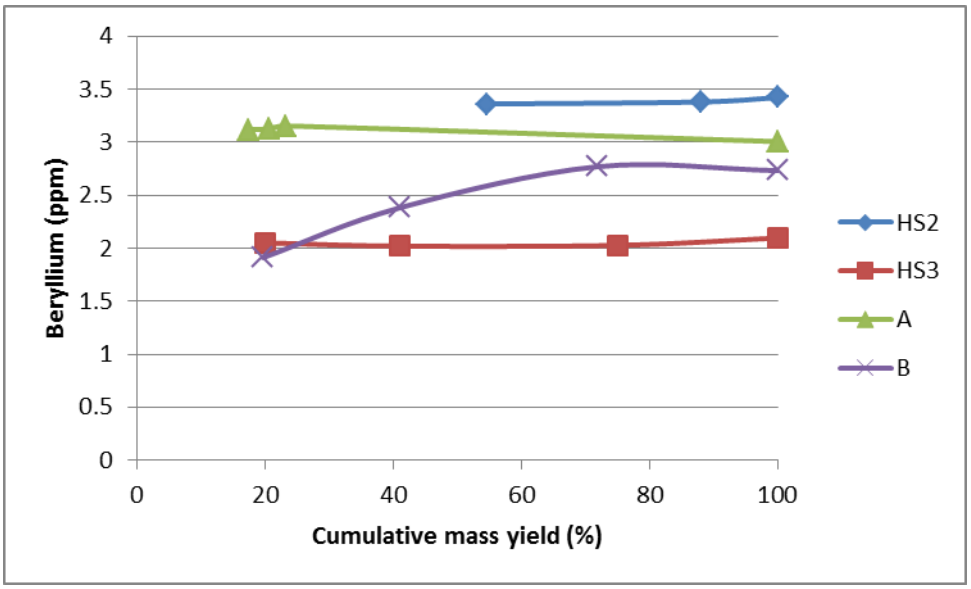

Figure 4.5: Be washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B

Table 4. 8: Correlation coefficient (r) Be: Macerals in Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

Be: Macerals	r
HS2	- 0.9988
HS3	- 0.9934
A	- 0.5664
B	- 0.0600

4.4.4 Cd Washability Curves

According to Finkelman (1994), Cd is associated with sphalerites. Sphalerite is a sulphide which mostly consists of Zn. Coal sample HS3 and B show increasing concentrations of Cd in higher densities (Table 4.5). The concentration of Cd decreases with increasing yield in coal sample A (Figure 4.6). Wagner and Tlotleng (2012) found that in SA coals, Cd exhibited an organic association and might have an affinity for pyrite in some SA coals. Correlation coefficients were determined (Table 4.9) to investigate the dependence of Cd with pyrites in both the Zimbabwe and SA samples. The correlation coefficients of all the selected samples suggest a strong dependence of Cd with pyrite.

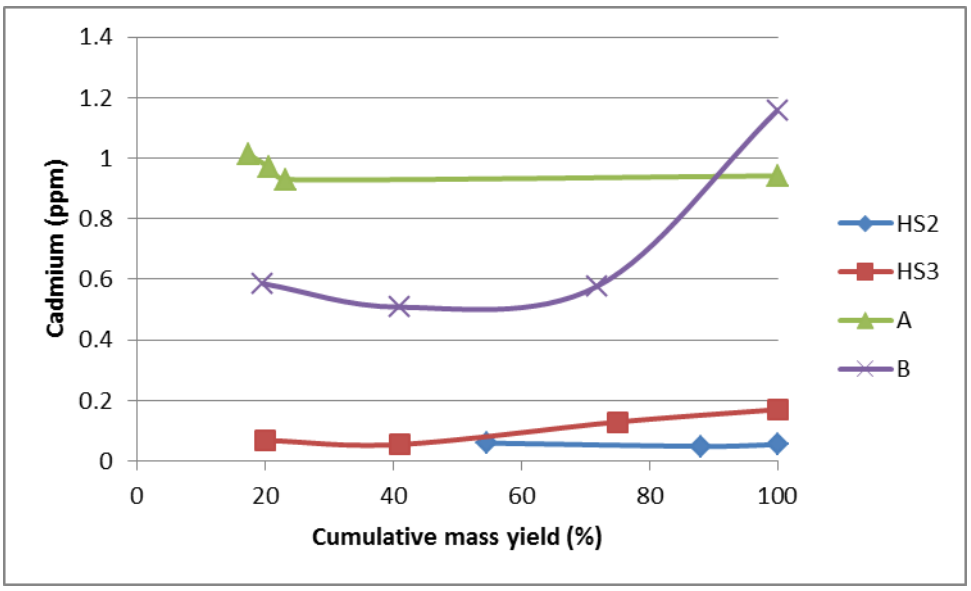

Figure 4.6: Cd washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B

Table 4.9: Correlation coefficient (r) of Cd: Pyrites in Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

Cd:Pyrites	r
HS2	0.73729
HS3	0.84652
A	0.85545
B	0.99262

4.4.5 Cr Washability Curves

Chromium has either an organic or clay association (Finkelman, 1994). Figure 4.7 shows the washability curves of coal samples HS2, HS3 and B show a slight increase in Cr concentration with increasing yield. The washability curve of coal sample A shows a decrease in Cr with increasing yield. The correlation coefficients in Table 4.10 show that Cr may not be associated with organic matter. The strong negative correlation coefficients of Cr: Kaolinite for coal samples HS2 (r= -1.0000), HS3 (r= -0.9129) and B (r= -0.7261), suggest that Cr may not be associated with kaolinite whilst for sample A it may be otherwise. The strong correlation coefficient r = 0.9192 for Cr: Muscovite in coal sample B suggests that Cr may be associated with muscovite in sample B. Muscovite is a silicate which could be inferred to be a type of clay (Mcdowell, 1983).

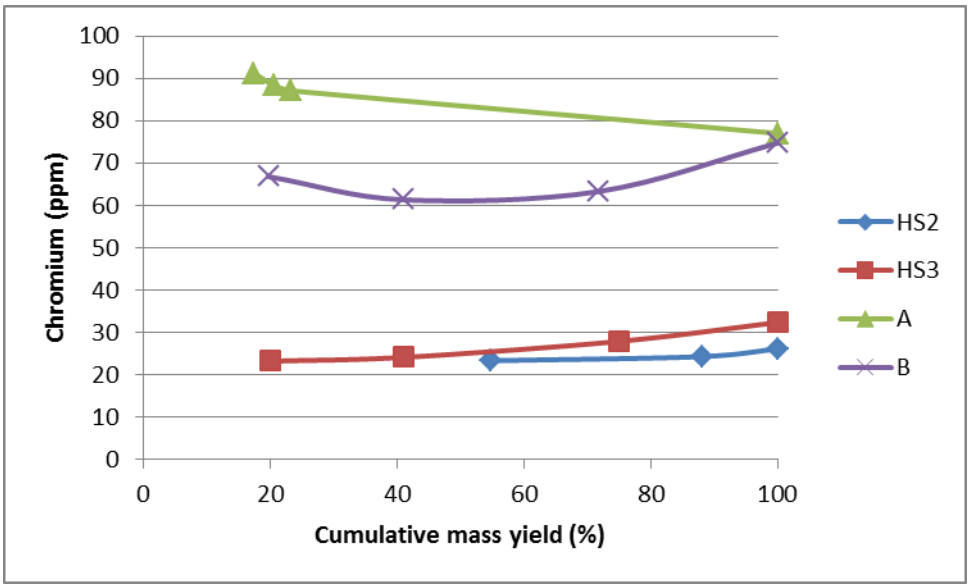

Figure 4.7: Cr washability curve for for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B.

Table 4.10: Correlation coefficient (r) of Cr:Maceral, Cr:Kaolinite, Cr:Muscovite in Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

	Cr:Maceral	Cr:Kaolinite	Cr:Muscovite
HS2	- 0.9973	- 1.0000	- 0.9995
HS3	- 0.9482	- 0.9129	- 0.4727
A	- 0.5461	- 0.2651	- 0.8198
B	- 0.9889	- 0.7261	0.9192

4.4.6 Co Washability Curves

Cobalt may be associated with pyrite, or may have an affinity for accessory sulphides (Finkelman, 1995). The washability curves of HS2 and B (Figure 4.8) show slight increases in Co concentration with increasing yield. The washability curve of HS3 shows a sharp decrease in Co in $\rho_{1.7}$ float and then increase in the sink fraction. This may be attributed to possible depletion of Co in the $\rho_{1.7}$ float sample. Cobalt concentration decreases with increasing yield for the washability curve of Co. The correlation coefficients of HS2 and HS3 suggest that Co may be associated with pyrite (Table 4.11) whilst r of A and B suggests that Co may not be associated with pyrite.

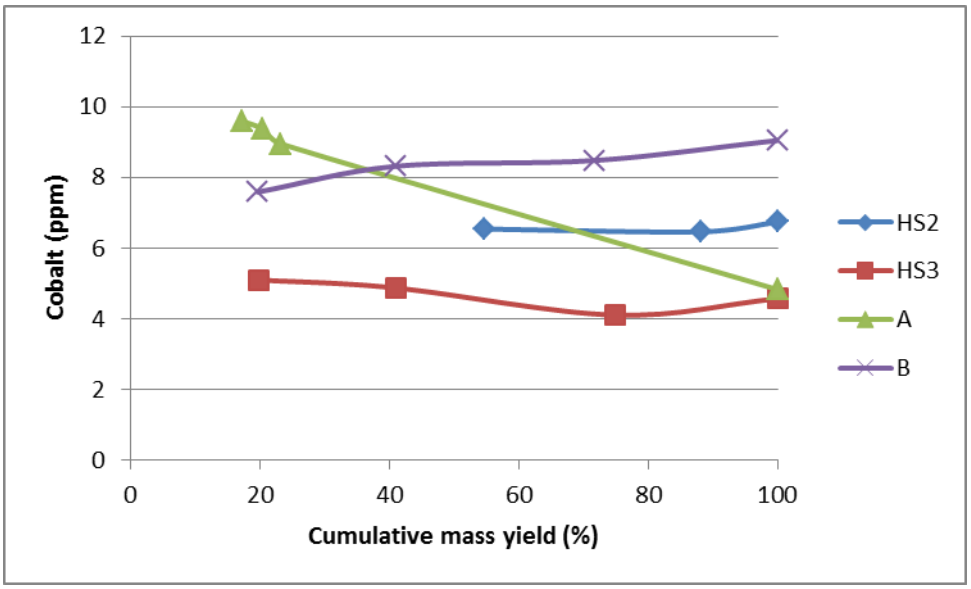

Figure 4.8: Co washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B

Table 4.11: Correlation coefficient (r) of Co:Pyrite, in Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

Co:Pyrites	r
HS2	0.9781
HS3	0.7569
A	- 0.2827
B	- 0.7745

4.4.7 Cu Washability Curves

According to Finkelman (1995), Cu is associated with chalcopyrite. The washability curves of coals HS2, HS3 and B show that Cu concentrates with increasing yield (Figure 4.9). The washability curve of A shows a decrease of Cu with increasing yield. The high positive correlation coefficients of all coal samples show that Cu is associated with pyrite (Table 4.12).

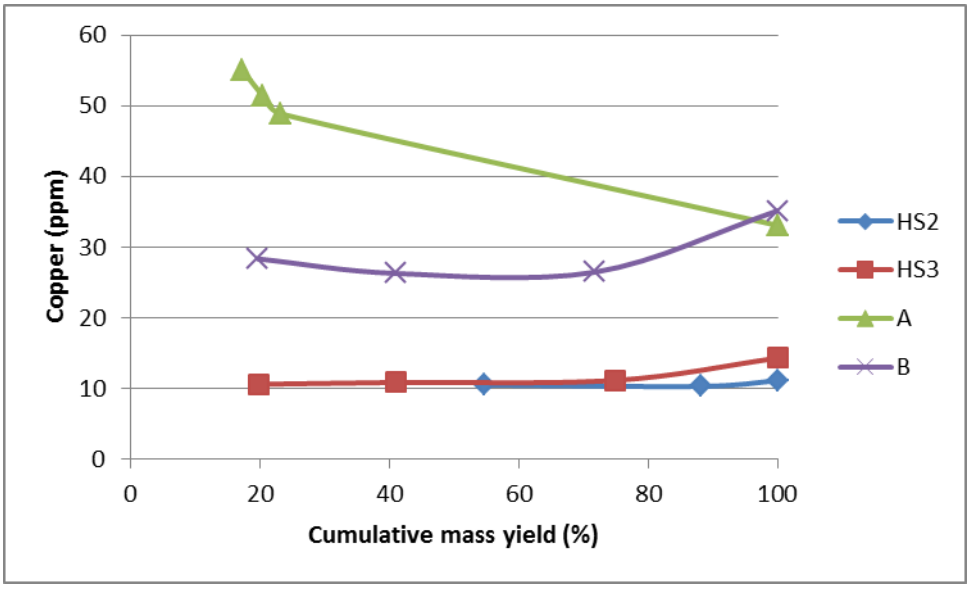

Figure 4.9: Cu washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B

Table 4.12: Correlation coefficient (r) of Cu:Pyrite, in Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

Cu:Pyrites	r
HS2	0.9794
HS3	0.9841
A	0.8193
B	0.9982

4.4.8 Hg Washability Curves

Table 4.13.a provides the Hg results as determined by FI-MH-AAS. According to literature, Hg is mostly associated with pyrite (Finkelman, 1994; Yudovich and Ketris, 2005a). Mercury in the Zimbabwean coal samples increases with increasing density (Table 4.13.a). The washability curves of the Zimbabwean coal samples show that Hg is dominant in the sink fractions, increasing with increasing yield (Figure 4.10). In the SA coal samples, the washability curves seem linear; Hg may be associated with both organic and inorganic matter. This trend was observed by Wagner and Tlotleng (2012) who found similar results in SA coals.

Table 4.13.a : Hg data from the FI-MH-AAS

Sample	Hg (ppm)
HS1 ROM	0.1497
HS2 ROM	0.5343
HS2 p1.3 float	0.3720
HS2 p1.5 float	0.7170
HS2 p1.5 sink	1.0457
HS3 ROM	0.6397
HS3 p1.3 float	0.1698
HS3 p1.5 float	0.1722
HS3 p1.7 float	0.2165
HS3 p1.7 sink	0.7399
Coal A ROM	0.4069
Coal A p1.5 float	0.2167
Coal A p1.7 float	0.1790
Coal A p1.9 float	0.1903
Coal A p1.9 sink	0.2401
Coal B ROM	0.4609
Coal B p1.3 float	0.1466
Coal B p1.5 float	0.1373
Coal B p1.7 float	0.0968
Coal B p1.7 sink	0.1511

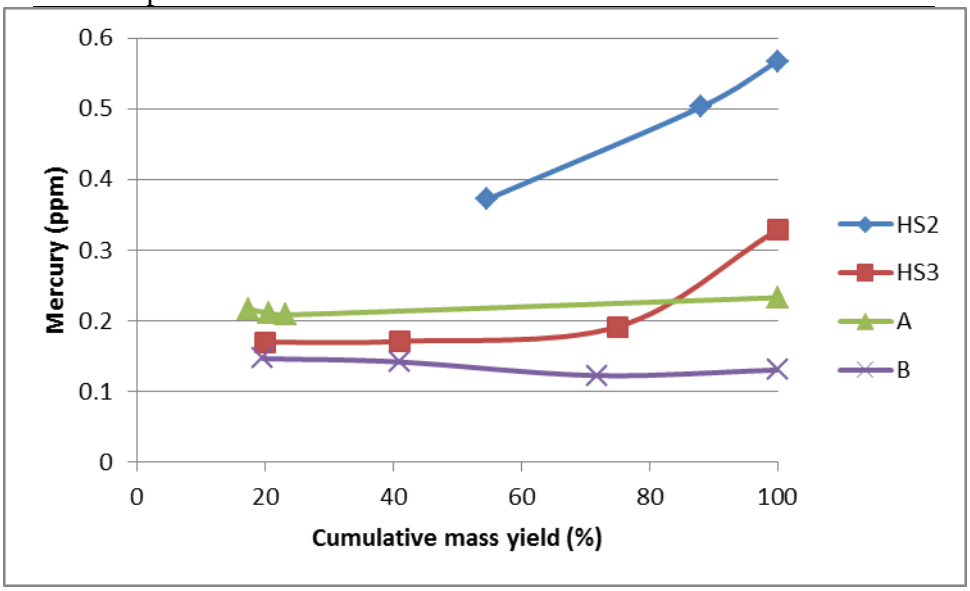

Figure 4.10: Hg washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B

Table 4.13.b: Correlation coefficient (r) of Hg:Pyrite, in Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

Hg:Pyrite	r
HS2	0.9207
HS3	0.9848
A	0.6785
B	0.4969

4.4.9 Mn Washability Curves

According to Finkelman (1994), Mn is associated with carbonates, especially siderite and ankerite. Coal A seems to give an almost flat washability curve, hence showing an equal distribution of Mn with all density fractions. In the Zimbabwean coal samples and coal sample B, Mn seems to concentrate with increasing yield (Figure 4.11.a). Ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$) is closely related to dolomite ($CaMg(CO_3)_2$) so correlation coefficients between Mn and dolomite were calculated for South African coals (Figure 4.11.b). The correlation coefficient r = 0.8381 for Mn: dolomite suggests a strong possible association of Mn with dolomites. With just density fractionation results, it is not sensible to make conclusions of Mn association with carbonates. Dolomite is closely related to ankerite which was not determined by XRD. Direct methods of determining modes of occurrence could help determine possible modes of occurrence in both Zimbabwean and SA coals.

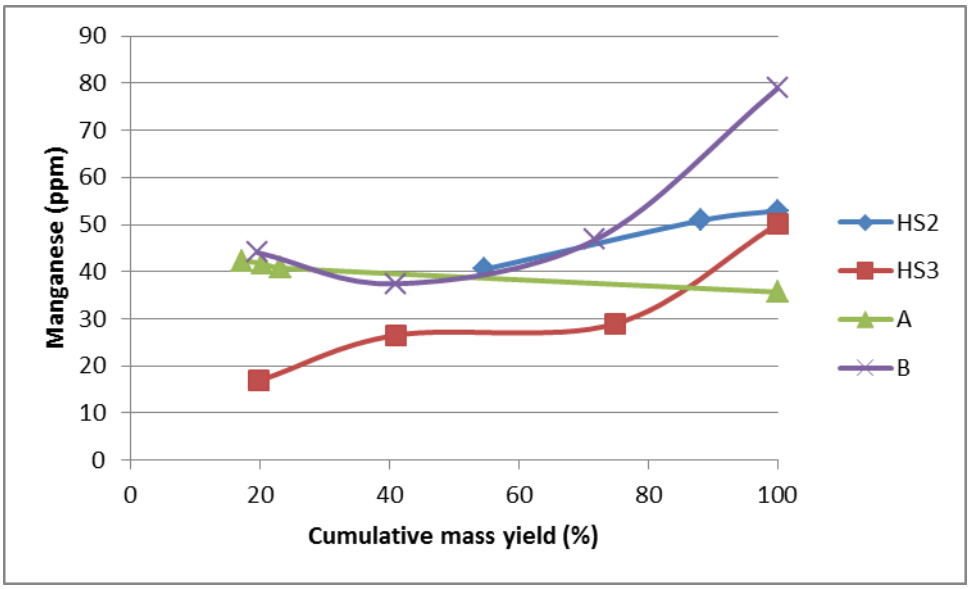

Figure 4.11.a: Mn washability curve for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B

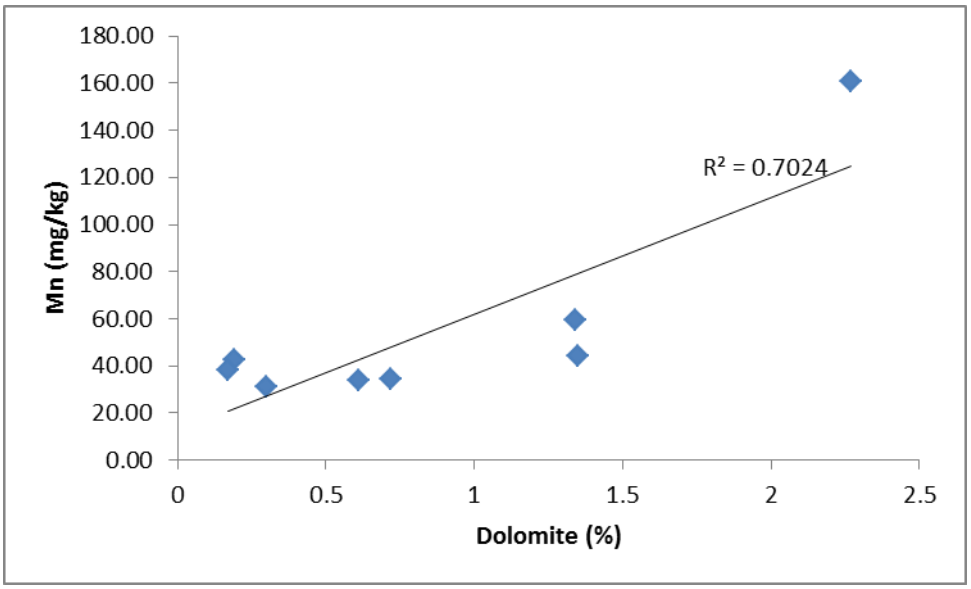

Figure 4.11.b: Correlation of Mn: Dolomite in South African coal samples A and B

4.4.10 Other trace elements Washability Curves

Molybdenum has a probable association with sulphides (Finkelman, 1995). In coal samples HS2, HS3 and B, Mo seems to associate with sink fractions (Table 4.5). The washability curves of samples HS2, HS3, and B show an increase in Mo

concentration with increasing yield (Figure 4.12.a). The washability curve of coal A shows that Mo is highly concentrated in the float fractions as it decreases with increasing yield.

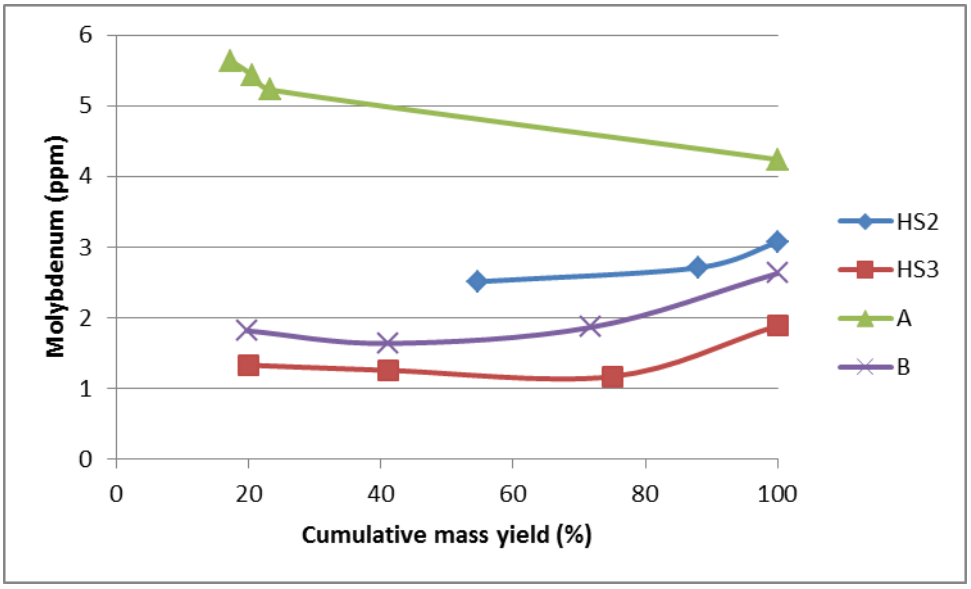

Figure 4.12.a: Mo washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B

According to Finkelman (1995), the mode of occurrence of Ni is unclear. The washability curves of Ni (Figure 4.12.b) in coal samples HS2, HS3 and B show an increase in Ni concentration with increasing yield. The washability curve of sample A shows decreasing Ni concentrations with increasing yield. Direct methods of determining modes of occurrence could assist in determining the modes of occurrence of Ni in coal.

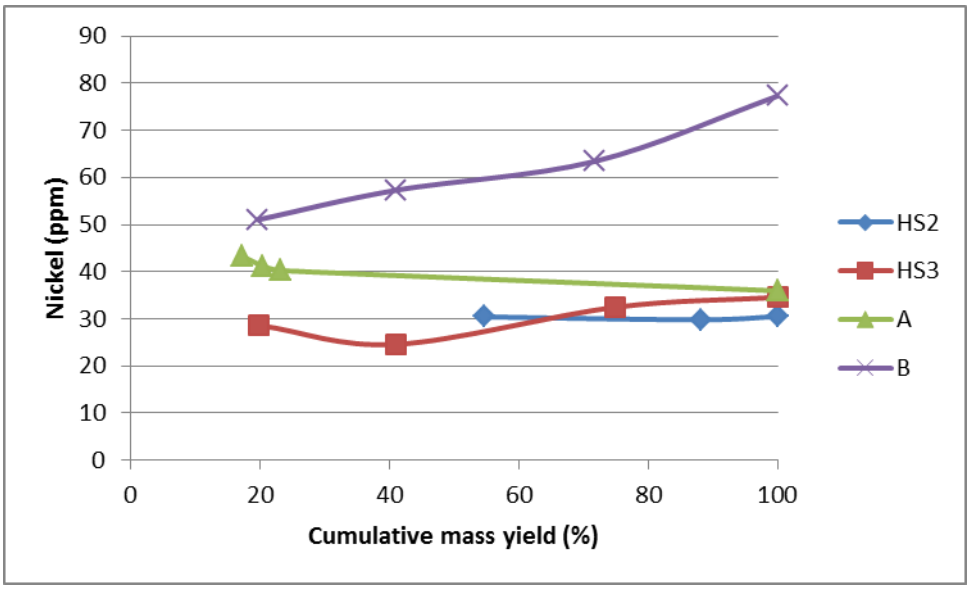

Figure 4.12.b: Ni washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B

The Pb washability curves (Figure 4.12.c) of coal samples HS2, HS3, and B show minimum increase in Pb content with increasing yield, whilst that of coal A shows a decrease in Pb content with increasing yield. The strong negative correlation coefficients of coal samples HS2, HS3 and A (Table 4.14.a) show that Pb may not be associated with sulphur. The strong coefficient of correlation of coal sample B ($r = 0.945$) shows that Pb may be associated with sulphur. Coal B ROM sample has the highest sulphur value of all five samples.

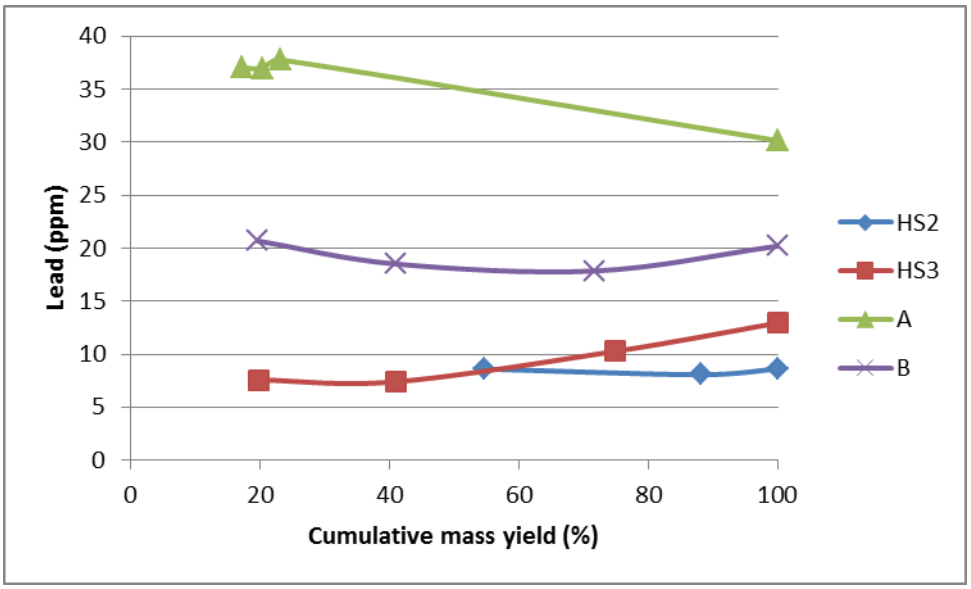

Figure 4.12.c: Pb washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B

Table 4.14. a: Correlation coefficient (r) of Pb: Sulphur, in Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

Pb:Sulphur	r
HS2	- 0.9083
HS3	- 0.8571
A	- 0.7163
B	0.9549

Antimony has a mode of occurrence with pyrite and accessory sulphides, whilst Se can be associated with organic matter, pyrite, accessory sulphides and selenides (Finkelman, 1994). In some SA coals, Se was found to report to middle fractions, and a silicate association was proposed by Wagner and Tlotleng (2012).

The washability curves (Figure 4.12.d) of coals HS3 and B show slight increases of concentration of Sb with increasing yield, whilst that of A shows a decrease with increasing yield. The washability curve of HS2 is almost flat, hence suggesting that washing the coal may have no effect on the concentration distribution of Sb in the clean coal. From Table 4.14.b, samples HS3 and B show very strong correlations ($r \approx +1$) of Sb with pyrite. Coal samples HS2 and A show that Sb may not be associated with pyrite, especially with $r = - 0.9357$ in HS2.

The washability curves of Se (Figure 4.12.e) show high concentrations in the float and sink fractions. The washability curve of A shows decreasing Se concentrations with increasing yield (Figure 4.12.e). The high correlation coefficients of Se: pyrite (Table 4.14.b) show that Se may be associated with pyrite for the Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

Selenium may not be associated with macerals in samples HS2 and HS3, as can be seen from their negative correlation, whilst for coals A and B, Se may also be associated with macerals.

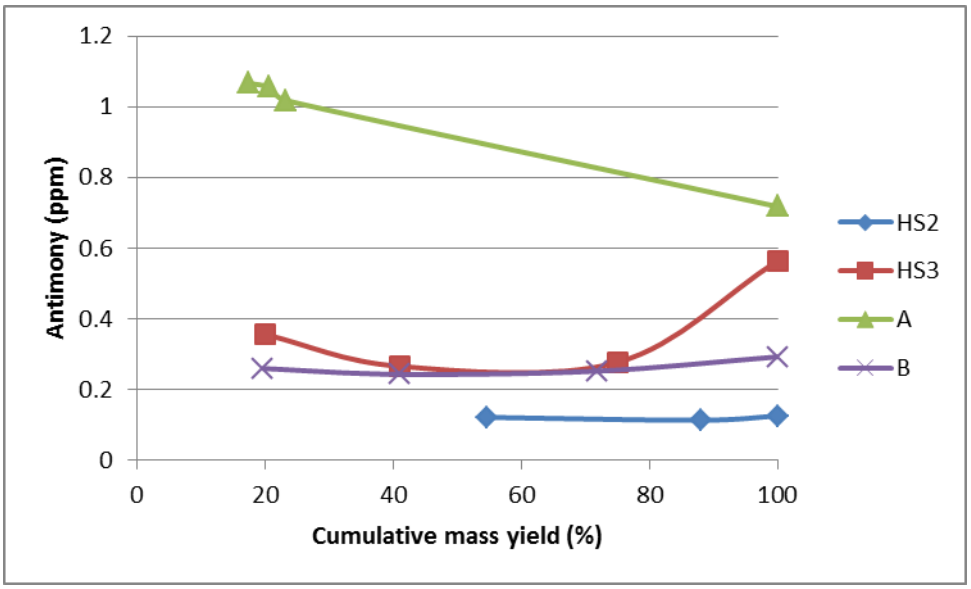

Figure 4.12.d: Sb washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B

Table 4.14. b: Correlation coefficient (r) of Sb: Pyrite, Se: Maceral, Se: Pyrite in Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

	Sb:Pyrite	Se:Maceral	Se:Pyrite
HS2	- 0.9537	- 0.6776	0.6314
HS3	0.9976	- 0.8370	0.8997
A	- 0.2600	0.6608	0.6404
B	0.9929	0.8864	0.9526

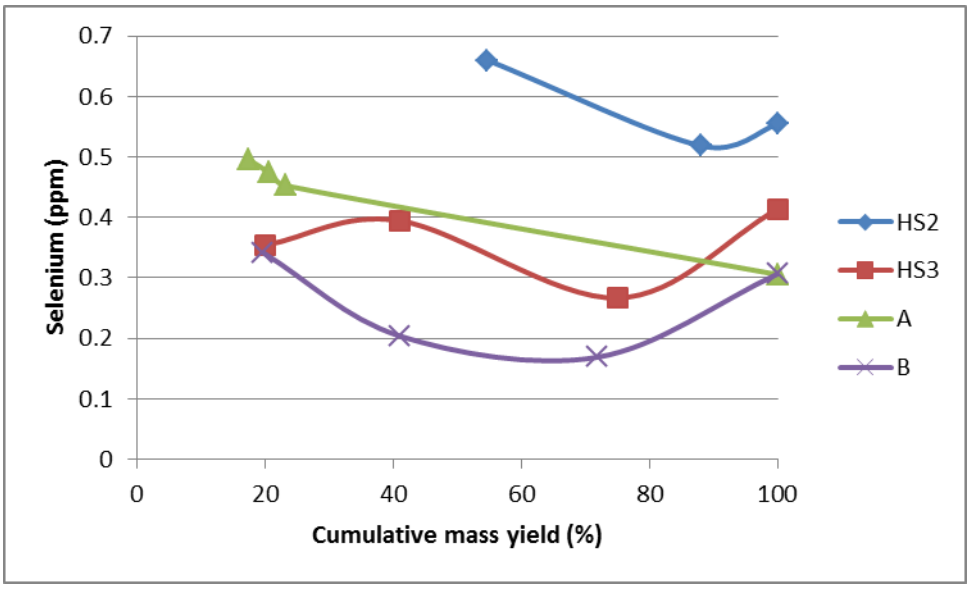

Figure 4.12.e: Se washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B

U may be organically bound or found in zircon whilst V may be associated with clays or organic matter (Finkelman, 1995). The washability curves of U (Figure 4.12.f) are almost flat in all coal samples suggesting that washing the coal may have no effect on the concentration distribution of U in the clean coal. Uranium in the Zimbabwean coal samples HS2 and HS3 and the selected SA coal samples does not show a correlation with the organic matter (Table 4.14.c).

The washability curves of V (Figure 4.12.g) in both the selected Zimbabwean and SA coal sample B, show an almost uniformly distribution of V with clays or organic matter (Figure 4.12.g). The washability curve of coal sample A shows a decrease in V concentration with increasing yield. From the correlation coefficients in Table 4.14.c, the values indicate possible association of V with both kaolinite and muscovite in the Zimbabwean coal samples HS2 and HS3 and SA coal samples A and B. Vanadium has a clay association in all selected coal samples analysed in this project.

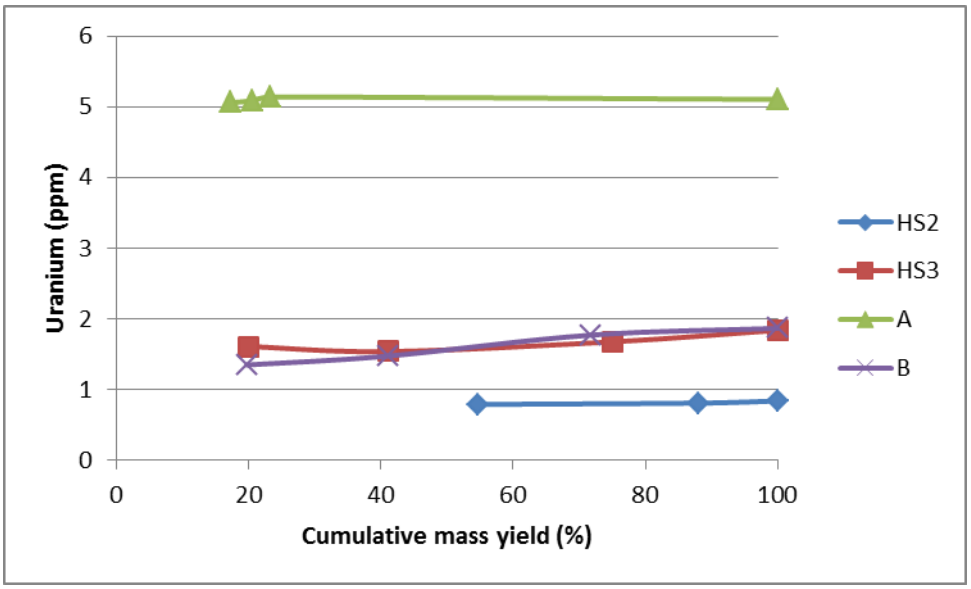

Figure 4.12.f: **U washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B**

Table 4.14.c: Coefficient of determination (R^2) of U: Maceral, V: Kaolinite and V: Muscovite in Zimbabwean coal samples HS2 and HS3, and South African coal samples A and B.

	Zimbabwe coal samples HS2 and HS3	South African coal samples A and B
U:Maceral	- 0.1118	- 0.4761
V:Kaolinite	0.7008	0.4893
V:Muscovite	0.5856	0.7033

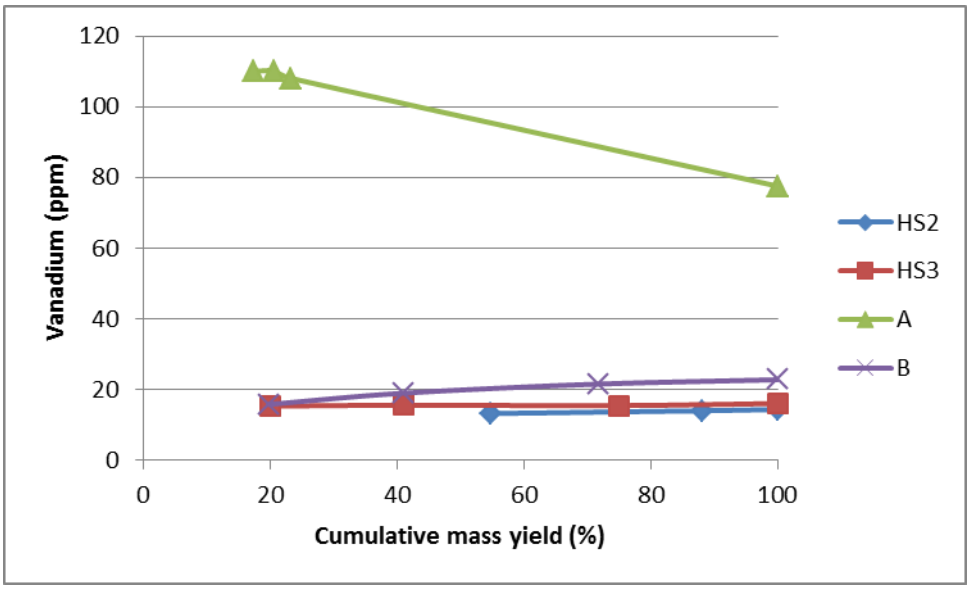

Figure 4.12.g: **V washability curves for Zimbabwean coal samples HS2, HS3 and South African coal samples A and B**

4.6 Sequential Leaching

The following TEs will be discussed, As, Be, Co, Cr, Cu, Mn, Mo, Ni and V. Table 4.15.a illustrates the percentages of TE extracted at each stage of leaching. The XRD data in Table 4.15.b shows mineral analysis results of ROM samples and leach residues. To try and maintain accuracy, all equipment was washed initially with 2 M HNO_3 and rinsed with deionised water. Care was taken while carrying out the sample preparation, and leachate bottles were stored in the fridge prior to being taken to UIS the next day for analysis. There is a concern regarding the results obtained, as the mass balances of several TEs either show huge losses or over balances. There is a possibility of errors, contamination and possible sample mishandling, especially in the external analytical laboratory[1]. Several samples, including the residues, were re-analysed and very different results were obtained. Some TEs like Hg are very volatile and may escape from solution; hence its mass balance could not get to 100%.

[1] **The external laboratory experienced several staff changes during the submission of the samples, which resulted in significant delays in the release of results and inconsistencies in the data. Samples were rerun, but time and costs prohibited a complete preparation and re-analysis of all the leachate samples. The commercial, certified laboratory closed down soon after completion of this project due to mismanagement.**

Table 4.15. a: Sequential leaching results (Trace elements, ppm)

Sample	Element	ROM	H_2O	% leached	CH_3COONH_4	% leached	HCl	% leached	HF	% leached	HNO_3	% leached	Total % leached	Residue	% in residue	Recovery(%)
Coal A	**As**	7.660	0.0000	0.0000	0.2520	3.2898	0.0210	0.2742	0.2520	3.2898	0.0210	0.2742	7.1279	6.4165	83.77	90.89
Coal B		3.580	0.0000	0.0000	0.0000	0.0000	0.0210	0.5866	0.0420	1.1732	0.0000	0.0000	1.7598	2.7577	77.03	78.79
HS1	**Be**	1.040	0.0000	0.0000	0.0000	0.0000	0.0420	4.0385	0.1890	18.1731	0.0420	4.0385	26.2500	0.6920	66.54	92.79
HS2		3.520	0.0000	0.0000	0.0000	0.0000	0.1680	4.7727	0.6720	19.0909	0.3360	9.5455	33.4091	2.2500	63.92	97.33
HS3		2.000	0.0000	0.0000	0.0000	0.0000	0.0840	4.2000	0.5460	27.3000	0.2100	10.5000	42.0000	1.3700	68.50	110.50
Coal A		3.340	0.0456	1.3644	0.0000	0.0000	0.5089	15.2363	0.7359	22.0337	0.1299	3.8894	42.5237	2.7326	81.81	124.34
Coal B		2.370	0.0000	0.0000	0.0000	0.0000	0.0774	3.2670	0.2666	11.2478	0.0474	2.0016	16.5165	2.5917	109.36	125.87
HS1	**Co**	5.030	0.0000	0.0000	0.0420	0.8350	0.2310	4.5924	0.5250	10.4374	0.1890	3.7575	19.6223	3.8100	75.75	95.37
HS2		7.540	0.0210	0.2785	0.0210	0.2785	0.1680	2.2281	0.4410	5.8488	0.3360	4.4562	13.0902	6.2600	83.02	96.11
HS3		5.000	0.0000	0.0000	0.2940	5.8800	0.9870	19.7400	1.0710	21.4200	0.4410	8.8200	55.8600	3.4100	68.20	124.06
Coal A		8.760	0.0421	0.4807	0.1970	2.2484	1.1820	13.4930	2.8784	32.8580	0.5047	5.7618	54.8419	5.5786	63.68	118.52
Coal B		10.900	2.7158	24.9158	1.0677	9.7952	0.8744	8.0218	1.6041	14.7170	0.5409	4.9626	62.4124	7.6523	70.20	132.62
HS1	**Cr**	25.500	0.0000	0.0000	0.0000	0.0000	4.5150	17.7059	7.5600	29.6471	6.1110	23.9647	71.3176	11.9000	46.67	117.98
HS2		57.700	0.0630	0.1092	0.0420	0.0728	5.0820	8.8076	17.4300	30.2080	13.4610	23.3293	62.5269	14.4000	24.96	87.48
HS3		42.900	0.0210	0.0490	0.0000	0.0000	3.6330	8.4685	11.9700	27.9021	7.1820	16.7413	53.1608	23.1000	53.85	107.01
Coal A		116.000	0.0458	0.0395	0.0357	0.0308	21.313	18.3730	33.5673	28.9373	7.8947	6.8058	54.1864	5.5786	4.81	59.00
Coal B		117.000	0.0818	0.0699	0.0406	0.0347	19.578	16.7336	18.5744	15.8756	8.1571	6.9718	39.6856	7.6523	6.54	46.23
HS1	**Cu**	10.700	0.0420	0.3925	0.1050	0.9813	1.0290	9.6168	1.5960	14.9159	0.5880	5.4953	31.4019	8.4800	79.25	110.65
HS2		12.000	0.0630	0.5250	1.7850	14.8750	1.3650	11.3750	1.3860	11.5500	0.8190	6.8250	45.1500	7.6100	63.42	108.57
HS3		13.800	0.0420	0.3043	0.1050	0.7609	1.5960	11.5652	1.1760	8.5217	0.5460	3.9565	25.1087	11.8000	85.51	110.62
Coal A		54.500	0.1417	0.2600	0.7412	1.3600	14.092	25.8567	11.4994	21.0998	3.4100	6.2569	54.8334	24.3696	44.71	99.55
Coal B		21.000	0.1132	0.5391	0.2603	1.2396	3.5859	17.0756	2.9801	14.1911	1.2292	5.8534	38.8988	20.2084	96.23	135.13
HS1	**Hg**	0.150	0.0029	1.9038	0.0029	1.9639	0.0139	9.2719	0.0047	3.1263	0.0048	3.2331	19.4990	0.1146	76.55	96.05
HS2		0.534	0.0027	0.4979	0.0027	0.5054	0.0138	2.5830	0.0039	0.7300	0.0030	0.5690	4.8852	0.3962	74.15	79.04
HS3		0.640	0.0110	1.7196	0.0110	1.7196	0.0210	3.2828	0.0190	2.9702	0.0140	2.1885	11.8807	0.5396	84.35	96.23
Coal A		0.407	0.0025	0.6164	0.0037	0.9019	0.0018	0.4378	0.0137	3.3648	0.0024	0.5942	5.9151	0.2622	64.44	70.35
Coal B		0.461	0.0029	0.6274	0.0033	0.7108	0.0025	0.5376	0.0144	3.1256	0.0030	0.6561	5.6575	0.2610	56.63	62.29
HS1	**Mn**	90.400	0.1890	0.2091	4.8930	5.4126	42.630	47.1571	23.3100	25.7854	9.3450	10.3374	88.9015	9.5500	10.56	99.47
HS2		123.000	0.4830	0.3927	1.5330	1.2463	53.130	43.1951	21.8400	17.7561	19.5510	15.8951	78.4854	6.3900	5.20	83.68
HS3		57.900	0.0630	0.1088	2.1000	3.6269	9.8070	16.9378	16.7790	28.9793	7.9800	13.7824	63.4352	12.2000	21.07	84.51
Coal A		106.000	1.2600	1.1887	10.5000	9.9057	39.270	37.0472	40.9500	38.6321	10.9200	10.3019	97.0755	26.0627	24.59	121.66
HS1	**Mo**	1.770	0.0000	0.0000	0.0210	1.1864	0.1680	9.4915	0.5670	32.0339	0.2100	11.8644	54.5763	0.8810	49.77	104.35
HS2		4.460	0.0000	0.0000	0.0000	0.0000	0.1050	2.3543	0.8820	19.7758	0.8190	18.3632	40.4933	2.0000	44.84	85.34
HS3		2.080	0.0000	0.0000	0.0000	0.0000	0.0840	4.0385	0.5880	28.2692	0.3360	16.1538	48.4615	1.6400	78.85	127.31
Coal B		6.630	0.0000	0.0000	0.0268	0.4045	0.6545	9.8722	3.2561	49.1118	1.0970	16.5457	75.9342	1.9860	29.95	105.89
HS1	**Ni**	35.400	0.0000	0.0000	0.0997	0.2817	1.8176	5.1345	5.0489	14.2625	2.7560	7.7854	27.4641	29.5000	83.33	110.80
HS2		35.200	0.1013	0.2879	0.0574	0.1629	1.2093	3.4354	5.6036	15.9192	4.4922	12.7621	32.5675	24.4000	69.32	101.89
HS3		25.000	0.0319	0.1277	0.7567	3.0267	2.2870	9.1479	5.8156	23.2623	2.8866	11.5464	47.1110	26.4000	105.60	152.71
Coal A		35.500	0.1191	0.3355	0.6615	1.8633	7.0657	19.9033	20.2415	57.0183	4.2202	11.8880	91.0084	31.4247	88.52	179.53
Coal B		83.700	8.7497	10.4536	3.4885	4.1679	7.0534	8.4270	19.7923	23.6467	6.7905	8.1129	54.8081	64.5410	77.11	131.92
HS2	**V**	11.700	0.0000	0.0000	0.0000	0.0000	0.2094	1.7900	1.9111	16.3342	0.9735	8.3207	26.4449	10.1000	86.32	112.77
HS3		17.100	0.0000	0.0000	0.0000	0.0000	0.2700	1.5787	4.7960	28.0468	1.8935	11.0728	40.6983	11.6000	67.84	108.53
Coal A		96.700	0.0000	0.0000	0.4200	0.4343	2.5200	2.6060	30.6600	31.7063	5.6700	5.8635	40.6101	77.1692	79.80	120.41
Coal B		22.300	0.0000	0.0000	0.6300	2.8251	0.4200	1.8834	4.2000	18.8341	1.0500	4.7085	28.2511	17.7913	79.78	108.03

Table 4.15. b: XRD data on ROM and leach residues (all values in wt%)

	Graphite	Anatase	Calcite	Dolomite	Kaolinite	Muscovite	Pyrite	Quartz
HS1 ROM	85.78	0.00	0.46	0.00	9.20	1.65	2.90	0.00
HS1 leach residue	98.13	0.00	0.00	0.00	0.00	0.00	1.87	0.00
HS2 ROM	78.76	0.00	0.88	0.00	10.6	1.77	2.12	5.87
HS2 leach residue	98.74	0.00	0.00	0.00	0.00	0.00	1.26	0.00
HS3 ROM	81.92	0.00	0.00	0.00	11.5	3.17	2.46	0.94
HS3 leach residue	92.89	0.00	0.00	0.00	4.31	0.77	1.60	0.42
A ROM	39.5	0.83	0.23	0.33	34.14	3.25	0.26	21.44
A leach residue	72.1	0.93	0.00	0.00	5.24	1.18	0.71	19.84
B ROM	68.32	0.09	0.05	1.53	21.24	0.75	3.93	4.10
B leach residue	92.44	0.05	0.00	0.00	2.4	0.09	2.07	2.94

5 g of coal was leached with 35 ml of each solution followed by 70 ml of distilled water to leach the previous solution completely; hence a dilution factor had to be factored into the calculations to cater for volumes used to get the concentration.

5 g was leached therefore with 105 ml of solution

Hence 5 g →105 ml

To account for the concentration of the leachates, the concentration obtained from the machine (ICP-OES, ICP-MS and FI-MH-AAS) is multiplied by (105/5), which is 21.

Mass balances of some elements like Co, Ni, and V are considerably more than 100%, suggesting possible mass accumulation of the elements or possible contamination during analysis. The TEs which gave mass balances slightly below 100% include As and Hg. All these results are shown in the Appendix E.

Various authors have used selective leaching to determine the modes of occurrence of TEs (Palmer et al., 1996; Norris et al., 2010; Jorjani et al., 2011; Spears, 2012). Pyrite is a great host of many TEs; pyrite was leached by dilute HNO_3 in stage 5 during sequential leaching. Some TEs may be removed by concentrated HF which is stage 4 of the sequential leaching process. Concentrated HF liberates elements associated with silicates (clays).

Arsenic is believed to be associated with pyrite in bituminous coals (Kolker et al., 2000). Coal A and B have over 75% of As remaining in the residue which still contains pyrites, hence indicating that the leaching was not effective. Hydrofluoric acid removed the highest percentage of As (3%) out of all chemicals used in coal A. Coal A has quite a high proportion of kaolinite (Figure 4.15.b), and As could be associated with clays in this coal sample.

Beryllium has an affinity for organic matter or it may be associated with clays in coal (Finkelman, 1994). Acids used to extract Be (HCl and HF) exhibit problems and issues such as interference and material compatibility when analysing by ICP-AES or ICP-MS (Archuleta and Duran, 2009). From the results, Be may be also associated with silicates as over 10% of Be was removed by HF in each sample

(Table 4.15.a), whilst more than 50% remained in the residue, hence also showing an association with the organic component or incomplete extraction.

Cobalt is associated with pyrite and some occur in accessory sulphides (Finkelman, 1995), hence most Co would be removed by HNO_3 during sequential extraction. For samples HS1, HS2, HS3 and A, high Co extraction occurred in stages 3 (HCl), 4 (HF), and 5 (HNO_3). Hence, some Co could occur with the carbonate minerals, clays, and pyrite. For sample B, 25% extraction occurred in the extraction process by H_2O. Possible contamination could have led to high observations of Co being extracted by H_2O.

According to Finkelman (1995), Cr has either an organic or clay association. It is expected that a high extraction of Cr would occur in stage 4 or some Cr would remain associated with organic matter in the residue. High levels of extraction of Cr occurred in stages 3, 4, and 5, with over 15% of Cr extraction occurring in stage 4 for all coal samples. In HS1 and HS2 no kaolinite (Table 4.15.b) was identified in the residue, hence Cr may have both clay and organic associations in these samples as some Cr still remained in the residue. Sample HS3 residue contains kaolinite which could still host Cr. The SA samples A and B had very low percentages of Cr in the residue, since most of the Cr was extracted by HF; Cr may be associated with clays in these SA coal samples.

It is expected that Cu could be removed by HNO_3 since Cu is associated with chalcopyrite (Finkelman, 1994). The extraction of Cu by HNO_3 was highest compared to extraction by the other chemicals. As some pyrite remained in the residues of all samples (Table 4.15.b), Cu could be associated with pyrite.

Although Hg was detected in the residues, HF and HNO_3 removed high percentages of Hg in all coal samples. Mercury may be associated with clays, pyrites and organic matter for these samples. In HS1, 9.3% extraction was observed in stage 3 (HCl), the highest of all chemicals hence suggesting a possible association of Hg with carbonates.

Manganese is associated with ankerite (Finkelman, 1994). Ankerite specifically was not identified in these coal samples by XRD; ankerite is a type of carbonate,

and carbonate minerals were determined by petrographic analysis of ROM samples (Table 4.1.c) in all samples except HS3. Dolomite and calcite are types of carbonates which were determined by XRD. Extraction of Mn using HCl (stage 3) was over 35% in samples HS1, HS2 and A giving an indication that Mn in these samples could be associated with carbonates. Less than 25% of Mn remained in the residue for all samples (Table 4.15.a). No petrographic analysis was done on the sequential leaching residues due to minimal samples remaining after sequential extraction. A greater percentage of Mn (28.97%) was removed by HF in HS3, hence suggesting a possible association of Mn with silicates in this sample. The analysis of coal B could not give comprehensive results possible due to mass accumulation of Mn or contamination during ICP-MS analysis

A probable association of Mo with sulphides was suggested by Finkelman (1995). Over 2% Mo extractions in samples HS1, HS2, HS3, and B were observed in stages 3, 4 and 5. The highest extraction of Mo in samples HS1, HS2, HS3, and B were observed in stage 4 (HF, Table 4.15.a); fairly high quantities of Mo were also extracted in stage 5; for a sulphide association, it is expected that major extraction would occur in stage 5. Molybdenum could be associated with silicates and sulphides in coal samples HS1, HS2 and B. It is difficult to make a sensible conclusion for sample HS3 as the mass balance is slightly higher than 100%; it is possible that some mass accumulation could have occurred in the residue which seems to have about 78.85% of Mo still present in the residue after 48.46% extraction from leaching.

According to Finkelman (1995), the association of Ni in coal is unclear. From sequential leaching results of all coal samples, most of the Ni still remained in the residue which unfortunately still contained mineral matter as well. It is difficult to make a sensible conclusion pertaining the association of Ni with any component in these coal samples, as the results show both high extraction of Ni by the chemicals used and still high proportion of Ni still remaining in the residue.

Vanadium may be associated with clays or the organic matter in coal (Finkelman, 1995). Very high proportions of V were removed by HF in coal samples HS2, HS3, A, and B (Table 4.15.a), hence suggesting a possible association of V with clays in these samples. Some V still remained in the residues (Figure 4.15.a) as well as kaolinite (Figure 4.15.b) in samples HS3, A and B. Some V could still remain in the kaolinite in the residue.

Some TEs and minerals remained in the residue possible due to low volumes of lixiviant (Riley et al., 2012). In future the volume of acids used could be comparable to those used by Riley et al. (2012) to increase the extraction of TEs and minerals.

Chapter 5

Conclusions and Recommendations

This is the concluding chapter of the dissertation, and will provide a summary of the work conducted, as well as the conclusions regarding the TE levels determined in these coal samples, with inference to the possible mode of occurrence of selected TE's. Three coal samples from Hwange coalfield, Zimbabwe, were compared to 2 South African coal samples.

The project aim and objectives have been fulfilled by determining TEs in ROM, density fractionated, and leached products for all 5 samples. Two Hwange, Zimbabwe coals were density fractionated along with the other 2 SA coals. All selected sampled were sequentially leached. ROM TE values were compared with average global and mean SA values. To infer modes of occurrence, two preparation techniques, density fractionation and sequential leaching were used and compared.

5.1 Conclusions

1. Proximate analysis of ROM samples show higher fixed carbon and lower ash content in the select Zimbabwean coals compared to the selected SA coals. The total %S in all selected coal samples is less than 3%. Petrographic analysis show that Zimbabwean coal ROM samples HS1, HS2, and HS3, and SA coal sample B are inertinite-rich coals compared to the SA coal sample A, which has high vitrinite content. Coal A has the highest ash content (55.80%) of all selected coal samples analysed in this project. XRD analysis show that coal A has the highest percentage of kaolinite (34.14%) and lowest graphite (39.50%) content compared to all selected coal samples in this project. Kaolinite is the highest dominant mineral in all the ROM samples followed by quartz except in sample HS1 and HS3. The coal ROM samples HS1 and B have the highest values of pyrite as well as sulphur content.

2. Trace element distribution between the ROM samples from both localities show some variations. Broadly speaking, TEs in the selected Zimbabwean

ROM samples appear consistent with published SA data, including higher Cr values and low As values, when compared to average global averages. Many of the TEs, especially in the selected SA coal samples, are above the global and mean SA values, including Co, Cr, Cu, Mo, Ni, Pb, and V. In comparison to the Waterberg coal samples analysed by Wagner and Tlotleng (2012), the TE values of Co, Cr, Ni, Pb, and V in the selected SA coals are high. The values of Hg (except in sample HS1) and Mn in all the coal samples analysed during the current project are above the global and SA average values. However, the selected SA coal samples analysed in this project showed lower Hg content compared Waterberg coals analysed in Wagner and Tlotleng (2012).

3. The values for Cd, Sb, and Se are within the global and SA mean averages. Coal A seems to show the highest values of Cu, Cd, Mn, Pb, and V, hence showing a great relationship of TEs with mineral matter as coal A has the highest ash content (from proximate analysis). At highly critical levels (for example 2 µg m^{-3} is the limit of exposure for an eight-hour time-weighted average for Be), these TEs are toxic to biological systems or have adverse environmental effects.

4. Petrographic analysis of float and sink fractions show a high concentration of inertinite in the float fractions of the inertinite-rich coals samples HS2, HS3 and B; whilst coal A shows a high vitrinite concentration in the float fractions, as expected. The %S and ash content increase with increasing densities. The XRD data of the density fractionated samples show an increase of minerals like pyrite, kaolinite and quartz with increasing densities.

5. An understanding of the mode of occurrence of TEs is important as it helps identify possible measures to utilise for prevention of environmental release of TEs during coal preparation and utilisation. Based on density fractionation, TEs seem to concentrate in higher densities in the Zimbabwean coal samples, hence showing that most TEs are inorganically bound. The washability curves of As and Pb for HS2, HS3, and coal

samples A and B show increasing concentrations with increasing yield. The washability curves of samples HS2, HS3, and coal B seem to show that the concentration of most TEs increase with increasing yield, especially for B, Be, Cd, Co, Cr, Cu, Mn, Mo and Ni. Coal A, perhaps because of its high ash content, shows some variations of modes of occurrence from those suggested in literature for some elements. In this coal sample, the least amount of pyrite was present (compared to the other 4 samples); according to literature, pyrite is believed to host most of the TEs (which include elements like As, B, Be, Cd, Cu, Hg, Mn, Mo, Ni, Pb, Se, U and V).

The correlation coefficients ($r \approx 1$) for coal samples HS2, HS3 and B show that As is associated with pyrite whilst $r = 0.0608$ for sample A is too low to suggest an association of As with pyrite. From the strong correlation coefficients of Hg and pyrite it may be concluded that Hg is associated with pyrite in Zimbabwean sample HS2 and HS3. In SA coals A and B, Hg could be associated with pyrite as well as other matter in coal.

Trace elements like Be and B, which are associated with organic matter according to Finkelman (1994), show no correlation with macerals in Zimbabwean coal samples HS2 and HS3. Boron and Be seem to show high association with mineral matter, especially in coal samples HS2, HS3, and A hence it may be concluded that these TEs may occur in association with mineral matter in these samples. From the correlation coefficients, South African coal sample B shows that B and Be may be associated with organic matter.

From the strong positive correlation coefficients of Cd, Co, Cu, and Se with pyrite in the Zimbabwean coal samples it can be concluded that these TEs occur in pyrite in samples HS2 and HS3. Correlation coefficients with sulphur show that Pb could be associated with other matter in samples HS2, HS3 and A besides sulphur. The correlation coefficient, $r = 0.945$ for Pb:S for sample B shows that Pb is highly associated with sulphur and sample B has the highest sulphur content of all samples (2.48%). The

correlation coefficients of V with kaolinite and muscovite suggest that in samples HS2, HS3, A and B, V may be associated with clays. It can be concluded that most of the TEs in Zimbabwean coals HS2 and HS3 are hosted by pyrite whilst in SA coals they may also occur in association with clays and other matter in coal.

6. Density fractionation seemed to give more comprehensible results compared to sequential leaching. Sequential leaching, due to the number of chemicals and handling techniques used, introduces higher levels of contamination compared to density fractionation. Interference of acids when taking the readings from the ICP-MS may make it impossible to obtain readings, especially with Be (Archuleta and Duran, 2009). Based on the results obtained, a major challenge appears to be the complete leaching of all minerals in each stage, to obtain a carbon residue. According to the results received, over 50% of some TEs remained in the residue after sequential leaching. The volume of acids used should have been comparable to those used by Riley et al. (2012). A high percentage of kaolinite, pyrite, and quartz remained in samples HS3, A and B after sequential leaching; in these samples over 7% of mineral matter remained in the residue after sequential leaching, whilst in coal samples HS1 and HS2 less than 2% of mineral matter remained in the residue. Some TEs may be present in the minerals remaining in the residue. A high proportion of pyrite remained in the residue which is a great host of TEs according to literature. Some kaolinite and quartz still remained in samples HS3, A and B these could still have been a host of some TEs.

7. During this research, a number of analytical techniques were investigated for TE determination. Generally TE values were determined by ICP-MS and ICP-OES (carried out by UIS), as these instruments are more sensitive to low level detection. The ICP-AES method used in the School of Chemistry was not as effective in determining TEs compared to ICP-MS, as most of the TEs were below the detection limit, as shown in Appendix F. Since Hg occurs in very low concentrations (ppb), the FI-MH-AAS

from the School of Chemistry was used for analysis. This technique proved to be an efficient and reliable method to analyse Hg compared to ICP-MS.

8. With most of the TEs reporting to the sink fractions, coal beneficiation may be an option to remove the TEs prior to coal utilisation. Proper disposal practices have to be factored in to make sure that the TEs do not leach to underground sources.

9. According to Goodarzi (1995), TEs in coal are greatly influenced by the geological settings, hydrological conditions and tectonic settings. Hence, different depositional environments may be the cause of variances in the modes of occurrence of TEs in both coalfields assessed in this investigation, namely the Hwange coalfield, and a coalfield in neighbouring SA. A detailed discussion regarding the influence of TE distribution during the formation of the coalfields is beyond the scope of this investigation, but could be a recommendation for future work.

5.2 Recommendations

In this project, indirect methods were employed to infer the modes of occurrence of TEs as these are cheaper and more readily available options. Direct methods could be applied, such as XAFS and the SEM-EDX to improve the reliability of results. XAFS was not available for this project. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) could also be explored for more accurate modes of occurrence determination; LA-ICP-MS can be applied directly to analyse the TEs in coal using polished sections.

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Appendices

Appendix A TGA profile

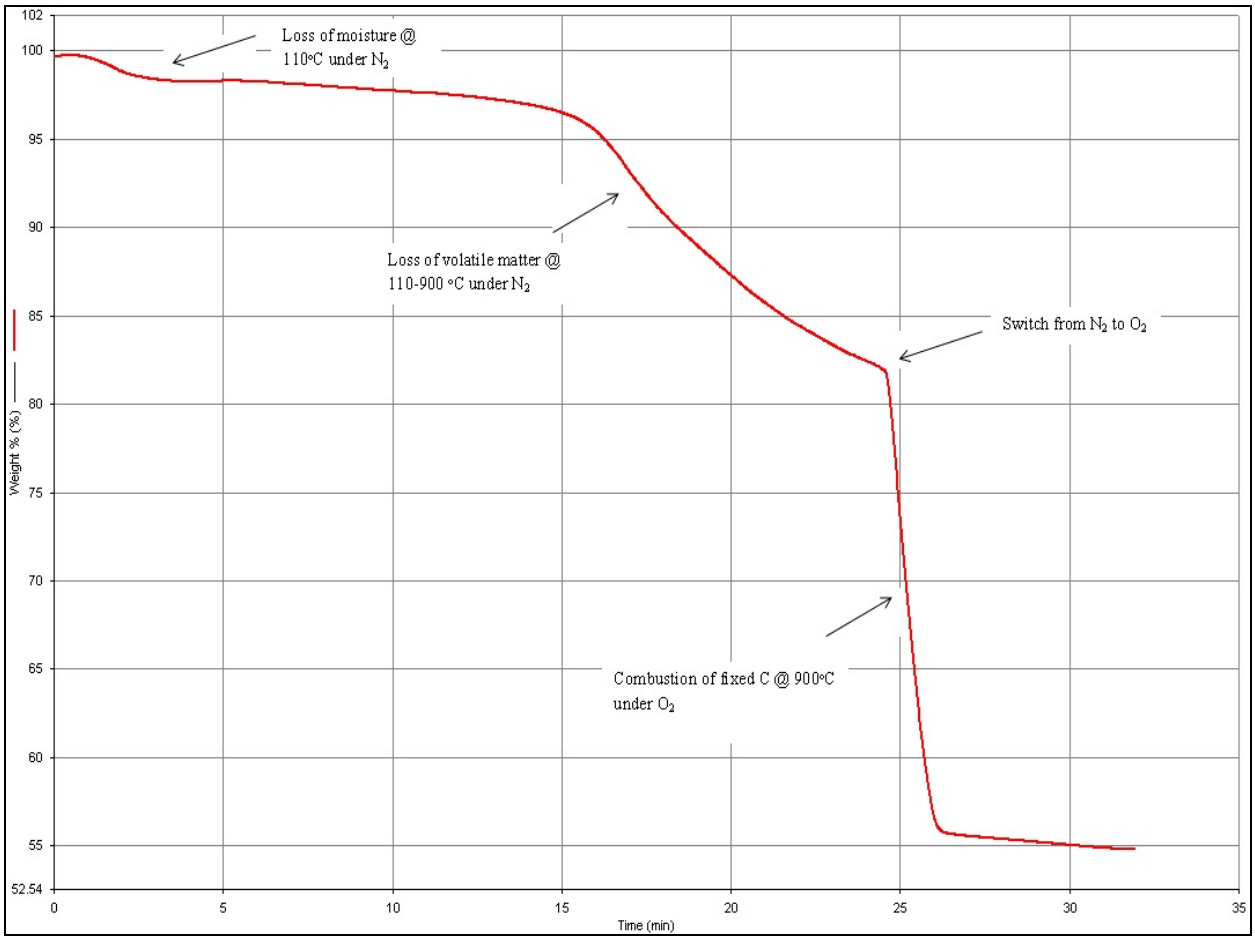

Figure Appendix A: Typical TGA graph obtained from the TGA machine

The remaining residue after the coal sample has undergone moisture loss, volatile matter loss and fixed carbon loss through all the TGA conditions is the ash.

Appendix B Leco CRM standards

Analytical Reference Materials International

Provisional Certificate of Analysis
Certified Reference Material

Grade: 0.25% Sulfur in Coal (Dry Basis Analysis)

Part Number: IARM HC-20025B, LECO No. 502-383

Certification Date: June 10, 2005 **Certificate No.: HC20025B-6102005-IARM-P** **Revision Date: June 10, 2005**

Interpretation of Data

1. Certified values listed below reflect analysis results submitted by qualified analytical laboratories using a combination of methods and instrumentation that emulate actual methods and instrumental techniques currently utilized in the analytical community.
2. The **"± Confidence Interval at 95%"** is enclosed by a **parentheses ( ) below the individual element's concentration.**
3. The "Inter-laboratory Analysis Program" (ILAP) utilized in the establishment of the data are an ongoing program with permanent membership. Certain elements may be selected by a consensus of the members for more extensive testing. Therefore the data in **brackets [ ] indicates further testing is in process.**
4. Any elemental data reported and enclosed by a **parentheses ( ) is a "best estimate" and is NOT CERTIFIED.** This data could not be quantified sufficiently for certification. It was however, reported by enough laboratories to be considered as potentially present in the matrix of the material being examined.

IMPORTANT: **A "USER REGISTRATION CARD" ACCOMPANIES ALL SHIPMENTS. THIS CARD SHOULD BE COMPLETED IMMEDIATELY UPON RECEIPT OF MATERIALS WITH THE APPROPRIATE USER INFORMATION. THIS IS THE ONLY WAY IN WHICH ARMI CAN GUARANTEE CUSTOMER UPDATES ON POSSIBLE DATA MODIFICATIONS!**

Mass/Mass %
Sulfur
0.28
(0.01)

The laboratories participating in the "Inter-Laboratory Analysis Program" (ILAP) and certification of this material are as follows:

Advanced Analytical Laboratories - Tyler, TX
Aquila Networks/Lake Road Gen. Sta. – St. Joseph, MO
G & C Laboratories - Somerville, PA
G & C Southern Division - Waynesburg, PA
LECO Corporation - St. Joseph, MI
Mineral Labs, Inc. - Salyersville, KY
SGS Minerals Services - Denver, CO
SGS Minerals Services - Gillette, WY
SGS Minerals Services - So. Holland, IL
Standard Laboratories/Gould Energy Div. - Casper, WY
Standard Laboratories/Gould Energy Div. - Cresson, PA
Standard Laboratories/Gould Energy Div. - Evansville, IN
Standard Laboratories/Gould Energy Div. - Salina, UT
Standard Laboratories/Gould Energy Div. - So. Charleston, WV
Wyoming Analytical Laboratories, Inc. - Laramie, WY

Traceability: Several members of the "Inter-Laboratory Analysis Program" (ILAP) listed above validate test methods and instrument performance utilizing SRMs produced by the National Institute of Standards and Technology (NIST), as well as other CRMs and RMs produced by recognized Certifying Bodies from around the world. The specific SRMs, CRMs and RMs applicable to the material covered by this certificate are: SRM - NIST 1632c, 1635, 2684b, 2776, 2683b, 2685b, CRM ARMI HP-20075A, RM – LQCRM027, ICRM 2004-4, MS249mvb, LECO 502-092, 501-0151, Benzoic Acid, MLI 205-05, VS6-066 and RC #1955-16.

A line of traceability is established to NIST and other Certifying Bodies for those elements that are noted as "Certified Values" on the Certificates of Analyses referenced above.

See Reverse Side for Statistical Data and Additional Information Regarding this Material.

700 Corporate Circle, Suite A • Golden, Colorado 80401-5636 • Telephone 303.216.2621 • FAX 303.216.2649

The following data and accompanying statements represent all pertinent information reported in the ILAP as it applies to th chemical and physical characterization of this material as of June 10, 2005.

HC-20075B	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15			MEAN	STDV.	CERTIFIED	95% C.I.
% S	0.32	0.28	0.30	0.30	0.251	0.276	0.28	0.27	0.246	0.27	0.283	0.288	0.274	0.26	0.2698			0.28	0.02	0.28	0.01

* Outlier Data – Not used in the calculation of the certified value or confidence interval.

The International Standards Organization (ISO) definitions, expressed in ISO Guide 30–1981-(E) list the following:

Certifying Body: A technically competent body (organization or firm, public or private) that issues a Reference Material Certificate. The only generally accepte certifying body in the United States for primary standards - Standard Reference Materials (SRM) is the U. S. Department of Commerce, National Institute of Standard & Technology, (NIST), Gaithersburg, MD. All other certifying bodies in the United States produce Reference Materials (RM) or Certified Reference Material (CRM).

Reference Material (RM): A material or substance with one or more properties which are sufficiently well established to be used for calibration of an apparatus, th assessment of a measurement method, or for assigning values to materials.

Certified Reference Material (CRM): A reference material with one or more properties whose values are certified by a technically valid procedure accompanied b or traceable to a certificate or other documentation that is issued by a Certifying Body.

Inter-Laboratory Analysis Program (ILAP): Although ASTM Standard E691-92 applies to inter-laboratory studies to "Determine the Precision of a Single Tes Method", it is also a well thought out and logical plan for conducting an inter-laboratory program involving multiple techniques. Therefore, the planning, conducting analyzing, protocol and treatment of data resulting from this inter-laboratory program were performed utilizing the guidelines established in ASTM E691-92.

Methods of Analysis: The methods utilized were a combination of ASTM Standard Methods D4239, D4239c and D2492. This CRM was prepared using ASTM Standard Method D3173-03 for the purpose of drying of coal.

Selection of Materials: A "Lot" is defined as a single quantity of hydrocarbon material, blended and tested as a single batch. No less than eight percent of the lot is sent for ILAP analysis by the above-referred ASTM Methods. This sampling procedure results in the overall statistics and certified data. The material used to manufacture this product was coal obtained from a Wyoming coal producing area.

Expiration Date: This refers to the date at which time this CRM will no longer be valid, provided this CRM is used and handled in accordance with proper laboratory procedures prescribed by ASTM and generally accepted Industry protocol. The expiration date appears on the label of each bottle.

Analysis Validity: The value shown for this CRM remains valid only if standard laboratory practices are observed and maintained during handling and storage of the material. Specifically, when in use the bottle should remain open for only the time needed to transfer the desired quantity required for testing. Also, this material should not be exposed to direct sunlight and remain in a controlled environment where possible. During non-use it should be stored under refrigeration.

Certified by: William D. Britt

William D. Britt, President & General Manager
Analytical Reference Materials International Corporation

Certificate No.: HC-20075B-IARM
Certification Date: June 10, 2005
Revision Date: June 10, 2005

Reference Material
Certificate of Analysis and Traceability

LECO Reference Materials are traceable to national or international standard reference materials whenever possible. When these reference materials do not exist or are inadequate for calibration purposes, other appropriate materials are used. The accuracy of the reported results for LECO Reference Materials is greatly influenced by the accuracy of the primary reference materials used. Sulfur results are reported on a dry basis and were determined by round robin exchange.

Part No: 502-435

Lot No: 21100D

Description: Coal Reference Material

Category	Reference Value	+/-	Participating Laboratories
% Sulfur	**0.95**	**0.04**	**4**

Date: June 2, 2008

Approved by: Dennis Lawrenz
Technical Services Laboratory Director

- *Expiration: This coal reference material is valid within the stated deviation until **June 2, 2018** provided the RM is stored in its original bottle at room temperature. This coal reference material is nullified if it is contaminated or otherwise altered.*
- *+/- indicates two times the standard deviation.*
- *Refer to the reverse side of certificate for additional information regarding calculations.*
- *No warranties of description, merchantability, or fitness for a particular purpose or any other express or implied warranties arise out of LECO's sale of this product. Remedies for any claimed defect in this product will be limited to replacement of the product or refund of the purchase price. In no event shall LECO be liable for incidental or consequential damages.*

LECO Corporation • Technical Services Laboratory • 3000 Lakeview Avenue • St. Joseph, MI 49085-2396 U.S.A.
Phone: 269-985-5496 • Fax: 269-982-8977 • info@leco.com • www.leco.com *LECO is a registered trademark of LECO Corporation.*

Sulfur results are reported on a dry basis. Average moisture at the time of certification was 1.25%. Since the moisture value can change over time, the sample should be dried @ 105° Celsius for one hour prior to analysis or moisture should be determined within 24 hours of the analysis for an accurate moisture correction. Please refer to the table below for additional details regarding the calculations.

	Laboratory Averages								
	1	2	3	4	Mean	Std. Dev. of Avg.	Reference Value	No. of Labs	95% CI
% Sulfur	**0.97**	**0.92**	**0.95**	**0.97**	**0.952**	**0.021**	**0.95**	**4**	**0.010**

Reference Material: NIST SRM 2692b @ 1.170% Sulfur

Method: ASTM D-4239

The following laboratories participated in the analysis of this material:

Consol Energy Inc. – South Park, PA
Hawk Mountain Labs Inc. – West Hazleton, PA
Leco Corporation – St. Joseph, MI
MVTL – Bismarck, ND

LECO Corporation • Technical Services Laboratory • 3000 Lakeview Avenue • St. Joseph, MI 49085-2396 U.S.A.
Phone: 269-985-5496 • Fax: 269-982-8977 • info@leco.com • www.leco.com *LECO is a registered trademark of LECO Corporation.*
Form No. 203-505-341

Analytical Reference Materials International

Certificate of Analysis

Certified Reference Material

Grade: 1% Sulfur in Coal (Dry Basis Analysis)

Part Number: **IARM HC-20100B**

Certificate Date: **10/09/2006** Certificate No.: **HC20100B-01009006-IARM-F** Revision Date: **07/16/2007**

Interpretation of Data

1. Certified values listed below reflect analysis results submitted by qualified analytical laboratories using a combination of methods and instrumentation that emulate actual methods and instrumental techniques currently utilized in the analytical community and are reported as % wt. unless otherwise noted.
2. The **"±Estimated Uncertainty"** is enclosed by a **parentheses ( ) below** the individual **element's concentration** and is based on a Confidence Interval at 95%. Included in this estimated uncertainty, are the combined effects of method imprecision, material inhomogeneity, and any bias between methods.
3. The "Inter-laboratory Analysis Program" (ILAP) utilized in the establishment of the data are an ongoing program with permanent membership. Certain elements may be selected by a consensus of the members for more extensive testing. Therefore the data in **brackets [ ] indicates further testing is in process.**
4. Any elemental data reported and enclosed by a **parentheses ( ) is a "best estimate" and is NOT CERTIFIED.** This data could not be quantified sufficiently for certification. It was however, reported by enough laboratories to be considered as potentially present in the matrix of the material being examined.

Important: A "User Registration Card" accompanies all shipments. This card should be completed immediately upon receipt of materials with the appropriate user information. This is the only way in which ARMI can guarantee customer updates or possible data modifications!

Sulfur
1.00
(0.03)

The laboratories participating in the "Inter-Laboratory Analysis Program" (ILAP) and certification of this material are as follows:

Consol Energy, Inc. – Library, PA
Kentucky Geological Survey / Univ. Kentucky – Lexington, KY
LECO Corporation - St. Joseph, MI
OKI Laboratory – Cincinnati, OH
SGS Minerals Services - Denver, CO
SGS Minerals Services - Gillette, WY
SGS Minerals Surveys – Huntington, UT
Standard Laboratories/Gould Energy Div. - Casper, WY
United States Geological Survey – Denver, CO
Wyoming Analytical Laboratories, Inc. - Laramie, WY

Traceability: Several members of the "Inter-Laboratory Analysis Program" (ILAP) listed above validate test methods and instrument performance utilizing SRMs produced by the National Institute of Standards and Technology (NIST), as well as other CRMs and RMs produced by recognized Certifying Bodies from around the world. The specific SRMs, CRMs, and RMs applicable to the material covered by this certificate are: **NIST 1632c, 1635, 1633b, 2684b, 2692b, 2683b, ARMI HC-30300B, RM – CANSPEC 2006-1 along with EDTA, Phenylalanie and, Benzoic Acid.**

A specific line of traceability is established to NIST and other Certifying Bodies for those elements that are noted as "Certified Values" on the Certificates of Analyses referenced above.

See Reverse Side for Statistical Data and Additional Information Regarding this Material.

700 Corporate Circle, Suite A • Golden, Colorado 80401-5636 • Telephone (303) 216-2621 • FAX (303) 216-2649

The following data and accompanying statements represent all pertinent information reported in the ILAP as it applies to the chemical and physical characterization of this material as of 07/16/2007.

HC-20100B	1	2	3	4	5	6	7	8	9	10		Mean	STDV.	Certified	95% C.I.
%S	1.01	0.9769	0.9342	0.97	0.997	1.02	1.056	0.956	0.982	1.065		0.9967	0.0419	1.00	0.03

The International Standards Organization (ISO) definitions, expressed in ISO Guide 30–1981-(E) list the following:

Certifying Body: A technically competent body (organization or firm, public or private) that issues a Reference Material Certificate. The only generally accepted certifying body in the United States for primary standards - Standard Reference Materials (SRM) is the U. S. Department of Commerce, National Institute of Standards & Technology, (NIST), Gaithersburg, MD. All other certifying bodies in the United States produce Reference Materials (RM) or Certified Reference Materials (CRM).

Reference Material (RM): A material or substance with one or more properties which are sufficiently well established to be used for calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

Certified Reference Material (CRM): A reference material with one or more properties whose values are certified by a technically valid procedure accompanied by or traceable to a certificate or other documentation that is issued by a Certifying Body.

Inter-Laboratory Analysis Program (ILAP): Although ASTM Standard E691-92 applies to inter-laboratory studies to "Determine the Precision of a Single Test Method", it is also a well thought out and logical plan for conducting an inter-laboratory program involving multiple techniques. Therefore, the planning, conducting, analyzing, protocol, and treatment of data resulting from this inter-laboratory program were performed utilizing the guidelines established in ASTM E691-92.

Methods of Analysis: The methods utilized were a combination of ASTM Methods D4239, D4239c, D5016, D5142, D3174, D3173, D3176, D3175, D5682, D5865, D2015, D1989, and D3286.

Selection of Materials: A **"Lot"** is defined as a single quantity of hydrocarbon material, blended, and tested as a single batch. No less than eight percent of the lot is sent for ILAP analysis by the above-referred ASTM Methods. This sampling procedure results in the overall statistics and certified data. The material used to manufacture this product was coal obtained from an Eastern Kentucky coal producing area.

Expiration Date: This refers to the date at which time this CRM will no longer be valid, provided this CRM is used and handled in accordance with proper laboratory procedures prescribed by ASTM and generally accepted Industry protocol. The expiration date appears on the label of each bottle.

Analysis Validity: The value shown for this CRM remains valid only if standard laboratory practices are observed and maintained during handling and storage of the material. Specifically, when in use the bottle should remain open for only the time needed to transfer the desired quantity required for testing. Also, this material should not be exposed to direct sunlight and remain in a controlled environment where possible. During non-use it should be tightly capped and stored in a controlled environment.

Certified by: William D Britt

William D. Britt, President & General Manager
Analytical Reference Materials International Corporation

Certificate No.: **HC20100C-10092006-IARM-F**
Certificate Date: **10/09/2006**
Revision Date: **07/16/2007**

Analytical Reference Materials International

Certificate of Analysis

Certified Reference Material

Grade: 5% Sulfur in Coal (Dry Basis Analysis)

Part Number: **IARM HC20500B**

Certificate Date: **08/10/2005** Certificate No.: **HC20500B-08102005-IARM-F** Revision Date: **08/21/2007**

Interpretation of Data

1. Certified values listed below reflect analysis results submitted by qualified analytical laboratories using a combination of methods and instrumentation that emulate actual methods and instrumental techniques currently utilized in the analytical community and are reported as % wt. unless otherwise noted.
2. The **"±Estimated Uncertainty"** is enclosed by a **parentheses ( ) below** the individual **element's concentration** and is based on a Confidence Interval at 95%. Included in this estimated uncertainty, are the combined effects of method imprecision, material inhomogeneity, and any bias between methods.
3. The "Inter-laboratory Analysis Program" (ILAP) utilized in the establishment of the data are an ongoing program with permanent membership. Certain elements may be selected by a consensus of the members for more extensive testing. Therefore the data in **brackets [ ] indicates further testing is in process.**
4. Any elemental data reported and enclosed by a **parentheses ( ) is a "best estimate" and is NOT CERTIFIED.** This data could not be quantified sufficiently for certification. It was however, reported by enough laboratories to be considered as potentially present in the matrix of the material being examined.

Important: A "User Registration Card" accompanies all shipments. This card should be completed immediately upon receipt of materials with the appropriate user information. This is the only way in which ARMI can guarantee customer updates or possible data modifications!

Sulfur
5.4
(0.1)

The laboratories participating in the "Inter-Laboratory Analysis Program" (ILAP) and certification of this material are as follows:

Advanced Analytical Labs - Tyler, TX
G & C Coal Analytical Lab
LECO Corporation - St. Joseph, MI
SGS Minerals Services - Denver, CO
SGS Minerals Services - So. Holland, IL
Std Labs / Gould Energy Div. - Cresson, PA
Std Labs / Gould Energy Div. - Salina, UT
Wyoming Analytical - Laramie, WY
Aquila Networks/Lake Road Gen-Station
G & C Southern Division
Mineral Labs Inc - Salyersville, KY
SGS Minerals Services - Gillette, WY
Std Labs / Gould Energy Div. - Casper, WY
Std Labs / Gould Energy Div. - Evansville,IN
Std Labs / Gould Energy Div. - So. Charleston,WV

Traceability: Several members of the "Inter-Laboratory Analysis Program" (ILAP) listed above validate test methods and instrument performance utilizing SRMs produced by the National Institute of Standards and Technology (NIST), as well as other CRMs and RMs produced by recognized Certifying Bodies from around the world. The specific SRMs, CRMs, and RMs applicable to the material covered by this certificate are: **NIST 1632c, 2682b, 1632c, 1635, 2684b, Benzoic Acid, NIST 2776, 2683b, 2685b, LQCRM027, Benzoic Acid, NIST 1632c, Benzoic Acid, NIST 2682b, 1632c, Benzoic Acid, ARMI HC20075A, NIST 1632c, 2685b, MLI 205-05, Vanguard VS6-066, LECO #501-015, ICRE 2004-4, MS-249mvb, (EDTA)#502009, Ricca Chem. Co. CAT# 1955-16, NIST 2682b, 1632c, 2684b, 2685b, Benzoic Acid, QA 1104, A20500, AR2782, 1191/1,1191/14, NIST 1632c, 2682b, 2685b, SLRR #0205/1, ARMI HC20025, SLRR #0205-1, AR1702**

A line of traceability is established to NIST and other Certifying Bodies for those elements that are noted as "Certified Values" on the Certificates of Analyses referenced above.

See Reverse Side for Statistical Data and Additional Information Regarding this Material.

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The following data and accompanying statements represent all pertinent information reported in the ILAP as it applies to the chemical and physical characterization of this material as of: 08/21/2007.

HC-20500B	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15		Mean	STDV.	Certified	95% C.I.
% S	5.50	5.59	5.12	5.153	5.402	5.42	5.46	5.46	5.48	5.388	5.64	5.614	5.905	4.99	5.33		5.4301	0.2264	5.4	0.1

The International Standards Organization (ISO) definitions, expressed in ISO Guide 30–1981-(E) list the following:

Certifying Body: A technically competent body (organization or firm, public or private) that issues a Reference Material Certificate. The only generally accepted certifying body in the United States for primary standards - Standard Reference Materials (SRM) is the U. S. Department of Commerce, National Institute of Standards & Technology, (NIST), Gaithersburg, MD. All other certifying bodies in the United States produce Reference Materials (RM) or Certified Reference Materials (CRM).

Reference Material (RM): A material or substance with one or more properties which are sufficiently well established to be used for calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

Certified Reference Material (CRM): A reference material with one or more properties whose values are certified by a technically valid procedure accompanied by or traceable to a certificate or other documentation that is issued by a Certifying Body.

Inter-Laboratory Analysis Program (ILAP): Although ASTM Standard E691-92 applies to inter-laboratory studies to "Determine the Precision of a Single Test Method", it is also a well thought out and logical plan for conducting an inter-laboratory program involving multiple techniques. Therefore, the planning, conducting, analyzing, protocol, and treatment of data resulting from this inter-laboratory program were performed utilizing the guidelines established in ASTM E691-92.

Methods of Analysis: The methods utilized were a combination of ASTM Methods D4239, D4239c, D5016, D5142, D3174, D3173, D3176, D3175, D5682, D5865, D2015, D1989, and D3286.

Selection of Materials: A **"Lot"** is defined as a single quantity of hydrocarbon material, blended, and tested as a single batch. No less than eight percent of the lot is sent for ILAP analysis by the above-referred ASTM Methods. This sampling procedure results in the overall statistics and certified data. The material used to manufacture this product was coal obtained from an eastern Kentucky coal producing area.

Expiration Date: This refers to the date at which time this CRM will no longer be valid, provided this CRM is used and handled in accordance with proper laboratory procedures prescribed by ASTM and generally accepted Industry protocol. The expiration date appears on the label of each bottle.

Analysis Validity: The value shown for this CRM remains valid only if standard laboratory practices are observed and maintained during handling and storage of the material. Specifically, when in use the bottle should remain open for only the time needed to transfer the desired quantity required for testing. Also, this material should not be exposed to direct sunlight and remain in a controlled environment where possible. During non-use it should be tightly capped and stored in a controlled environment.

Certified by: William D Britt

William D. Britt, President & General Manager
Analytical Reference Materials International Corporation

Certificate No.: **HC20500B-08102005-IARM-F**
Certificate Date: **08/10/2005**
Revision Date: **08/21/2007**

Appendix C Petrographic analysis results

MACERAL ANALYSIS (PERCENT BY VOLUME) & RANK DETERMINATION (%RoVmr)

CLIENT:	NG. Mguni, MSc student, Wits
PROJECT:	Trace elements in Zimbabawe coals
DATE:	15-Oct-12
JOB / SAMPLE NUMBERS:	**Job 1232**
ANALYST:	Prof NJ Wagner; Coal & Carbon Research Group, School of Chemical & Metallurgical Engineering, University of the Witwatersrand
ICCP ACCREDITATION:	ICCP/SCAP-056/AB (expires Dec 2012); ICCP/CBAP/056

THESE RESULTS RELATE ONLY TO THE SAMPLES ANALYSED

MACERAL ANALYSIS (ISO 7404 PART 3)

MACERAL GROUP	MACERAL SUB GROUP	SAMPLE NUMBER / ID								
		HS1 ROM	HS2 ROM	HS3 ROM	B5 ROM	B11 ROM				
		1232	**1233**	**1234**						
VITRINITE	VITRINITE (collotelinite)	32	24.2	11.6	11.8	9.5				
	PSEUDOVITRINITE	0	0	0	**0**	0.3				
	VITRODETRINITE	2.8	2.8	1.8	2.3	5				
	CORPOGELINITE	1.2	0	0.2	0	0				
	OTHER VITRINITE	1.6	0.4	0.4	0	0				
	% TOTAL VITRINITE	**37.6**	**27.4**	**14.0**	**14.1**	**14.8**	**0.0**	**0.0**	**0.0**	**0.0**
LIPTINITE	CUTINITE	0.8	0.4	0	6.3	1.5				
	SPORINITE	0.2	0	2	0	**0**				
	RESINITE	0	0.6	1.4	0	**0**				
	ALGINITE	0	0	0	0	**0.5**				
	LIPTODETRINITE	0	0	0	0	**0**				
	OTHER LIPTINITE	0	0	0	0	**0**				
	% TOTAL LIPTINITE	**1.0**	**1.0**	**3.4**	**6.3**	**2.0**	**0.0**	**0.0**	**0.0**	**0.0**
INERTINITE	R. SEMIFUSINITE	8.6	5.2	4	0.3	**3**				
	I. SEMIFUSINITE	18.8	28.4	40.2	8	33.3				
	FUSINITE	13.4	12.6	6.8	0.8	1.8				
	SECRETINITE	5.4	5	3.4	**2.5**	5				
	MACRINITE	3.4	2.2	4.2	0	0				
	MICRINITE	1	0.6	0.8	0	1.3				
	FUNGINITE	0	0	0	0	0				
	R.INERTODETRINITE	1.6	2.8	6.6	0	2.8				
	I.INERTODETRINITE	5.8	6.8	8.6	14.8	27.3				
	% TOTAL INERTINITE	**58.0**	**63.6**	**74.6**	**26.4**	**74.5**	**0.0**	**0.0**	**0.0**	**0.0**
% TOTAL REACTIVE MACERALS		**48.8**	**36.4**	**28.0**	**20.7**	**19.8**	**0.0**	**0.0**	**0.0**	**0.0**
MINERAL MATTER	CLAYS	0.2	1	0.2	**4.5**	**0.3**				
	QUARTZ	1	1.6	2.8	**46.5**	**4**				
	PYRITE	1.6	4.4	4.8	1.8	1.5				
	CARBONATES	0.6	1	0	1	3				
	OTHER	0	0	0.2	0	0.3				
% TOTAL MINERAL MATTER		**3.4**	**8.0**	**8.0**	**53.3**	**9.1**	**0.0**	**0.0**	**0.0**	**0.0**

TABLE 2: RANK DETERMINATION (ISO 7404 - 5, 1994)

		HS1	HS2	HS3	B5 ROM
		1232	**1233**	**1234**	
RoVmr%		**0.82**	**1.01**	**0.90**	0.73
Standard deviation		0.061	0.087	0.109	0.06
Range	**high**	0.98	1.28	1.22	0.70
	low	0.68	0.84	0.73	0.06
RANK CATEGORY		med vol bit C	med vol bit B	med vol bit C	med vol bit C
Heat affected	**y / n**	no	no	no	

KEY: MACERAL GROUP ANALYSIS

Total Reactives = Vitrinite + Liptinite + R.Semifusinite + R. inertodetrinite

Other vitrinite includes telinite, collodetrinite, gelinite

Other liptinite includes suberinite and exsudatinite

COMMENTS

MACERAL ANALYSIS (PERCENT BY VOLUME) & RANK DETERMINATION (%RoVmr)

CLIENT:	NG. Mguni, MSc student, Wits
PROJECT:	Trace elements in Zimbabawe coals
DATE:	30-Jul-13
JOB / SAMPLE NUMBERS:	**Job 1349**
ANALYST:	Prof NJ Wagner; Coal & Carbon Research Group, School of Chemical & Metallurgical Engineering, University of the Witwatersrand
ICCP ACCREDITATION:	ICCP/SCAP-056/AB; ICCP/CBAP/056

THESE RESULTS RELATE ONLY TO THE SAMPLES ANALYSED

MACERAL ANALYSIS (ISO 7404 PART 3)

MACERAL GROUP	MACERAL SUB GROUP	SAMPLE NUMBER / ID								
		1A	2B	5E	3C	4D	10J	11K		
		HS2 1.3 FLT	HS2 1.5 FLT	HS2 1.5 SINK	HS3 1.3 FLT	HS3 1.5 FLT	HS3 1.7FLT	HS3 1.7 SINK		
VITRINITE	VITRINITE (collotelinite)	24.5	32	16.3	22.2	20	7.1	9.3		
	PSEUDOVITRINITE	0	0.0	0.5	0	0	0.3	0		
	DETROVITRINITE	2.5	1.5	2.8	2.2	1	0.5	**1.3**		
	CORPOGELINITE	0	0	0	0.2	0.5	0.5	0		
	OTHER VITRINITE	0.3	0	0.5	0.2	0	0.8	0.3		
	% TOTAL VITRINITE	**27.3**	**33.5**	**20.1**	**24.8**	**21.5**	**9.2**	**10.9**	**0.0**	**0.0**
LIPTINITE	CUTINITE	0	**0**	0	0.5	1.5	0.5	0.3		
	SPORINITE	0	0	0	1	0.8	0.3	0.3		
	RESINITE	0.3	1.3	0	2.7	1	2.5	0		
	ALGINITE	0	0	0	0	0	0	0		
	LIPTODETRINITE	0	0	0	0	0	0	**0**		
	OTHER LIPTINITE	0	0	0	0	0	0	0		
	% TOTAL LIPTINITE	**0.3**	**1.3**	**0.0**	**4.2**	**3.3**	**3.3**	**0.6**	**0.0**	**0.0**
INERTINITE	R. SEMIFUSINITE	6	7.8	0.8	1.7	2.3	4.3	2		
	I. SEMIFUSINITE	27.3	**26.5**	16.3	40.1	39	36.5	20.5		
	FUSINITE	11.5	5.5	3.5	2	2.8	2.5	2.3		
	SECRETINITE	4.5	3.8	3	11	11.3	11.8	5		
	MACRINITE	1	0.3	0	0.2	0	0.8	0		
	MICRINITE	0.5	1.8	0	0.7	1.8	2	0.3		
	FUNGINITE	0	0	0.5	0	0	0	0.3		
	R.INERTODETRINITE	1.5	1	10	2.7	6.3	14.2	7.3		
	I.INERTODETRINITE	15	10	0	8.1	9.5	9.1	**20.8**		
	% TOTAL INERTINITE	**67.3**	**56.7**	**34.1**	**66.5**	**73.0**	**81.2**	**58.5**	**0.0**	**0.0**
% TOTAL REACTIVE MACERALS		**33.6**	**42.6**	**21.4**	**30.7**	**27.1**	**16.8**	**13.8**	**0.0**	**0.0**
MINERAL MATTER	CLAYS	2	0.3	4.8	0	0.3	0.8	**0.5**		
	QUARTZ	1.3	4	8.8	2	0.8	3.5	**6**		
	PYRITE	2.1	**4.5**	10.3	1.5	1	2.5	**22.8**		
	CARBONATES	0	**0**	22	0.5	0	0	**1**		
	OTHER	0	**0**	0	0.2	0.5	0.3	**0.3**		
	% TOTAL MINERAL MATTER	**5.4**	**8.8**	**45.9**	**4.2**	**2.6**	**7.1**	**30.6**	**0.0**	**0.0**

MACERAL ANALYSIS (PERCENT BY VOLUME) & RANK DETERMINATION (%RoVmr)

CLIENT:	NG. Mguni, MSc student, Wits		
PROJECT:	Trace elements in Zimbabawe coals		
DATE:	30-Jul-13	16-Jan-14	
JOB / SAMPLE NUMBERS:	**Job 1349**	**1401**	
ANALYST:	Prof NJ Wagner; Coal & Carbon Research Group, School of Chemical & Metallurgical Engineering, University of the Witwatersrand		
ICCP ACCREDITATION:	ICCP/SCAP-056/AB; ICCP/CBAP/056		

THESE RESULTS RELATE ONLY TO THE SAMPLES ANALYSED

MACERAL ANALYSIS (ISO 7404 PART 3)

MACERAL GROUP	MACERAL SUB GROUP	SAMPLE NUMBER / ID								
		6F	7G	8H	9I	12L	13M	14N	15O	
		B11 1.3 FLT	**B11 1.5 FLT**	**B11 1.7 FLT**	**B11 1.7 SINK**					
VITRINITE	VITRINITE (collotelinite)	**12**	8.8	7.3	5	**61.8**	54.8	23.1	10	
	PSEUDOVITRINITE	0.3	1.3	0.3	0	1.5	0.3	0	1.5	
	DETROVITRINITE	3.8	2.3	**3**	0.8	2.3	3	3.8	0.5	
	CORPOGELINITE	0.5	0	0	0	0.3	0	**0.3**	0	
	OTHER VITRINITE	0	**0**	0	0.3	0	**0**	0.3	**0**	
	% TOTAL VITRINITE	**16.6**	**12.4**	**10.6**	**6.1**	**65.9**	**58.1**	**27.5**	**12.0**	**0.0**
LIPTINITE	CUTINITE	4	1.5	0	0	4.8	5.3	6.6	9	
	SPORINITE	0	0	2	3.5	**0**	0	0	0	
	RESINITE	0.5	0	0	0	0	0	0	0	
	ALGINITE	**0**	0	0	0	0	0	0	0	
	LIPTODETRINITE	**0**	0	**0**	0	0.5	0	0	0	
	OTHER LIPTINITE	**0**	0	0	**0**	0	**0**	0	0	
	% TOTAL LIPTINITE	**4.5**	**1.5**	**2.0**	**3.5**	**4.8**	**5.3**	**6.6**	**9.0**	**0.0**
INERTINITE	R. SEMIFUSINITE	3.8	5	2.5	0.8	0.8	1.8	0.9	0	
	I. SEMIFUSINITE	29	39.3	31.8	22.5	5.8	15.5	22.2	8	
	FUSINITE	**1.8**	3.5	3.8	2.3	**3.3**	5.5	2.5	1.5	
	SECRETINITE	6.5	5.3	2.3	1.3	2	2.8	5.4	1.5	
	MACRINITE	1.3	0.5	0	0	0	0.5	0	0	
	MICRINITE	0.8	2.5	0.5	0.8	0	0	0	0	
	R.INERTODETRINITE	0	**0**	4.8	1.5	0.5	0.3	2.5	0.5	
	I.INERTODETRINITE	4.5	3.5	33	35	3.3	1.5	9.2	11	
	FUNGINITE	26	24.8	**0**	0	0	0	**0**	0	
	% TOTAL INERTINITE	**73.7**	**84.4**	**78.7**	**64.2**	**15.7**	**27.9**	**42.7**	**22.5**	**0.0**
% TOTAL REACTIVE MACERALS		**24.9**	**18.9**	**19.9**	**11.9**	**72.0**	**65.5**	**37.5**	**21.5**	**0.0**
MINERAL MATTER	CLAYS	**1.8**	1	3.5	3.3	9.5	5.5	9.8	30.5	
	QUARTZ	**1.8**	0	2.3	7.8	3	2.8	12.3	24.5	
	PYRITE	**1**	0.3	2.3	11.8	0	0.3	0	1	
	CARBONATES	**0.8**	0.8	0.8	2.8	0.8	0.3	0.9	0.5	
	OTHER	0.3	0	0.3	1	0.3	0.3	0	0	
	% TOTAL MINERAL MATTER	**5.7**	**2.1**	**9.2**	**26.7**	**13.6**	**9.2**	**23.0**	**56.5**	**0.0**

Appendix D UIS results on density fractionated samples and leach residues

To:	University Of Witwatersrand															Date of Request	17.07.2013								
Attention:	Nonhlanhla Mguni																								
ORDER REF:																									
Tel:	+27 11 717 7397																								
Cell:																									
																Certificate of analysis:	8047								
Lims ID	Sample ID	Note: all results in parts per million (ppm) unless specified otherwise																							
		Ag	As	Au	B	Ba	Be	Bi	Cd	Ce	Co	Cr	Cs	Cu	Ga	Ge	Hf	Hg	Ho	Ir	La	Li	Mn	Mo
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
8047 - 351701	08/07/2013/HS3/p1.7/float	0.016	4.73	2.78	25.1	82.0	2.04	0.868	0.219	7.03	3.18	32.4	8.37	11.5	4.85	2.85	2.44	0.071	0.067	0.015	2.41	53.0	32.0	1.06
8047 - 351702	08/07/2013/HS3/p1.7/sink	0.015	34.3	0.076	29.5	31.9	2.30	0.558	0.295	15.2	5.97	45.7	5.67	23.7	6.63	3.44	2.21	0.515	0.163	0.010	6.35	67.9	113.5	4.04
8047 - 351703	08/07/2013/B11/p1.3/float	0.012	2.31	0.026	14.7	39.0	1.91	0.410	0.586	9.35	7.59	66.8	0.366	28.4	5.15	1.380	1.79	0.067	0.207	0.003	4.71	9.4	44.1	1.82
8047 - 351704	08/07/2013/B11/p1.5/float	0.019	1.83	0.016	12.2	40.0	2.82	0.518	0.437	8.38	8.99	56.3	0.170	24.4	7.11	2.06	2.61	0.182	0.147	0.008	3.06	10.4	31.3	1.47
8047 - 351705	08/07/2013/B11/p1.7/float	0.016	2.04	0.023	12.3	38.3	3.28	0.602	0.668	10.5	8.70	65.9	0.103	26.7	7.80	1.563	2.78	0.178	0.179	0.008	3.75	14.6	59.2	2.17
8047 - 351706	08/07/2013/B11/p1.7/sink	0.018	6.72	0.030	11.9	345	2.64	0.820	2.64	19.5	10.49	104	0.459	57.2	7.87	1.405	2.71	0.31	0.399	0.005	13.2	16.0	161	4.57
8047 - 351707	08/07/2013/B5/p1.5/float	0.050	3.65	0.026	27.4	368	3.12	1.64	1.01	19.4	9.59	91.2	1.88	55.0	17.2	3.36	8.03	0.142	0.280	0.010	7.41	18.4	42.3	5.63
8047 - 351708	08/07/2013/B5/p1.7/float	0.049	2.81	0.024	27.7	385	3.16	1.57	0.742	15.0	8.16	72.9	1.35	31.6	17.2	3.45	8.30	0.125	0.182	0.010	5.10	16.6	38.4	4.37
8047 - 351709	08/07/2013/B5/p1.9/float	0.041	5.56	0.032	28.5	403	3.37	1.74	0.616	10.4	5.83	77.7	0.487	30.2	17.0	2.30	7.28	0.100	0.118	0.010	2.95	32.1	33.8	3.65
8047 - 351710	08/07/2013/B5/p1.9/sink	0.036	6.45	0.024	29.4	255	2.96	1.46	0.945	9.22	3.58	73.9	0.524	28.3	15.4	1.532	6.93	0.217	0.016	0.009	2.11	37.1	34.1	3.94
8047 - 351711	08/07/2013/B5/residue	0.054	6.42	0.036	54.5	557	2.73	0.995	0.894	39.4	5.58	67.9	4.17	24.4	9.23	2.22	9.51	0.367	0.422	0.011	21.2	9.1	26.1	4.33
8047 - 351712	08/07/2013/B11/residue	0.019	2.76	0.013	39.2	59.8	2.59	0.332	0.461	26.3	7.65	42.9	1.16	20.2	4.36	1.497	2.51	0.261	0.153	0.005	4.54	3.60	77.5	1.99
8047 - 351713	02/02/2013/B15	0.031	4.73	0.016	91.4	363	2.39	1.20	0.171	81.3	7.47	63.6	1.94	17.7	15.8	1.537	5.06	0.231	0.519	0.007	32.6	90	77.7	1.28
		Mo	Na	Nb	Nd	Ni	Pb	Pt	Rb	Sb	Sc	Se	Sn	Sr	Ta	Te	Th	Tl	U	V	W	Y	Zn	Zr
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
8047 - 351701	08/07/2013/HS3/p1.7/float	1.06	261	5.52	1.68	42.0	13.8	0.011	22.8	0.290	2.06	0.113	1.41	35.3	0.533	0.079	1.76	0.729	1.84	15.4	664	2.62	728	81.8
8047 - 351702	08/07/2013/HS3/p1.7/sink	4.04	120	6.39	4.88	40.9	20.9	0.007	33.5	1.43	4.42	0.85	1.82	31.8	0.574	0.138	8.39	3.727	2.32	17.7	1135	4.83	805	75.8
8047 - 351703	08/07/2013/B11/p1.3/float	1.82	192	4.18	4.04	51.0	20.7	0.006	1.29	0.260	2.68	0.34	1.42	14.3	0.531	0.097	2.18	0.175	1.35	15.8	2506	6.87	228	59.5
8047 - 351704	08/07/2013/B11/p1.5/float	1.47	452	5.71	2.67	63.1	16.5	0.007	0.447	0.228	2.86	0.077	2.16	18.6	0.561	0.110	3.21	0.052	1.59	21.9	2183	4.40	112.3	106.9
8047 - 351705	08/07/2013/B11/p1.7/float	2.17	346	6.78	3.52	71.6	17.0	0.010	0.57	0.264	4.46	0.122	1.99	18.3	0.777	0.135	3.72	0.195	2.17	25.0	3712	5.18	1082	92.2
8047 - 351706	08/07/2013/B11/p1.7/sink	4.57	989	7.23	9.68	112.5	26.2	0.009	1.69	0.396	6.3	0.66	2.09	23.3	0.95	0.140	5.53	0.423	2.10	25.9	6203	14.4	1539	88.6
8047 - 351707	08/07/2013/B5/p1.5/float	5.63	346	15.6	6.68	43.3	37.0	0.019	6.90	1.07	7.2	0.50	7.06	89.6	1.13	0.202	7.96	0.341	5.06	110	1663	8.75	257	275
8047 - 351708	08/07/2013/B5/p1.7/float	4.37	442	15.4	5.09	30.1	36.7	0.020	7.44	1.00	5.75	0.36	6.06	65.3	1.04	0.194	9.6	0.461	5.24	111	1137	5.39	810	274
8047 - 351709	08/07/2013/B5/p1.9/float	3.65	315	17.9	3.94	33.1	43.7	0.016	6.56	0.732	9.5	0.29	6.33	58.7	1.49	0.272	13.8	0.997	5.53	92.0	2111	2.89	1157	228
8047 - 351710	08/07/2013/B5/p1.9/sink	3.94	286	19.1	0.465	34.6	27.8	0.014	5.61	0.627	10.1	0.26	5.95	12.4	1.53	0.323	3.57	0.768	5.09	68.3	83.8	0.345	1241	188
8047 - 351711	08/07/2013/B5/residue	4.33	192	25.1	13.7	31.4	31.4	0.019	13.2	0.872	5.82	0.40	4.38	104.0	2.02	0.192	12.9	0.565	5.50	77.2	72.7	15.0	219	292
8047 - 351712	08/07/2013/B11/residue	1.99	237	6.23	3.03	64.5	13.5	0.010	4.96	0.277	1.45	0.35	1.50	31.8	0.539	0.090	0.78	0.216	1.90	17.8	40.2	4.52	113.6	87.4
8047 - 351713	02/02/2013/B15	1.28	1136	15.2	16.8	25.7	278.2	0.012	9.18	0.429	8.8	0.79	3.66	298	1.24	0.201	20.7	0.312	4.19	45.7	3.19	27.4	16.3	177
								Chemical elements:	Ag, As, Au, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Ga, Ge, Hg, Ho, Ir, La, Li, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pt, Rb, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr													
								Instrument:	ICP-MS Perkin Elmer NexION 300D															
Date:	20.08.2013							Date:	20.08.2013															
Analysed by:	Walter Masoga							Authorised :	JJ Oberholzer								Page 1 of 1							

ANALYTICAL REPORT: ORE SAMPLE

No unauthorised copies may be made of this report.

To:	**WITS University**	Date of Request: 05.11.2012	From : UIS Analytical Services
Attention:	Sibongile Maswanganye		Analytical Chemistry
Order No.:	3293671		Laboratories 4, 6
			Tel: (012) 665 4291
Tel:	(011) 717 7587		Fax: (012) 665 4294
Fax:	+27 86 553 6475		

Certificate of analysis: 6654

Note: all results in parts per million (ppm) unless specified otherwise

Sample ID	Lims ID	Ag	Al	As	Au	B	Ba	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs	Cu	Fe	Ga	Ge	Hf	Hg	Ho	Ir	K	La	Li	Mg
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
	Det. Lim	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<1.0	<0.01	<0.10	<0.10	<0.10	<0.10	<0.10	<1.0	<0.10	<0.10	<0.10	<0.01	<0.10	<0.10	<1.0	<0.10	<0.10	<1.0
Hwange/Sample/3/p1.3/float	6654-321624	<0.1	20400	8.17	<0.1	15.2	34	2.05	0.13	696	0.069	7.2	5.10	23	7.60	10.6	8180	5.0	5.16	1.37	5.46	<0.1	<0.1	2880	1.99	54.9	21
Hwange/Sample/3/p1.5/float	6654-321625	<0.1	17700	3.77	<0.1	14.30	58.6	1.99	0.14	1090	0.042	11.3	4.7	25	5.87	11.1	4840	4.82	4.19	1.60	5.48	<0.1	<0.1	3660	1.1	39.2	15
Hwange/Sample/2/p1.3/float	6654-321626	<0.1	10500	3.76	<0.1	22.50	21	3.36	0.13	1990	0.060	9.7	6.5	23.3	4.29	10.5	8360	10.00	29.20	1.07	15.7	<0.1	<0.1	1300	1.8	21.7	20
Hwange/Sample/2/p1.5/sink	6654-321627	<0.1	27100	12.20	<0.1	28.90	31.7	3.73	0.16	35100	0.101	18.7	8.8	39.7	2.99	17.2	44600	10.60	23.40	1.05	248.0	<0.1	<0.1	1900	5.2	51.7	178
Hwange/Sample/2/p1.5/float	6654-321628	<0.1	21900	5.68	<0.1	19.3	29.8	3.41	0.14	5780	0.031	12.90	6.34	25.9	3.00	10.0	13300	10.90	29.70	0.93	73.30	<0.1	<0.1	1090	3.94	25.6	55
Hwange/Sample/1/leach/residue	6654-321629	<0.1	4460	1.52	<0.1	15.6	18.3	0.69	<0.1	713	0.013	16.40	3.81	11.9	1.00	8.5	7490	3.7	7.7	0.85	1.10	<0.1	<0.1	72	2.56	1.0	35
Hwange/Sample/2/leach/residue	6654-321630	<0.1	4320	1.94	<0.1	5.2	12.8	2.25	<0.1	710	0.011	14.00	6.26	14.4	0.37	7.6	5760	4.98	21.70	0.66	0.40	<0.1	<0.1	4	2.54	0.9	33
H/Sample/3/HIC/residue/from/leaching	6654-321631	<0.1	10000	6.97	<0.1	9.13	20.2	1.37	0.19	598	0.052	27.1	3.41	23.1	2.26	11.8	8300	2.56	2.83	1.49	0.18	<0.1	<0.1	1210	1.44	16.10	15
B/5/residue/from/leaching	6654-321632	<0.1	16300	6.910	<0.1	25.80	144.0	2.58	0.432	1030	1.120	15.50	7.05	80.4	3.200	29.2	6280	11.40	2.07	9.06	0.288	<0.1	<0.1	1480	3.91	12.3	11.9

Sample ID	Lims ID	Mn	Mo	Na	Nb	Nd	Ni	Pb	Pt	Rb	Sb	Sc	Se	Si	Sn	Sr	Ta	Te	Th	Ti	Tl	U	V	W	Y	Zn	Zr
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
	Det. Lim	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<5.0	<0.10	<0.10	<0.10	<0.10	<0.01	<5.0	<0.10	<0.01	<0.10	<0.10	<0.10	<0.10	<0.10
Hwange/Sample/3/p1.3/float	6654-321624	16.90	1.33	416.00	4.80	0.69	28.60	7.5600	<0.1	20.3000	0.356	5.84	0.354	24700	1.2800	12.9000	0.3430	<0.1	1.0780	1280.0000	0.4830	1.6090	15.3000	513.0000	0.9580	10.8000	50.7000
Hwange/Sample/3/p1.5/float	6654-321625	36	1.19	828	4.7	0.49	20.8	7.3	<0.1	12.6	0.18	5.6	0.43	23000	1.18	23.9	0.33	<0.1	1.06	1250	0.27	1.47	15.8	514.0	0.39	11	62
Hwange/Sample/2/p1.3/float	6654-321626	40.5	2.51	412	3.44	0.9	30.4	8.6	<0.1	10.70	0.12	6.79	0.66	30900	0.98	18.2	0.26	<0.1	1.03	944	0.99	0.79	13.2	2540.0	2.0	8	44.1
Hwange/Sample/2/p1.5/sink	6654-321627	68	5.74	1330	6.00	2.46	35.8	12.7	<0.1	14.50	0.22	17.00	0.82	72300	1.90	53.3	0.70	0.116	2.75	1810	1.81	1.05	17.1	55300	5.2	6	42.0
Hwange/Sample/2/p1.5/float	6654-321628	67.8	3.04	459	3.59	2.00	28.8	7.2	<0.1	9.54	<0.1	8.26	0.29	32200	1.23	20.4	0.31	<0.1	2.65	1020	1.15	0.84	15.3	13800	4.6	4	40.1
Hwange/Sample/1/leach/residue	6654-321629	9.6	0.88	238	2.62	1.56	29.5	2.99	<0.1	1.75	<0.1	1.35	0.18	2880	1.02	29.4	0.18	<0.1	0.66	726	0.17	0.63	10.90	88.5	0.84	2.21	47.4
Hwange/Sample/2/leach/residue	6654-321630	6	2.00	77	3.28	1.42	24.4	3.00	<0.1	1.6	<0.1	1.46	0.16	2160	0.69	20.4	0.23	<0.1	1.01	880	0.26	0.70	10.1	22.5	2.02	3.30	30.3
H/Sample/3/HIC/residue/from/leaching	6654-321631	12.2	1.64	130	5.50	0.80	26.4	5.8	<0.1	5.4	0.23	3.20	0.68	9640	0.95	20.6	0.38	<0.1	1.73	1380	0.23	1.24	11.6	5.1	0.45	6.6	61.9
B/5/residue/from/leaching	6654-321632	9.6	4.02	357	28.60	1.39	128.0	28.50	<0.1	10.50	0.82	9.81	1.64	40900	4.11	32.5	1.92	0.135	2.27	4890	0.16	3.22	109.0	4.4	2.00	56.00	335.0

Comments / additional information: **Results reported on an as received basis**

		Chemical elements:	Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe,Ga, Ge, Hg, Ho, In, Ir, K, La, Li, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pt, Rb, Sb, Sc, Se, Si, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr
Identification of test methods:		Instrument:	ICP-MS Perkin Elmer Nexlon 300D, ICP-OES
		Documentation:	
Analysed by:	W Masoga	Authorised :	E Kgosana
Date:	15.11.2012	Date:	15.11.2012

Appendix E UIS TEs results on ROM and leachates

ANALYTICAL REPORT: ORE SAMPLE

No unauthorised copies may be made of this report.

To:	WITS University	Date of Request: 08.08.2012	From : UIS Analytical Services
Attention:	Sibongile Maswanganye		Analytical Chemistry
Order No.:	3279820		Laboratories 4, 6
			Tel: (012) 665 4291
Tel:	(011) 717 7587		Fax: (012) 665 4294
Fax:	+27 86 553 6475		

Certificate of analysis: 6174

Note: all results in parts per million (ppm) unless specified otherwise

Sample ID	Lims ID	Ag	Al	As	Au	B	Ba	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs	Cu	Fe	Ga	Ge	Hf	Hg	Ho	Ir	K	La	Li	Mg
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
	Det. Lim	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<1.0	<0.01	<0.10	<0.10	<0.10	<0.10	<0.10	<1.0	<0.10	<0.10	<0.10	<0.01	<0.10	<0.10	<1.0	<0.10	<0.10	<1.0
B5/ROM	6174 - 309273	<0.10	91057	7.66	<0.10	19.7	395	3.34	1.09	4244	0.239	24.2	8.76	116	2.06	54.5	8806	22.9	1.77	5.40	0.49	0.20	<0.10	4624	7.97	41.3	1452
B11/ROM	6174 - 309274	<0.10	29323	3.58	<0.10	3.70	19.8	2.37	0.37	3191	0.219	64.3	10.9	117	0.18	21.0	16218	8.56	1.24	1.72	0.20	0.47	<0.10	785	27.3	13.3	1803
Bench/11/sink/p1.3	6174 - 309275	<0.10	30633	3.25	<0.10	4.46	121	2.53	0.43	3649	0.274	25.5	11.2	70.4	0.45	28.3	17607	7.49	1.21	2.01	27.9	0.29	<0.10	472	13.2	15.4	1907
Bench/11/float/p1.3	6174 - 309276	<0.10	13263	3.29	<0.10	4.56	25.2	2.51	0.46	1439	0.285	42.4	10.3	86.7	0.67	30.6	7848	9.00	1.39	1.78	36.9	0.33	<0.10	208	18.1	16.2	774
Hwange/Sample/1/ROM/HCC	6174 - 309277	<0.10	14027	3.45	<0.10	29.3	29.2	1.04	0.15	2897	0.029	2.63	5.03	25.5	5.28	10.7	11398	5.05	9.00	0.80	0.24	<0.10	<0.10	259	1.27	28.8	194
Sample/2/ROM/3/Main/Coal/LP	6174 - 309278	<0.10	15495	3.17	<0.10	20.9	26.6	3.52	0.19	6420	0.028	3.03	7.54	57.7	5.09	12.0	9187	10.3	25.9	0.91	0.19	<0.10	<0.10	966	2.04	42.9	204
Sample/3/ROM/HIC/Coal	6174 - 309279	<0.10	24044	8.15	<0.10	18.9	10.7	2.00	0.29	957	0.053	8.99	5.00	42.9	8.69	13.8	11629	6.42	3.22	1.48	0.16	0.12	<0.10	3903	8.60	56.9	393
NW/B11/float/p1.5	6174 - 309280	<0.10	15557	0.63	<0.10	6.07	21.6	2.22	0.31	508	0.024	11.1	9.42	27.7	0.25	14.4	309	9.20	1.54	1.62	0.17	0.11	<0.10	205	9.50	9.45	283

Sample ID	Lims ID	Mn	Mo	Na	Nb	Nd	Ni	Pb	Pt	Rb	Sb	Sc	Se	Si	Sn	Sr	Ta	Te	Th	Ti	Tl	U	V	W	Y	Zn	Zr
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
	Det. Lim	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<5.0	<0.10	<0.10	<0.10	<0.10	<0.01	<5.0	<0.10	<0.01	<0.10	<0.10	<0.10	<0.10	<0.10
B5/ROM	6174 - 309273	106	4.66	1130	21.1	7.10	35.5	33.7	<0.10	40.2	0.51	19.4	0.91	164278	6.08	177.4	1.31	0.309	10.21	4651	0.47	3.71	96.7	51.5	4.77	98	234
B11/ROM	6174 - 309274	95.0	6.63	147	6.43	13.5	83.7	15.1	<0.10	1.70	0.17	6.15	0.36	40971	1.50	52.3	0.38	0.141	3.60	1668	0.14	1.39	22.3	16.0	19.5	115	66.5
Bench/11/sink/p1.3	6174 - 309275	117	3.30	412	7.13	7.76	73.5	13.2	<0.10	2.40	0.16	6.64	0.49	43855	2.06	38.4	0.48	0.173	2.32	1710	0.13	1.45	22.5	3039	11.3	138	68.3
Bench/11/float/p1.3	6174 - 309276	41.0	3.20	612	6.83	9.36	67.8	15.2	<0.10	4.32	0.17	6.16	0.37	18671	1.60	41.5	0.43	0.174	2.88	781	0.16	1.46	22.7	4454	15.7	149	72.2
Hwange/Sample/1/ROM/HCC	6174 - 309277	90.4	1.77	1399	2.65	1.32	35.4	4.16	<0.10	8.89	<0.10	2.93	0.20	15227	0.69	58.5	0.13	<0.10	0.53	743	1.10	0.57	9.71	18.0	1.84	7.21	24.4
Sample/2/ROM/3/Main/Coal/LP	6174 - 309278	123	4.46	1013	3.54	1.78	35.2	5.17	<0.10	35.5	<0.10	4.58	0.38	30898	0.93	62.2	0.16	0.107	0.61	938	1.65	0.66	11.7	13.8	2.38	7.11	33.1
Sample/3/ROM/HIC/Coal	6174 - 309279	57.9	2.08	366	5.75	3.47	25.0	10.2	<0.10	31.8	0.31	3.95	0.35	31237	1.31	25.0	0.36	0.120	1.55	1565	1.15	1.48	17.1	11.0	6.08	21.2	57.8
NW/B11/float/p1.5	6174 - 309280	25.9	0.67	134	4.97	3.18	51.0	8.07	<0.10	2.07	<0.10	3.60	0.49	20368	1.47	31.8	0.32	0.107	0.89	1150	<0.10	1.07	20.6	12.9	5.74	8.65	57.6

Comments / additional information: **Results reported on an as received basis**

Identification of test methods:		Chemical elements:	Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe,Ga, Ge, Hg, Ho, In, Ir, K, La, Li, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pt, Rb, Sb, Sc, Se, Si, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr
		Instrument:	ICP-MS Perkin Elmer Nexlon 300D, ICP-OES
		Documentation:	
Analysed by:	W Masoga	Authorised :	E Kgosana
Date:	03.10.2012	Date:	03.10.2012

ANALYTICAL REPORT: ICP-MS FULL

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To:	**University of Witwatersrand**	Date of request: 05.12.2012	From : UIS Analytical Services
Attention:	Nonhlanhla Mguni		Analytical Chemistry
Order No.:	3298065		Laboratories 4, 6
			Tel: (012) 665 4291
Tel:	+27 11 717 7397		Fax: (012) 665 4294
Fax:			

Certificate of analysis: 6825

Note: all results in parts per million (ppm) unless specified otherwise

Sample ID	LIMS ID	As	B	Ba	Be	Cd	Ce	Co	Cr	Cs	Cu	Fe	Ga	Gd	Ge	Hg	Mn	Mo	Nb	Ni	P	Pb	Pd	Sb	Sc	Se	Sn	Th	Tl	U	V	Zn
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
	Detection Limits	< 0.001	< 0.001	< 0.001	< 0.001	<0.0001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.01	< 0.001	< 0.001	< 0.001	<0.0001	< 0.001	< 0.001	< 0.001	< 0.001	<0.001	<0.001	<0.001	< 0.001	< 0.001	< 0.001	< 0.001	<0.0001	< 0.001	<0.0001	<0.001	< 0.001
1.HS1/H2O/leachate	6825 - 324456	< 0.001	0.025	0.010	<0.001	<0.0001	<0.001	<0.001	<0.001	< 0.001	0.002	0.032	<0.001	<0.001	<0.001	0.0016	0.009	<0.001	<0.001	< 0.001	0.455	0.001	<0.001	<0.001	<0.001	0.001	< 0.001	<0.0001	<0.001	<0.0001	<0.001	<0.001
2.HS2/CH3COONH3/leachate	6825 - 324457	0.001	0.029	0.168	<0.001	0.0002	<0.001	0.002	< 0.001	0.016	0.005	0.072	<0.001	<0.001	<0.001	0.0013	0.233	0.001	<0.001	0.005	2.56	0.005	<0.001	<0.001	0.003	0.003	< 0.001	<0.0001	0.005	0.0002	<0.001	<0.001
3.HS1/HCl/leachate	6825 - 324458	0.033	0.092	0.475	0.002	0.0008	0.018	0.011	0.215	0.028	0.049	3.06	0.002	0.006	0.004	0.0015	2.03	0.008	<0.001	0.087	9.27	0.034	<0.001	0.001	0.004	0.004	0.026	0.0009	0.003	0.0034	0.007	0.165
4.HS1/HF/leachate	6825 - 324459	0.407	1.86	0.136	0.009	0.0007	0.001	0.025	0.360	0.079	0.076	6.95	0.017	<0.001	0.034	0.0025	1.11	0.027	0.008	0.240	5.85	0.162	<0.001	0.001	0.090	0.011	0.077	0.0007	0.007	0.0035	0.029	0.142
5.HS1/HNO3l/leachate	6825 - 324460	0.021	0.150	0.300	0.002	0.0004	0.017	0.009	0.291	0.031	0.028	2.18	0.004	0.003	0.007	0.0009	0.445	0.010	< 0.001	0.131	3.10	0.057	<0.001	<0.001	0.018	0.002	0.026	0.0040	0.003	0.0020	0.007	0.051
6.HS2/H2O/leachate	6825 - 324461	0.002	0.028	0.021	<0.001	0.0000	<0.001	0.001	0.003	0.001	0.003	0.291	<0.001	<0.001	<0.001	0.0015	0.023	< 0.001	<0.001	0.005	2.08	0.001	<0.001	<0.001	< 0.001	0.002	< 0.001	<0.0001	<0.001	0.0002	<0.001	<0.001
7.HS2/CH3COONH4/leachate	6825 - 324462	0.001	0.038	0.134	<0.001	0.0002	<0.001	0.001	0.002	0.006	0.085	0.061	<0.001	<0.001	<0.001	0.0040	0.073	< 0.001	<0.001	0.003	6.72	0.002	<0.001	<0.001	0.003	0.003	<0.001	<0.0001	0.001	0.0003	<0.001	<0.001
8.HS2/HCl/leachate	6825 - 324463	0.020	0.099	0.302	0.008	0.0005	0.018	0.008	0.242	0.026	0.065	2.53	0.003	0.005	0.007	0.0028	2.53	0.005	<0.001	0.058	10.7	0.042	<0.001	< 0.001	0.006	0.004	0.006	0.0006	0.002	0.0064	0.010	0.165
9.HS2/HF/leachate	6825 - 324464	0.338	1.61	0.098	0.032	0.0005	< 0.001	0.021	0.830	0.075	0.066	7.28	0.091	<0.001	0.104	0.0013	1.04	0.042	0.004	0.267	7.37	0.116	<0.001	0.001	0.110	0.014	0.028	0.0005	0.011	0.0049	0.091	0.075
10.HS2/HNO3/leachate	6825 - 324465	0.078	0.467	0.143	0.016	0.0003	0.008	0.016	0.641	0.059	0.039	4.09	0.048	<0.001	0.057	0.0014	0.931	0.039	0.002	0.214	4.45	0.092	<0.001	< 0.001	0.053	0.005	0.015	0.0024	0.008	0.0043	0.046	0.035
11.HS3/H2O/leachate	6825 - 324466	0.002	0.037	0.012	<0.001	0.0000	<0.001	<0.001	<0.001	0.004	0.002	0.083	<0.001	<0.001	<0.001	0.0045	0.003	<0.001	<0.001	0.002	1.41	< 0.001	<0.001	<0.001	<0.001	0.001	<0.001	<0.0001	<0.001	0.0002	<0.001	<0.001
12.HS3/CH3COONH4/leachate	6825 - 324467	0.002	0.046	0.143	<0.001	0.0002	<0.001	0.014	< 0.001	0.106	0.005	0.072	<0.001	<0.001	<0.001	0.0051	0.100	< 0.001	<0.001	0.036	8.24	< 0.001	<0.001	<0.001	0.002	0.003	<0.001	<0.0001	0.005	0.0004	<0.001	<0.001
13.HS3/HCl/leachate	6825 - 324468	0.046	0.088	0.235	0.004	0.0008	0.042	0.047	0.173	0.078	0.076	8.66	0.003	0.022	0.004	0.0061	0.467	0.004	<0.001	0.109	14.7	0.060	<0.001	0.002	0.003	0.004	0.004	0.0024	0.001	0.0093	0.013	0.330
14.HS3/HF/leachate	6825 - 324469	0.359	1.59	0.200	0.026	0.0007	0.010	0.051	0.570	0.108	0.056	33.0	0.111	0.001	0.026	0.0033	0.799	0.028	0.004	0.277	16.1	0.211	<0.001	0.003	0.167	0.018	0.030	0.0132	0.005	0.0203	0.228	0.283
15.HS3/HNO3/leachate	6825 - 324470	0.062	0.395	0.399	0.010	0.0004	0.062	0.021	0.342	0.125	0.026	14.9	0.045	0.021	0.011	0.0033	0.380	0.016	0.003	0.137	6.56	0.100	<0.001	0.002	0.064	0.004	0.011	0.0344	0.005	0.0119	0.090	0.135

		Chemical elements:	
Identification of test methods:		Instrument:	ICP-MS Perkin Elmer Elan NexION 300D
		Documentation:	
Date:	16.01.2013	Date:	16.01.2013
Analysed by:	W Masoga	Authorised :	E.Kgosana

ANALYTICAL REPORT: ICP-MS FULL

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To:	University Of Witswatersrand	Date of request: 20.03.2013	From : UIS Analytical Services
Attention:	Nonhlanhla Mguni		Analytical Chemistry
Order No.:	3309881		Laboratories 4, 6
			Tel: (012) 665 4291
Tel:	+27 11 717 7397		Fax: (012) 665 4294
Fax:			

Certificate of analysis:

Note: all results in parts per million (ppm) unless specified otherwise

Sample ID	LIMS ID	Ag	Al	As	Au	B	Ba	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs	Cu	Fe	Ga	Ge	Hf	Hg	Ho	Ir	K	La
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
	Detection Limits	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.01	<0.0001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.01	< 0.001	< 0.001	<0.001	<0.0001	< 0.001	< 0.001	< 0.01	< 0.001
1/B5/Distilled/H2O/leachate	7316 - 335716	<0.001	2.64	0.008	< 0.001	0.034	0.040	0.002	< 0.001	21.3	0.0001	0.003	0.002	0.002	< 0.001	0.007	0.110	< 0.001	< 0.001	< 0.001	0.0036	<0.001	<0.001	2.97	< 0.001
2/B5/CH3COONH4	7316 - 335717	<0.001	0.700	0.028	< 0.001	0.033	0.330	< 0.001	< 0.001	142	0.0008	< 0.001	0.009	0.002	0.011	0.035	0.040	< 0.001	< 0.001	< 0.001	0.0024	<0.001	0.003	5.91	<0.001
3/B5/HCl/Leachate	7316 - 335718	0.001	13.4	0.732	0.001	0.078	0.800	0.024	0.035	162	0.0022	0.036	0.056	1.01	0.010	0.671	39.5	0.006	0.003	< 0.001	0.0021	0.012	<0.001	2.53	0.013
4/B5/HF/leachate	7316 - 335719	0.012	2825	0.430	<0.001	0.828	2.90	0.035	0.026	17.2	0.0023	0.564	0.137	1.60	0.053	0.548	145	1.02	0.038	0.058	<0.0001	0.003	<0.001	90.3	0.203
5/B5/HNO3/leachate	7316 - 335720	0.001	485	0.102	< 0.001	0.154	5.85	0.006	0.006	39.0	0.0006	0.848	0.024	0.376	0.116	0.162	37.9	0.149	0.007	0.013	<0.0001	0.005	<0.001	20.3	0.411
6/B11/distilled/H2O/leachate	7316 - 335721	<0.001	0.16	0.020	<0.001	0.024	0.050	< 0.001	< 0.001	50.3	0.0007	0.008	0.129	0.004	< 0.001	0.005	50.7	< 0.001	< 0.001	< 0.001	<0.0001	<0.001	<0.001	1.90	0.003
7/B11/CH3COONH4	7316 - 335722	<0.001	0.18	0.014	<0.001	0.026	0.220	< 0.001	< 0.001	165	0.0005	0.002	0.051	0.002	0.001	0.012	6.69	< 0.001	< 0.001	< 0.001	0.0003	<0.001	< 0.001	5.30	0.001
8/B11/HCl/leachate	7316 - 335723	0.001	2.88	0.708	0.002	0.059	0.320	0.004	0.012	150	0.0010	0.321	0.042	0.932	0.001	0.171	53.8	0.008	0.004	< 0.001	0.0095	0.009	<0.001	1.60	0.078
9/B11/FH/Leachate	7316 - 335724	0.002	895	0.407	< 0.001	0.875	0.090	0.013	0.008	6.56	0.0008	0.020	0.076	0.884	0.003	0.142	43.8	0.298	0.015	0.019	<0.0001	<0.001	<0.001	9.12	0.004
10/B11/HNO3/leachate	7316 - 335725	<0.001	208	0.078	<0.001	0.115	0.230	0.002	0.003	38.0	0.0003	0.235	0.026	0.388	0.005	0.059	13.2	0.052	0.004	0.005	<0.0001	0.004	<0.001	3.28	0.082
	7316 - 335725 QC	<0.001	205	0.073	<0.001	0.116	0.230	0.002	0.003	37.7	0.0003	0.241	0.025	0.377	0.005	0.058	13.1	0.052	0.004	0.005	<0.0001	0.004	<0.001	3.13	0.086

Sample ID	LIMS ID	Li	Mg	Mn	Mo	Na	Nb	Nd	Ni	Pb	Pt	Rb	Sb	Sc	Se	Si	Sn	Sr	Ta	Te	Th	Ti	Tl	U	V	W	Y	Zn	Zr
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
	Detection Limits	< 0.001	< 0.01	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.05	< 0.001	< 0.001	< 0.001	< 0.001	<0.0001	< 0.05	< 0.001	<0.0001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
1/B5/Distilled/H2O/leachate	7316 - 335716	0.018	8.38	0.060	< 0.001	34.6	< 0.001	< 0.001	0.006	0.002	<0.001	0.008	<0.001	0.003	0.006	4.78	<0.001	0.243	<0.001	<0.001	0.0005	0.030	< 0.001	0.0004	< 0.001	0.495	< 0.001	0.092	0.005
2/B5/CH3COONH4	7316 - 335717	0.018	28.1	0.500	0.003	42.0	<0.001	<0.001	0.031	0.002	<0.001	0.028	<0.001	0.006	0.007	5.92	<0.001	0.820	<0.001	<0.001	<0.0001	0.060	< 0.001	0.0014	0.020	0.297	<0.001	0.076	< 0.001
3/B5/HCl/Leachate	7316 - 335718	0.042	37.7	1.87	0.025	16.5	< 0.001	0.037	0.336	0.641	<0.001	0.018	0.003	0.024	0.013	18.5	0.023	0.883	<0.001	0.002	0.0103	0.190	< 0.001	0.0691	0.120	0.285	0.192	0.586	0.019
4/B5/HF/leachate	7316 - 335719	1.75	19.4	1.95	0.162	16.1	0.161	0.226	0.964	0.794	<0.001	0.921	0.006	0.783	0.653	4290	0.150	2.85	0.012	0.007	0.168	20.5	0.012	0.1335	1.46	0.622	0.078	0.751	1.46
5/B5/HNO3/leachate	7316 - 335720	0.235	16.7	0.520	0.034	6.74	0.032	0.374	0.201	0.471	<0.001	0.527	0.002	0.133	0.025	894	0.030	3.00	0.003	0.001	0.145	3.68	0.005	0.0369	0.270	0.336	0.111	0.443	0.243
6/B11/distilled/H2O/leachate	7316 - 335721	0.003	21.2	0.840	<0.001	26.1	<0.001	0.005	0.417	0.002	<0.001	0.006	<0.001	0.003	0.002	25.2	<0.001	0.562	<0.001	<0.001	0.0005	0.010	< 0.001	0.0001	< 0.001	0.023	0.005	0.452	< 0.001
7/B11/CH3COONH4	7316 - 335722	0.002	47.5	0.960	0.001	76.5	<0.001	0.002	0.166	0.001	<0.001	0.005	<0.001	0.005	0.001	32.8	<0.001	0.710	<0.001	<0.001	<0.0001	0.010	< 0.001	0.0010	0.030	0.154	0.001	0.144	<0.001
8/B11/HCl/leachate	7316 - 335723	0.004	69.6	2.32	0.031	20.9	<0.001	0.382	0.336	0.611	<0.001	0.003	0.003	0.012	0.008	15.0	0.008	1.10	<0.001	0.002	0.0156	0.030	< 0.001	0.0230	0.020	0.831	0.155	0.899	0.010
9/B11/FH/Leachate	7316 - 335724	0.515	7.96	1.22	0.155	9.07	0.026	0.013	0.942	0.649	<0.001	0.267	0.003	0.216	0.737	1300	0.052	0.091	0.002	0.010	0.0516	3.66	0.001	0.0406	0.200	0.692	0.011	0.625	0.539
10/B11/HNO3/leachate	7316 - 335725	0.103	16.9	0.450	0.052	7.05	0.006	0.166	0.323	0.293	<0.001	0.032	< 0.001	0.048	0.022	332	0.012	0.307	< 0.001	< 0.001	0.0659	0.920	< 0.001	0.0119	0.050	0.469	0.074	0.189	0.114
	7316 - 335725 QC	0.103	16.9	0.450	0.053	6.92	0.007	0.170	0.322	0.296	<0.001	0.032	< 0.001	0.051	0.018	326	0.012	0.316	< 0.001	< 0.001	0.0661	0.900	< 0.001	0.0120	0.050	0.477	0.076	0.191	0.116

Sample ID	LIMS ID	Ag	Al	As	Au	B	Ba	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs	Cu	Fe	Ga	Ge	Hf	Hg	Ho	Ir	K	La
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
	Detection Limits	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.001	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01	<0.1	<0.1	<0.1	<0.1
HS1/Leaching/residue	7316 - 335726	0.25	3445	8.96	<0.1	16.9	22.9	1.40	0.493	1240	0.108	25.8	3.78	21.0	3.73	15.2	11173	2.64	2.30	1.39	0.697	0.129	<0.1	699	3.27
HS2/Leaching/residue	7316 - 335727	0.25	3296	9.08	<0.1	16.4	35.3	1.40	0.575	1605	0.109	22.8	4.02	23.9	2.98	14.2	11021	2.72	2.42	1.73	0.696	0.062	<0.1	867	1.91
HS3/Leaching/residue	7316 - 335728	0.19	5695	5.32	<0.1	24.8	33.3	0.749	0.337	1585	0.081	17.8	4.63	13.0	6.43	9.71	11682	4.67	8.03	0.656	1.35	0.062	<0.1	509	3.55
	7316 - 335728 QC	0.15	5602	5.17	<0.1	24.5	33.8	0.747	0.330	1570	0.090	18.1	4.52	13.0	6.36	9.67	11688	4.60	8.10	0.650	1.35	0.062	<0.1	516	3.55

Sample ID	LIMS ID	Li	Mg	Mn	Mo	Na	Nb	Nd	Ni	Pb	Pt	Rb	Sb	Sc	Se	Si	Sn	Sr	Ta	Te	Th	Ti	Tl	U	V	W	Y	Zn	Zr
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
	Detection Limits	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01	<0.1	<0.1	<0.01	<0.1	<0.1	<0.1	<0.1	<0.1
HS1/Leaching/residue	7316 - 335726	10.4	196	28.0	1.05	109	5.80	2.81	14.6	4.72	<0.1	7.95	0.278	1.74	0.222	3094	0.76	55.1	0.440	0.457	0.194	1650	2.79	1.31	10.45	67.4	2.61	9.19	39.8
HS2/Leaching/residue	7316 - 335727	9.85	196	22.7	1.12	173	6.31	1.92	16.6	4.99	<0.1	9.27	0.274	1.47	0.240	3473	0.79	53.6	0.470	0.374	0.043	1793	2.69	1.49	11.48	68.1	0.90	9.88	56.9
HS3/Leaching/residue	7316 - 335728	8.72	176	22.2	1.05	706	2.77	2.72	31.2	2.18	<0.1	4.09	0.091	1.36	0.192	5364	0.95	74.3	0.210	0.305	1.39	1058	2.29	0.311	9.98	114.1	1.10	5.89	10.6
	7316 - 335728 QC	8.66	176	22.7	1.06	701	2.75	2.72	31.5	2.12	<0.1	4.03	0.081	1.40	0.210	5332	1.00	69.0	0.207	0.310	1.39	1068	2.32	0.316	9.85	114.6	1.13	5.83	11.0

Identification of test methods:		Chemical elements:	Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, GA, Ge, Hg , K, Li, Mg, Mn, Mo, Na, Ni, Pb, S , Sb, Se, Si, Sn, Sr,Th, U, Ti, Tl, V, W, Zn, Zr
		Instrument:	ICP-MS Perkin Elmer NEXION 300D
		Documentation:	ICP-MS FULL
Date:	20.05.2013	Date:	20.05.2013
Analysed by:	W Masoga	Authorised :	E.Kgosana

Appendix F ICP-AES results

Element Conc. Unit	As ppm	Be ppm	Cd ppm	Co ppm	Cr ppm	Cu ppm	Hg ppm	Mn ppm	Mo ppm	Ni ppm	Pb ppm	Sb ppm	Se ppm	U ppm	V ppm
Blank	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**
0.1 ppm	**0.115**	**0.113**	**0.112**	**0.11**	**0.107**	**0.126**	**0.107**	**0.107**	**0.106**	**0.11**	**0.11**	**0.11**	**0.123**	**0.105**	**0.1**
1 ppm	**1.084**	**1.045**	**1.06**	**1.05**	**1.051**	**1.052**	**1.042**	**1.052**	**1.068**	**1.04**	**1.011**	**1.04**	**1.073**	**1.009**	**1.018**
B5 ROM	**nd**	**nd**	**nd**	**6.53**	**86.8**	**55.692**	**nd**	**84.252**	**nd**	**19.5**	**28.76**	**nd**	**nd**	**126.9**	**81.91**
B11 ROM	**nd**	**nd**	**nd**	**3.06**	**76.91**	**29.682**	**nd**	**79.9**	**nd**	**58.3**	**12.75**	**nd**	**nd**	**148.2**	**18.87**
B11 float 1.3	**nd**	**nd**	**nd**	**nd**	**78.44**	**29.784**	**nd**	**71.4**	**nd**	**55.5**	**nd**	**nd**	**1428**	**145.8**	**15.1**
B11 sink 1.3	**nd**	**nd**	**nd**	**nd**	**59.67**	**23.664**	**nd**	**7680.6**	**nd**	**48.1**	**nd**	**nd**	**1102**	**135.2**	**15.4**
HS 2 Rom	**nd**	**nd**	**nd**	**nd**	**68.14**	**13.26**	**nd**	**94.146**	**nd**	**34.3**	**7.446**	**nd**	**nd**	**142.4**	**10.2**
HS3 Rom Hic	**nd**	**nd**	**nd**	**nd**	**40.5**	**16.463**	**nd**	**48.985**	**nd**	**19.5**	**nd**	**nd**	**nd**	**137.7**	**15.05**

nd = not detected

The concentrations are reported as average concentrations for 3 measurements

The relative standard deviation (RSD) is shown below concentration

Element Conc. Unit	As ppm	Ba ppm	Be ppm	Ca ppm	Cd ppm	Co ppm	Cr ppm	Cu ppm	Fe ppm	Hg ppm	K ppm	Mg ppm	Mn ppm
Blank	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**	**nd**
0.1 ppm	**0.115**	**0.112**	**0.113**	**0.118**	**0.112**	**0.111**	**0.107**	**0.126**	**0.105**	**0.107**	**0.115**	**0.112**	**0.107**
1 ppm	**1.084**	**1.086**	**1.045**	**1.061**	**1.06**	**1.049**	**1.051**	**1.052**	**1.057**	**1.042**	**1.02**	**1.058**	**1.052**
B5 ROM	**nd**	**744.6**	**nd**	**2626.5**	**nd**	**6.528**	**86.802**	**55.692**	**9883.8**	**nd**	**3299.7**	**780.3**	**84.252**
		0.3		0.422		4.896	0.175	0.86	0.787		1.876	0.772	0.135
B11 ROM	**nd**	**34.272**	**nd**	**1224**	**nd**	**3.06**	**76.908**	**29.682**	**19074**	**nd**	**622.2**	**632.4**	**79.9**
		0.391		4.679		9.264	0.634	1.222	2.083		3.141	2.37	0.126
B11 float 1.3	**nd**	**37.026**	**nd**	**724.2**	**nd**	**nd**	**78.438**	**29.784**	**17860.2**	**nd**	**632.4**	**795.6**	**71.4**
		0.159		1.457			0.094	0.6	0.347		0.788	0.334	0.59
B11 sink 1.3	**nd**	**27.54**	**nd**	**244.8**	**nd**	**nd**	**59.67**	**23.664**	**18329.4**	**nd**	**530.4**	**520.2**	**7680.6**
		4.311		5.487			6.711	7.426	0.518		13.31	0.855	5.984
HS 2 Rom	**nd**	**14.994**	**nd**	**2555.1**	**nd**	**nd**	**68.136**	**13.26**	**9781.8**	**nd**	**856.8**	**100.776**	**94.146**
		3.878		1.588			0.777	1.857	1.127		0.894	1.905	1.368
waterberg ash	**nd**	**2063.09**	**nd**	**4923.4**	**nd**	**nd**	**394.49**	**62.006**	**38831**	**nd**	**196.833**	**78.486**	**59.843**
		1.117		28.169			0.702	0.999	1.972		1.505	1.425	1.037
Witbank	**nd**	**2134.16**	**nd**	**48451.2**	**nd**	**nd**	**137.608**	**63.757**	**42085.8**	**nd**	**4696.8**	**14739.3**	**421.27**
		1.357		2.03			3.145	3.425	3.175		2.419	0.788	1.836
HS3 Rom Hic	**nd**	**23.331**	**nd**	**161.6**	**nd**	**nd**	**40.501**	**16.463**	**13635**	**nd**	**3040.1**	**166.757**	**48.985**
		1.941		1.385			1.526	3.474	1.334		1.748	1.728	1.933