

**The partition behavior and the chemical speciation of selected  
trace elements in a typical coal sample during pyrolysis**

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in fulfilment of the requirements for the degree Master of Science  
(chemistry)**

**By**

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## Declaration

I the undersigned declare that the work contained in this thesis is my own original work and has not already been submitted to any other university for a degree.

  
TB Hlatshwayo

Date 09/03/2008

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## Synopsis

Sasol is by far the world's leading company in upgrading of low-grade coal into high value chemicals and fuels. Such plants also utilise fine particles or pulverised coal in the combustion process to generate steam and electricity for their processes.

Certain trace elements released from coal during utilisation may be of environmental concern. From the literature findings it appears that the elements of interest are mercury, arsenic and selenium due to their potential health hazard and as they are included in the United States of America, Europe and China Clean Air Act for their potential hazardous effects. It has been observed in the literature that these elements show a nature of high volatility compared to the rest of the elements and further mercury provides an important chemistry to investigate as it has the ability to accumulate in the food chain. It is likely that environmental legislation in South Africa could be implemented soon to control environmental pollution of selected trace element from coal plants.

The toxicity of heavy metals is dependent on the chemical form in which the metal is released. Available analytical techniques for the measurement of trace metals are in many cases not able to differentiate between different chemical species in which the elements occur and are not very reliable at low concentration levels. This makes it difficult to estimate the real environmental impact of the emission of heavy metals as the result of coal processing.

The project centred on a study of the partition behaviour of mercury during coal pyrolysis. Some other environmentally important trace elements, e.g. selenium and arsenic were also investigated.

The stated aims of the project were reached by the following objectives:

1. Testing of suitable pyrolysis instrumentation.
2. Testing of absorption apparatus.
3. Testing of analytical methods.
4. Comparison of two coal types with regard to trace metal emission.
5. Obtaining mass-balance closure with regard to mercury during pyrolysis.

## 6. Application of the FACTSAGE modelling package

Samples were prepared and analysed for trace elements concentrations using advanced analytical techniques including modeling packages for comparison purposes.

The conclusions of the project can be summarised as follows:

- The partitioning behaviour of trace elements on a plant scale was successfully determined.
- The modes of occurrence of some elements of environmental concern were successfully determined. It was not easy to compare these results with literature findings in this area as the coal used in this work was different from that used by other researchers.
- The coal pyrolysis process was well understood.
- The FACTSAGE package was applied successfully in this project in that it predicted the species of trace elements thus explaining the observed experimental findings, especially the analytical method used to analyse the concentration of mercury in solution. It can be concluded that research should start with theoretical studies like a model than an actual experiment as the model predicts direction of the reaction.

## OORSIG

Sasol is verreweg die wêreld se voorste maatskappy betreffende die verwerking in hoë kwaliteit chemikalieë en brandstof uit laegraadse steenkool. Aanlegte soos Sasol maak in die verbrandingsproses ook gebruik van die kleiner deeltjies van steenkool of die fyngemaalde steenkool om stoom en elektrisiteit vir hulle prosesse te verwek.

Sekere spoorelemente wat tydens die verbruik van steenkool afgeskei word, mag van omgewingsbelang wees. Uit die bevindings van literatuur lyk dit asof kwik, arseen en seleen, as gevolg van hulle gesondheidsgevaar, die interessantste van dié elemente is. Om hierdie rede is hulle ook ingesluit in die "Clean Air Act" van die Verenigde State van Amerika, Europa en China. Uit die literatuur blyk dit ook dat hierdie elemente 'n hoë vlugtigheid toon in vergelyking met ander elemente. Verder is kwik ook van chemiese navorsingsbelang, omdat dit die vermoë het om in die voedselketting op te hoop. Dit is hoogs waarskynlik dat omgewingswetgewing binnekort in Suid-Afrika geïmplementeer sal word, om beheer uit te oefen oor omgewingsbesoedeling deur spoorelemente uit steenkoolaanlegte.

Die giftigheid van swaar metale is afhanklik van die chemiese vorm waarin die metal afgeskei word. Beskikbare analitiese tegnieke vir die meting van spoormetale kan in baie gevalle nie onderskei tussen die chemiese soorte waarin die elemente voorkom nie. Hierdie tegnieke is nie baie betroubaar by lae konsentrasie vlakke nie. Dit is dus moeilik om 'n skatting te maak van die ware omgewingsimpak wat die afskeiding van swaar metale in die verwerkingsproses het.

Die projek is gebaseer op 'n studie van die verdelingsgedrag van kwik gedurende steenkoolpirolise. Sommige ander spoorelemente wat van belang is vir die omgewing, bv. seleen en arseen, is ook ondersoek.

Die bepaalde doelwitte van die projek is bereik deur:

1. toetsing van geskikte pirolise instrumentasie
2. toetsing van absorpsie apparaat
3. toetsing van analitiese metodes
4. vergelyking van twee steenkooltipes betreffende die afskeiding van spoormetaal

5. behaling van massa-balans sluiting gedurende pirolise, met betrekking tot kwik
6. toepassing van die FACTSAGE modelleringspakket

Toetsstukke is deur die gebruik van gevorderde analitiese tegnieke, insluitend modelleringspakkette vir vergelykingsdoeleindes, voorberei en ontleed vir spoorelement konsentrasies.

Die gevolgtrekkings van die projek kan as volg opgesom word:

- Die verdelingsgedrag van spoorelemente in 'n aanlegsituasie is suksesvol bepaal.
- Die voorkomsvorme van sommige omgewingsbelangrike elemente is suksesvol bepaal. Dit was nie maklik om hierdie uitslae met literatuurbevindings te vergelyk nie, aangesien die steenkool wat in dié werk gebruik is anders is as dié wat deur ander navorsers gebruik is.
- Die pirolise-proses van steenkool is goed verstaan.
- Die FACTSAGE-pakket is suksesvol toegepas in hierdie projek, aangesien die fases waarin spoorelemente verwag is, korrek voorspel is. Die eksperimentele bevindings wat waargeneem is, veral deur die analitiese metode wat gebruik is om die konsentrasie van kwik in vloeistof te analiseer, is so verduidelik.

Die slotsom is dat navorsing met teoretiese studies, soos 'n model, eerder as met 'n ware eksperiment, moet begin. Die rede hiervoor is dat die model die rigting van die reaksie voorspel.

# CONTENTS

Synopsis .....	1
OORSIG.....	3
Contents.....	5
Motivation.....	7
Background.....	9
Aim.....	15
Chapter 1 .....	16
Literature Overview .....	16
1.1 The Origin and Structure of Coal.....	16
1.2 Organic and Inorganic Part of Coal.....	22
1.3 Trace Elements Origin in Coal .....	27
1.4 Mode of occurrence of trace elements in coal.....	32
1.5 Trace element emission during coal utilization.....	35
1.6 Trace element emission during coal combustion .....	37
1.7 Trace element release behaviour during coal pyrolysis .....	40
1.8 Trace element partitioning behaviour during gasification .....	44
1.9 Trace element content comparison in Lignite and sub-bituminous coal .....	46
1.10 Modeling of trace elements during coal processing .....	46
1.11 South Africa's coal geological setting and typical coal properties .....	50
Chapter 2 .....	57
Experimental .....	57
2.1 Analytical Techniques for Identifying Trace Elements in Coal & its Products.....	57
2.2 Analytical Methods Selected for this Project .....	71
2.2.2 Information on the Coal used in this Work.....	71
2.2.5 Methods for determining the Mode of Occurrence of Trace Elements in Coal.....	77
2.3 Pyrolysis Process.....	79
2.3.1 Pyrolysis Experimental Set-up .....	81
2.4 Methods for determination of Mercury in Gas Streams (Gold tube and activated carbon tube).....	85

2.4.2.1 Comparison of DMA 80 mercury analyzer and the SIR GALAHAD mercury analyzer.....	88
2.5 Modeling of Trace Elements during Coal Processing.....	89
2.5.1 FACTSAGE Thermodynamic Modeling Package.....	89
2.5.2 SimuSage.....	90
2.6 Coal Pyrolysis Modeling.....	90
2.6.1 Comparison of the Actual and Modeled Pyrolysis Experiment.....	91
Chapter 3 .....	93
Results.....	93
3.1 Coal Characterisation.....	94
3.3 American Society for Testing and Materials standard test methods (ASTM)	99
3.4 Arsenic, Selenium determination (D4606–95) and Mercury determination (D6414–99) .....	100
3.5 Methods for determining the mode of occurrence of trace elements in coal .....	102
3.6 Mode of Occurrence of Trace Elements in the Investigated Coal .....	107
3.7 Methods for determination of Mercury in Gas Streams (Gold tube and activated carbon tube).....	111
3.8 Pyrolysis Experimental Results .....	115
Mercury Mass Balance.....	119
3.11 Thermodynamic Modeling of the Behavior of Trace Elements during Coal Pyrolysis - Modeled Results Compared to Experimental Results.....	122
CHAPTER 4 .....	130
Conclusions.....	130
4.3.1 Project successes .....	132
4.3.2 Project failures .....	133
References.....	134
Appendix A.....	142
Appendix B.....	148

## Motivation

On November 15, 1990, the President of the United States of America signed into law sweeping revisions of the Clean Air Act (CAA). The new law contains titles that:

- strengthen measures for attaining air quality standards (Title I),
- set forth provisions relating to mobile sources (Title II),
- expand the regulation of hazardous air pollutants (Title III),
- require substantial reductions in power plant emissions for control of acid rain (Title IV),
- establish operating permits for all major sources of air pollution (Title V),
- establish provisions for stratospheric ozone protection (Title VI), and
- expand enforcement powers and penalties (Title VII).

Of most interest to this project is pollution that is emitted from fossil fuel usage. Understanding the nature of the pollutants will go a long way into limiting their emissions. The USA Clean Air Act Amendment of 1990 aims to reduce air pollution through the reduction or elimination of pollutants produced or created at the source. It offers a comprehensive plan for achieving significant reductions in emissions of hazardous air pollutants from major sources. In the Act, 189 potentially hazardous air pollution substances are listed. Eleven of these are inorganic elements potentially originating from coal utilisation. These are antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni) and selenium (Se). As, Hg and Se emitted from coal-fired utilities have been shown to cause severe health problems in Europe and Asia. Millions of people suffer from fluorosis, thousands suffer from arsenism and hundreds from selenosis (Wagner, 2001).

It appears that coal will keep its important position as the world's energy source because of its relatively abundant reserves in comparison to the decreasing reserves of both petroleum and natural gas. World politics have also contributed negatively in cutting back other cleaner fuel technologies like nuclear for energy generation. The gasification technology is being marketed around the world where there are enough coal reserves. South Africa uses coal in the order of million tons per annum especially in energy production and fuel conversion processes like gasification. With a large increase in industrialization and urbanisation it has also become necessary to expand power stations and fuel plants to keep up with the demand. South Africa is the world's sixth largest producer, producing 245.3 million short tons of coal in 2002. There are several contradicting figures in literature with regard to the amount of coal reserves in

South Africa: The South African minerals bureau (Department of minerals and energy) estimates 28293 millions tonnes in 2004, while the Energy Information Administration of America (EIA) website estimates 54.6 billion short tons in 2005, which is approximately 5% of the world's total (EIA-Country Analysis briefs, 2005). It is calculated that South Africa produces an average 224 million tonnes of marketable coal annually (ESKOM fact sheet, 2006). It has been highlighted in the Clean Air Act that the pollution emission from coal utilization may cause serious environmental and health risks. The emissions of SO<sub>x</sub>, NO<sub>x</sub>, CO<sub>2</sub> and volatile organic compounds in flue gases from coal combustion may have serious environmental impacts, such as ozone exposure at ground-level, soil acidification and eutrophication due to the deposition of acid and nitrogen, respectively. Global temperatures rising and direct hazards of volatile organic compounds to agriculture, soil and water, are all environmental impacts (Xu et al., 2003). In addition to the above mentioned pollutants there is a large concern about the fate of trace elements during coal combustion or gasification. The partitioning, environmental impacts and emission control technologies are not yet well understood. Understanding the behaviour of the so called trace elements in coal has drawn more interest from scientist because of the great concern for their toxicological and environmental effects. Therefore, the demand of studying trace elements behaviour in this work was driven by:

- the 1990 Clean Air Act legislation (anticipated similar South African legislation)
- the need to understand mode of occurrence of trace elements in coal
- understanding the behaviour and environmental effects of the more volatile elements in coal i.e. Hg, As and Se

## **Background**

Sasol is by far the world's leading company in upgrading low-grade coal into high value chemicals and fuels. Such plants also utilise coal in the combustion process to generate steam and electricity for their processes.

As mentioned earlier, certain trace elements released from coal during utilisation may be of environmental concern. From the literature findings (Huggins, 2002), it appears that the elements of concern are mercury, arsenic and selenium. This is as a result of their potential health hazard. These elements are included in the United States of America, Europe and China Clean Air Act amendment of 1990. It has been observed in the literature that these elements (Hg, As and Se) show relatively higher volatility compared to the rest of the elements present in coal. And in addition mercury provides an important chemistry to investigate as it has the ability to accumulate in the food chain.

It is likely that environmental legislations in South Africa could be implemented soon to control environmental pollution of selected trace element from coal plants. The legislation is likely to have a great impact on coal plants, especially petrochemical industries. Increased environmental concerns as well as legislations have accelerated research on the determination of trace elements in coal or fuels and the subsequent recovery or capturing of these elements during gasification of coal. There are secondary products from various Sasol processes where heavy metals could accumulate. These products include tar and gas liquor (water streams that condense out when the high temperature gas products from the coal gasification process is cooled). An efficient and environmentally friendly way of using coal can only be realized through good of the chemistry of trace elements in coal.

The toxicity of heavy metals is dependent on the chemical form in which the metal is released. Available analytical techniques for the measurement of trace metals are in many cases not able to differentiate between different chemical species in which the elements occur and are not very reliable at low concentration levels. This makes it difficult to estimate the real environmental impact of the emission of heavy metals as the result of coal processing. Computational thermodynamics chemical modeling packages have been successfully used to investigate and understand the different

chemical species of elements in a system at equilibrium, overcoming the limitations of analytical techniques.

The environmental impact, behaviour and healthy hazard of some trace elements of major concern are briefly reviewed:

### ***Mercury***

Mercury is a persistent substance that comes from natural and anthropogenic sources. It can be found in cinnabar and other ores containing compounds of zinc, tin and copper in rocks such as limestone, sand stones, calcareous shales and basalt; and in fossil fuels such as coal. Mercury is a high-priority regulatory concern because of its persistence and bio-accumulation in the environment and evidence of serious adverse effects on the neurological development of children. The Council of Scientific Industrial Research (CSIR) recently organised the South African Mercury Assessment (SAMA) workshop programme.

The following were some of the workshop's objectives:

- Development of a framework for mercury research in SAMA, focusing initially on the transport, fate and consequences of Hg from coal-fired power plants in South Africa
- Assisting the regulatory body in drawing up the mercury regulations.
- Identifying mercury in high point sources especially in coal utilization and mining.

Mercury is present in trace amounts in all environmental media. The bulk of global atmospheric mercury is elemental mercury in the vapour form. From the atmosphere elements are removed through precipitation, resulting in deposition to water bodies, the soil, and vegetation. The ultimate depository of mercury is the sediment of oceans, seas, and lakes, where inorganic mercury is readily transformed into highly toxic organic methylmercury through bacterial synthesis and other enzymic and nonenzymic processes. Organic mercury rapidly accumulates in the aquatic biota and biomagnifies upward through aquatic food chain, attaining its highest concentrations in fish, especially in large predatory species, where it often exceeds 2.0 micrograms per gram ( $\mu\text{g/g}$ ), and in such species as dolphins, reaching 10  $\mu\text{g/g}$ . Average levels of 0.07-0.17

µg/g mercury are found in fish, largely (over 70%) in the form of organic methylmercury (pollution prevention report, 1998).

Any risk management of the source of anthropogenic mercury needs to be based on an understanding of the source and transportation mechanism of airborne mercury. The global atmospheric mercury from anthropogenic sources is estimated between 40 to 75% of the total atmospheric mercury content. Table 1 gives some of the properties of atmospheric mercury (Environmental and Occupational Health report, 2005).

Table 1: Properties of atmospheric mercury (Environmental and Occupational Health report, 2005)

<b>Type of Mercury</b>	<b>Residence time in atmosphere</b>	<b>Transport distance</b>	<b>Method for deposit</b>
Hg (Elemental mercury vapour)	One year	global	Wet precipitation
Hg <sub>p</sub> (Mercury in atmospheric particulates)	Hours up to years, dependent on particle size	Local, regional, and global	Dry and wet precipitation
Hg <sup>2+</sup> (divalent mercury)	Days	Regional	Dry and wet precipitation

The natural emissions of mercury, mainly as a result of the degassing of the Earth's crust and evaporation from water bodies, are two to four times larger than those from anthropogenic sources (pollution prevention report, 1998). About half of the atmospheric mercury generated by anthropogenic sources can be attributed to fossil fuel combustion (pollution prevention report, 1998). Emissions from fossil fuel combustion vary according to the mercury content of the fuel. Mercury levels in coal tend to be one to four orders of magnitude greater than those in fuel oil and natural gas.

The main human health hazard of mercury has been associated with exposure to highly toxic organic methylmercury through food, primarily through the ingestion of aquatic organisms, mainly fish. Methylmercury in human diet is almost completely

absorbed into the blood stream and distributed to all tissues, the main accumulation taking place in the brain, liver and kidneys (pollution prevention report, 1998).

Methylmercury poisoning affects the central nervous systems and the areas associated with the sensory, visual, auditory and coordinating functions. Increasing doses results in parasthesia, ataxia etc. The effects of methyl mercury poisoning are in most cases irreversible because of the destruction of neuronal cells. The development of a child's brain is significantly affected by methylmercury (pollution prevention report, 1998).

### ***Arsenic***

Arsenic is a metalloid that is distributed widely in the Earth's crust. Pure arsenic is rarely found in the environment. More commonly it bonds with various elements such as oxygen, sulphur and chlorine to form inorganic arsenic compounds and with carbon and hydrogen to form organic arsenic compounds. The water soluble trivalent and pentavalent oxidation states of inorganic arsenic are the most toxic arsenic compounds. Atmospheric arsenic exists primarily in inorganic form and is absorbed by particulate matter, while soluble arsenate and arsenite salts are the most typical forms in water. Atmospheric arsenic deposits in the soil and is then absorbed by plants, leached to groundwater and surface water and taken up again by plants and animals (pollution prevention report, 1998).

The highest concentration of arsenic mineral can be found as arsenides of copper, lead, silver and gold but high levels may also be found in some coal. According to the United States Geological Survey, there is a lot of evidence of coals containing high levels of arsenic in China. The greatest part of anthropogenic arsenic emissions originate from stationary sources, especially combustion of low grade brown coal. There is also the contribution of agriculture in which arsenic is released through the burning of vegetation and wood treated with arsenic-containing preservatives. The largest contributors of arsenic in terrestrial waters are land fills, mines and pit heaps wastewater from smelters (pollution prevention report, 1998).

Ingestion is the main route of exposure to arsenic for the general population. Arsenic can have both acute and chronic toxic effects on humans. It affects many organs

including the respiratory, cardiovascular, nervous and hematopoietic systems. When ingested in dissolved form, both inorganic and organic soluble arsenic compounds are readily absorbed from the gastrointestinal tract; less soluble forms have lower absorption rates. The carcinogenic potential of inorganic arsenic is considered the key criterion in assessing the hazard from both environmental and occupational exposures (pollution prevention report, 1998).

### **Selenium**

According to the Wikipedia Encyclopedia, 2007 selenium occurs only rarely in the free form in nature. It is a nonmetal that is chemically related to sulphur and tellurium. It is toxic in large amounts, but trace amounts of it, forming the active center of certain enzymes, are necessary for the function of all cells in (probably) all animals. Selenium requirements in plants differ by species, with some plants apparently requiring none.

Isolated selenium occurs in several different forms, but the most stable of these is a dense purplish-gray semimetal (semiconductor) form that is structurally a trigonal polymer chain. It conducts electricity better in the light than in the dark, and is used in photocells. Selenium also exists in many nonconductive forms: a black glass-like substance, as well as several red crystalline forms built of eight-membered ring.

Selenium is found in economic quantities partially replacing sulphur in sulfide ores such as pyrite ( $\text{FeS}_2$ ). Minerals that are selenide ( $\text{Se}^{2-}$  ion) or selenate ( $\text{SeO}_4^{2-}$  ion) compounds are also known, but all are rare. Selenium occurs naturally in a number of inorganic forms, including selenide and selenate. In soils, selenium most often occurs in soluble forms like selenate (analogous to sulfate), which are leached into rivers very easily by runoff. Selenium has a biological role which is not part of this project. It is found in organic compounds such as dimethyl selenide, selenomethionine ( $\text{C}_5\text{H}_{11}\text{NO}_2\text{Se}$ ) and selenocysteine. In these compounds selenium plays an analogous role to sulphur.

Selenium is most commonly produced from selenide in many sulfide ores, such as those of copper, silver, or lead. It is obtained as a byproduct of the processing of these ores, from the anode mud of copper refineries and the mud from the lead chambers of

sulphuric acid plants. Natural sources of selenium include certain selenium-rich soils, and selenium that has been bioconcentrated by certain toxic plants such as locoweed. Anthropogenic sources of selenium include coal burning and the mining and smelting of sulfide ores.

Although selenium is an essential trace element it is toxic if taken in excess. Exceeding the Tolerable Upper Intake Level of 400 micrograms per day can lead to selenosis. Symptoms of selenosis include a garlic odour on the breath, gastrointestinal disorders, hair loss, sloughing of nails, fatigue, irritability and neurological damage. Extreme cases of selenosis can result in cirrhosis of the liver, pulmonary edema and death.

Elemental selenium and most metallic selenides have relatively low toxicities because of their low bioavailability. In contrast, selenate is very toxic, and has modes of action similar to those of arsenic. Hydrogen selenide is an extremely toxic, corrosive gas. Selenium also occurs in organic compounds such as dimethyl selenide, selenomethionine and selenocysteine, all of which have high bioavailability and are toxic in large doses.

Selenium poisoning of water systems may result whenever new agricultural runoff courses through normally-dry undeveloped lands. This process leaches natural soluble selenium compounds (such as selenates) into the water, which may then be concentrated in new "wetlands" as it evaporates. High selenium levels produced in this fashion have been found to have caused certain congenital disorders in wetland birds (Wikipedia, Encyclopedia, 2007)

## **Aim**

The project centred on the measurement and prediction of the partition behaviour of mercury and other environmentally important metals during coal pyrolysis.

The strategy used to reach the aims was:

1. Development/testing of suitable pyrolysis instrumentation.
2. Development/testing of absorption apparatus.
3. Testing of analytical methods.
4. Comparison of several coal types with regard to trace metal emission.
5. Identification of the trace element containing pyrolysis products.
6. Obtaining mass-balance closure with regard to mercury.
7. Application of a computation thermodynamic modeling package in a coal pyrolysis system (FACTSAGE).

# CHAPTER 1

## Literature Overview

### Chapter Summary

This chapter looks at the literature of:

- composition of coal with an emphasis on trace elements.
- emission of trace elements during coal utilisation.
- application of computational thermodynamic modeling calculation in the coal utilization processes

### ***1.1 The Origin and Structure of Coal***

#### ***1.1.1 Coal Origin***

Coal is classified in geological science as a rock. Coal as described by Valkovic (1983) represents the accumulation of organic material in sedimentary strata. Figure 1.1 shows the deposition environment needed for coal formation, while Figure 1.2 depicts the actual situation of coal formation in the Karoo region in South Africa.



Figure 1.1: Rich depositional environment required for coal formation

Although there is no satisfactory definition of coal, it can be generally described as a mixture of organic and mineral materials produced by a natural process of growth and decay, accumulation of debris both vegetal and mineral, with some sorting and stratification and accomplished by chemical, biological, bacteriological and metamorphic action.

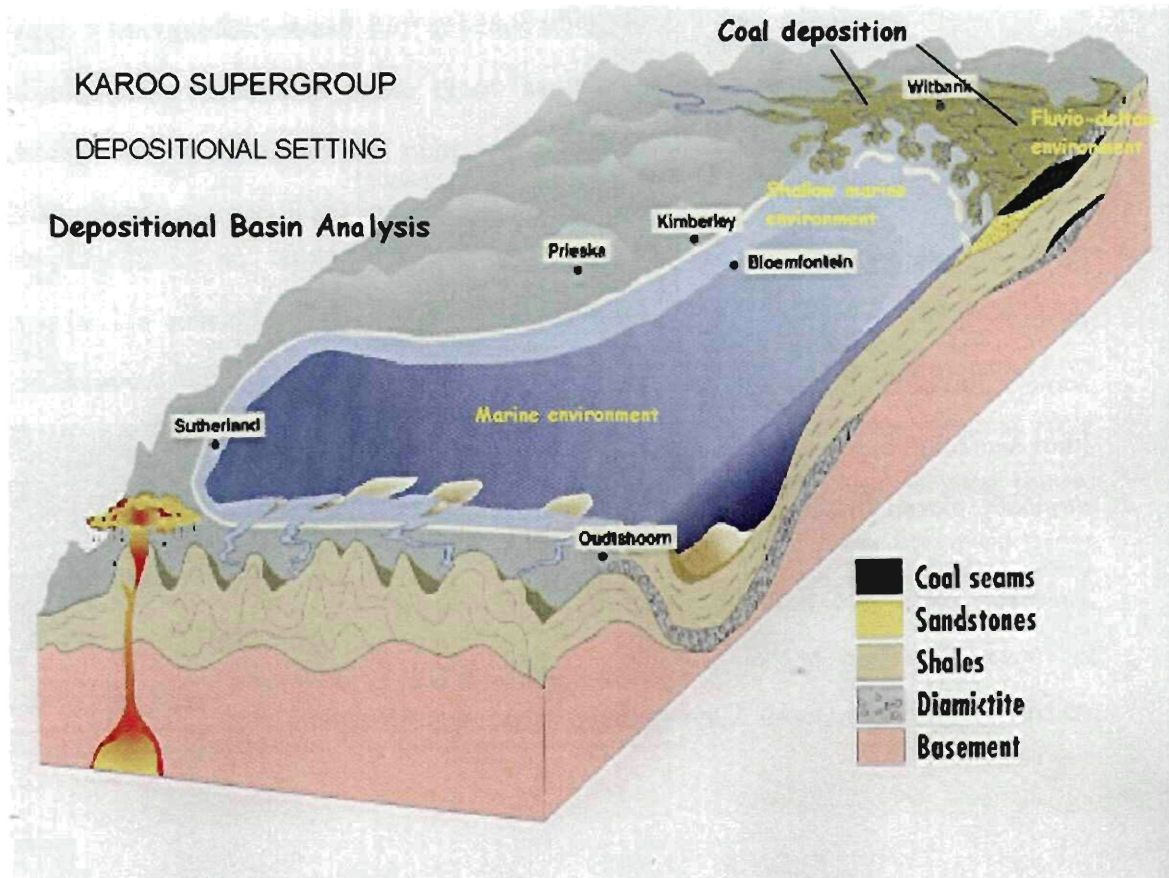


Figure 1.2: Depiction of the actual environmental of coal formation in the Karoo region in South Africa

Figure 1.3: Illustrating the formation of coal from debris to actual coal. Peat is the result of the accumulation of important debris in swamps. Once peat is formed it must be buried under mineral sediments, clay, silt, and sand. After a long period of time under pressure and heat from sediments, peat form beds of coal that range from a few centimetres to many meters in thickness. In most cases the coal is mixed with shale, sandstone, and other sedimentary rocks (Valkovic, 1983). The mixing of coal with such debris is as a result of the meandering of the river bringing with it; some sand on top of the plant debris (see Figure 1.1). The stages of transforming peat can be described or

characterised at various levels of resolution from living material: peat> lignite> bituminous coal> anthracite (Figure 1.3 and Figure 1.4).

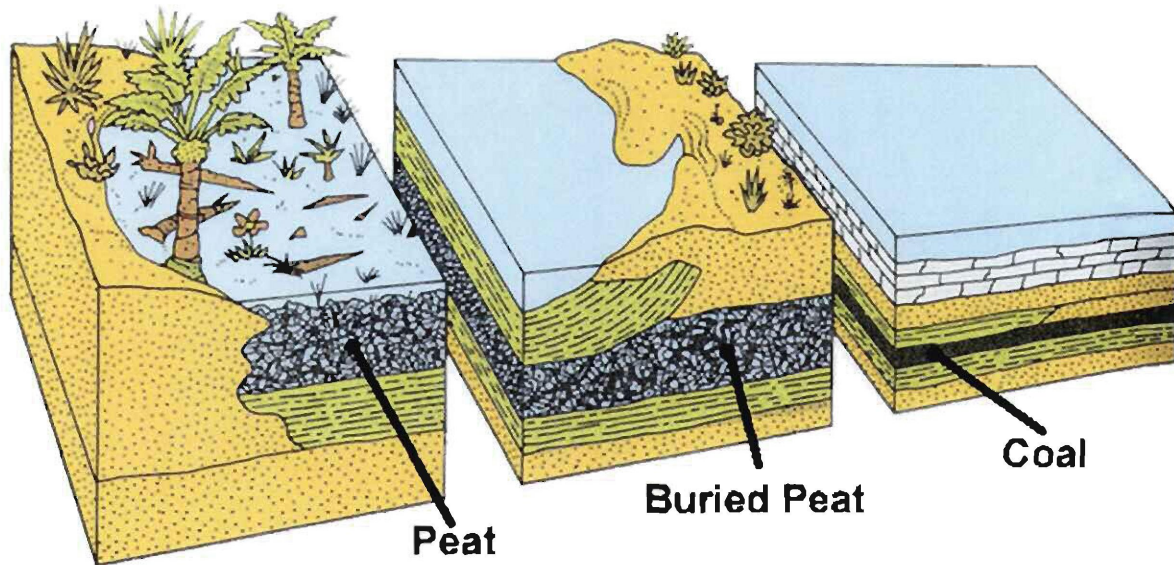


Figure 1.3: Illustrating the formation of coal from debris to actual coal

The change in the properties and structure of coal is called metamorphism. The extent of metamorphism is called the rank. The rank and the relative amount of mineral matter that may be present in coal is reflected by the physical appearance of the coal and determines its behaviour during utilization (Figure 1.4). Therefore anthracite as it is the last stage of coal development under high pressure and for longer period of time, is a higher rank coal. The pressure effects are related to the decrease in moisture content and porosity of the coal (Valkovic, 1983). Temperature cannot be accounted for in the rank of coal although it is an important factor in transforming peat to coal.

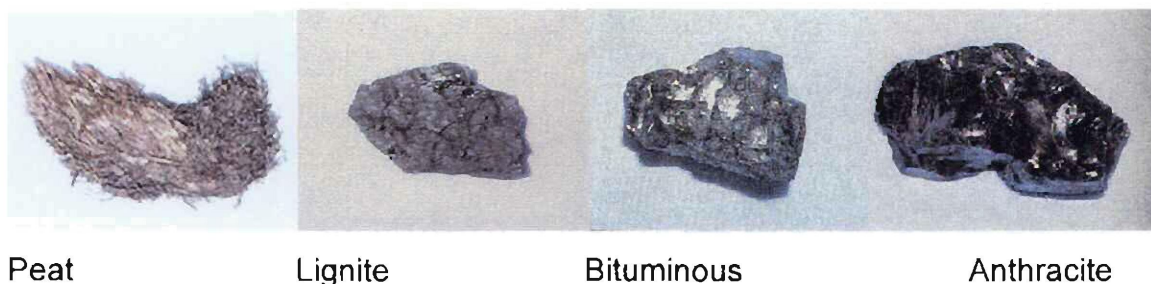


Figure 1.4: The formation of coal in terms of rank (maturity) type (organic composition)

### **1.1.1.1 The chemical composition of coal**

The chemical composition of coal is defined in terms of its proximate and ultimate (elemental) analyses;

- The proximate analysis gives relative amounts of light organic compounds (volatile matter). It also gives the amount of moisture in the coal and an indication of the inorganic components remaining as residue or ash when the coal is burned.
- The Proximate Analysis of any coal i.e. the percent content of Moisture, Ash (A), Volatile Matter (VM), Fixed Carbon (FC) - also Sulphur (S) and Calorific Value (CV) - can be expressed on any of the following bases:
  - As Received (ar): includes Total Moisture (TM)
  - Air Dried (ad): includes Inherent Moisture (IM) only
  - Dry Basis (db): excludes all Moisture
  - Dry Ash Free (daf): excludes all Moisture & Ash

### **1.1.2 Coal Structure**

The history of the coal structure dates back to the 1940's yet it is still a complex issue even today (Mathews, 2005). Mathews (2005) came up with a coal structure represented in Figure 1.5. There is still some difficulty in coming up with the true structure of coal because of its extremely heterogeneous nature. Many molecular subgroups have been identified with the most prominent being the benzene ring, condensed ring such as naphthalene, anthracene and larger-ring compounds (Valkovic, 1983). These subgroups are interlinked or bonded in an almost infinite variety of ways (Figure 1.6). Atoms of elements, for example oxygen, sulphur and nitrogen are placed throughout the representation of a coal molecule. The elements can be present in heterocyclic rings or can be part of a functional group. Mathews et al., 2005 have recently proposed molecular models of the structure of coal (Figure 1.7). In all molecular structures in the literature, there is no indication of the trace elements in the structure. It could therefore be assumed that such inorganic elements are trapped in the coal matrix, attaching themselves to the nitrogen atoms forming some chelates.

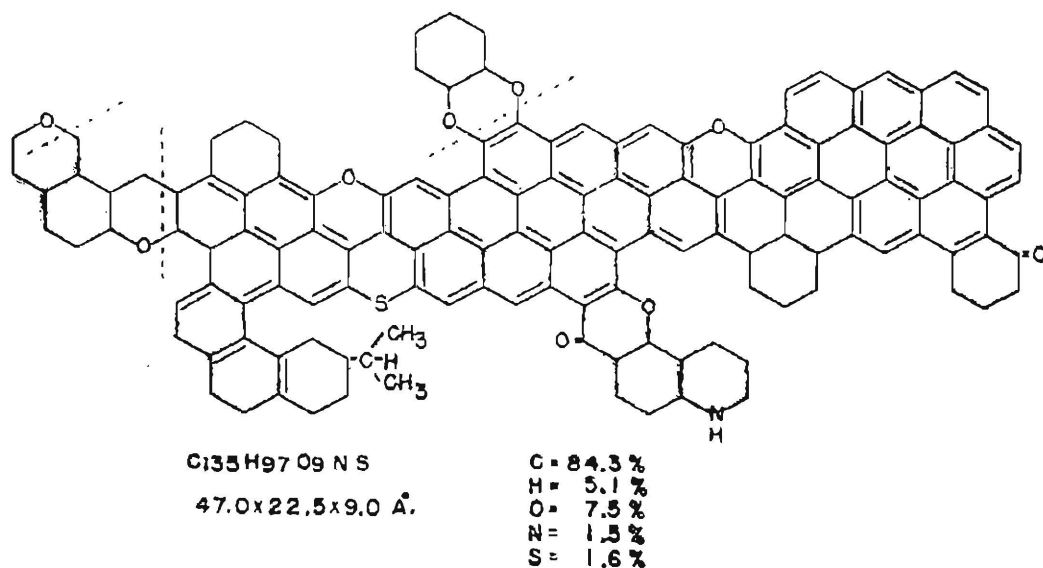


Figure 1.5: Fuch, W. and Sandoff, A. G., Theory of coal pyrolysis, *Industrial Engineering Chemistry*, 1942, **34**, 567 (in Mathews 2005).

Coal has been viewed as an organic chemical substance containing the classical organic functional groups mainly carbonyl and hydroxide, aromatic and heterocyclic ring units and aliphatic bridges. It can be viewed as a solid colloid which has large volume porosity and can adsorb gases and vapours as well as liquid (Valkovic, 1983). The organic coal matrix may be characterised as a cross-linked polymer (formed from the cellulosic polymer present in plant material) which, in the absence of degradation, is essentially insoluble and non-volatile. In order to understand the chemistry of coal, it is helpful to consider the chemicals found in plants: carbohydrates, lignins, proteins, waxes and resins (Valkovic, 1983). While closely understanding the structure of coal, it would be of great value to also briefly consider the destruction of the structure of coal during coal pyrolysis.

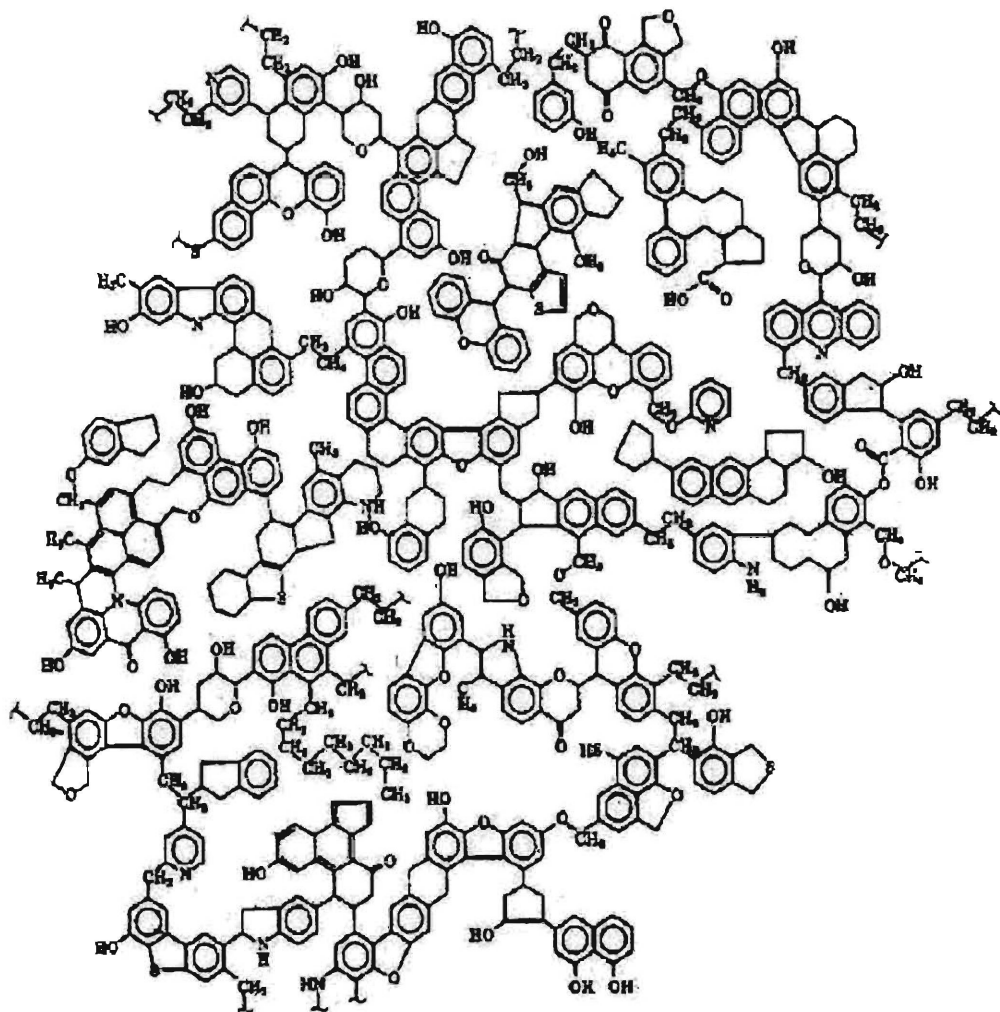


Figure 1.6: Hypothetical structure of bituminous coal (Kirk-Othmer, 1995)

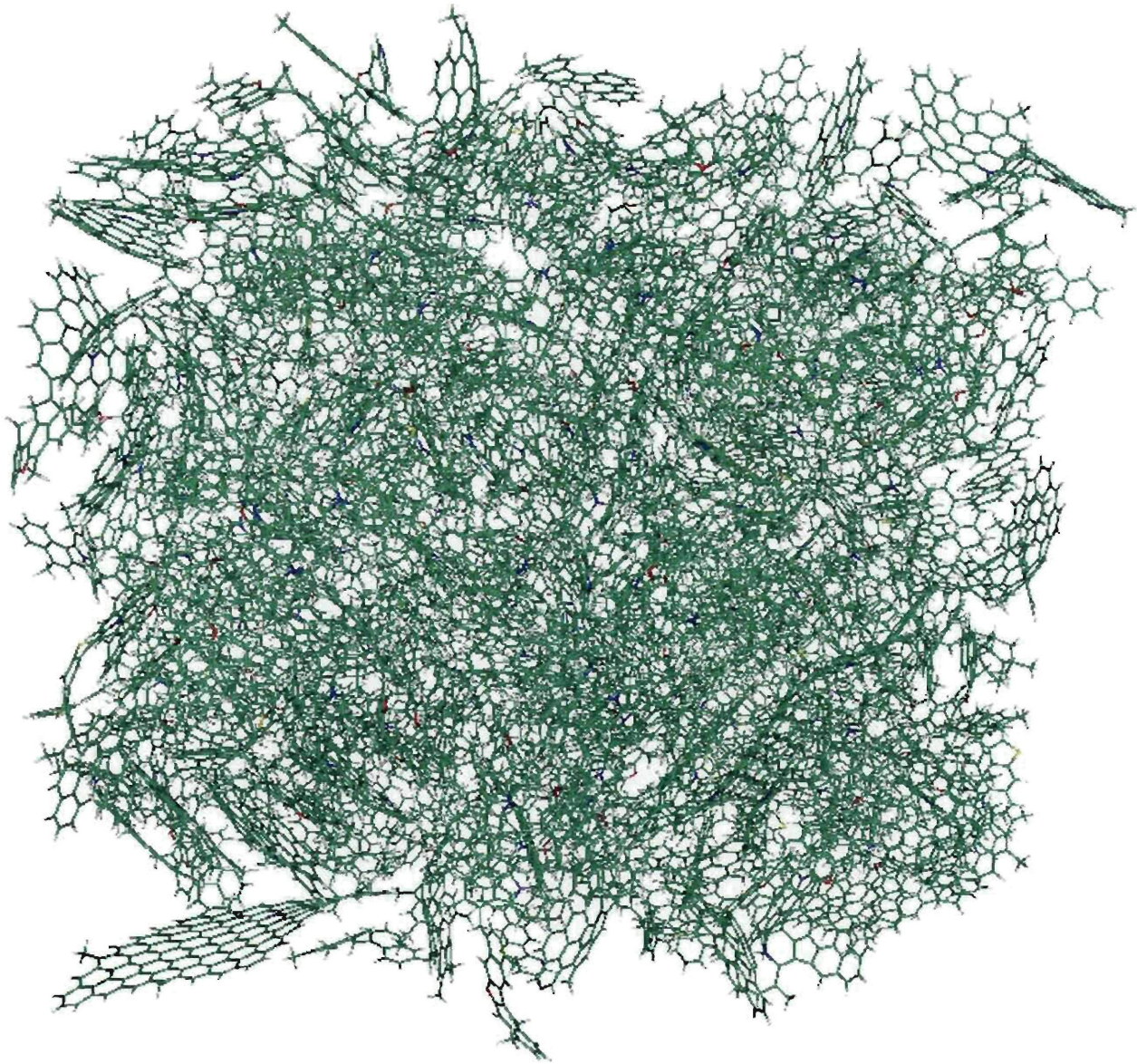


Figure 1.7: 2-D structure of coal by Narkiewicz & Mathews (2005)

## ***1.2 Organic and Inorganic Part of Coal***

### ***1.2.1 Organic Matter in Coal***

Coal is composed of discrete organic constituents termed macerals. Macerals are entities which evolve from different organs or tissues of the original plant material during the course of the primary accumulation and early stages of biochemical degradation and early coalification. Maceral defines coal in its chemical composition and physical properties. It should be noted that macerals are crystalline like most minerals. Macerals describe at the same time both the shape and nature of the

microscopically recognizable constituents of the coal (Stach et al., 1982). Factors influencing the formation of maceral during coalification include type of plant community, climatic controls, ecological conditions, the acidity and the redox or *Eh* value. The widely used method for determining maceral content of coal is by measurement of reflected light. Valkovic (1983) reports that each maceral reflects characteristic amounts of light when direct light is applied to polished coal surface. The reflectance of macerals increases with increasing rank of the coal. Once the accumulating plant material is buried at depth below 1 metre, processes of biochemical degradation cease to function and chemico-physical changes of geochemical coalification or maturation takes over. Most maceral once formed undergo progressive physical chemical optical changes with increasing rank, but their proportions and shapes with minor exceptions remain the same. Their names are descriptive and conventionally end in *-inite*. The distinction of the group macerals is based on the reflectance, but the names are derived from morphologic and genetic considerations and to some extent on their technological characteristics (Falcon and Snyman, 1986). These groups of macerals are termed *vitrite*, *exinite* and *inertinite*. Each group includes a series of macerals which can be regarded as belonging together, either because of similar origin or because of the mode of conservation (Stach et al., 1982).

#### **1.2.1.1 Vitrite**

Vitrite is one of the primary components of coals. Vitrite is a type of maceral, where "macerals" are organic components of coal analogous to the minerals of rocks. Vitrite has a shiny appearance resembling glass (vitreous). It is derived from the cell-wall material or woody tissue of the plants from which coal was formed. Chemically, it is composed of polymers, cellulose and lignin.

Vitrite forms diagenetically by the thermal alteration of lignin and cellulose in plant cell walls. It is therefore common in sedimentary rocks that are rich in organic matter, such as shales and marls with a terrigenous origin, or some terrigenous content.

#### **1.2.1.2 Exinite**

Refers to the finely-ground and macerated remains, originally formed by spores, pollen, dinoflagellate cysts, leaf cuticles, plant resins and waxes, as found in coal deposits.

### **1.2.1.3 Inertinite**

It is found as tiny flakes within sedimentary rocks. The presence of inertinite is significant in the geological record, as it signifies that wildfires occurred at the time that the host sediment was deposited. Inertinite is a common maceral in most types of coal.

The optical properties of inertinite are very similar to those of vitrinite. They differ in that inertinite is black, whereas vitrinite is brown and visually shiny, and inertinite also has a higher reflectance than vitrinite.

### **1.2.2 Inorganic Matter (Mineral Matter) in Coal**

The term mineral matter includes all inorganic non-coal material found in coal as mineral phases and also all elements in coal that are considered inorganic (Gluskoter, 1975). The definition of the term encompasses three fundamentally different types of constituents, namely (Ward, 2002):

- Dissolved salts and other inorganic substances in the coal's pore water.
- Inorganic elements incorporated within the organic compounds of the coal.
- Discrete inorganic particles (crystalline or non crystalline) representing true mineral components.

Gluskoter (1975) mentions that most mineral matter occurs in coal as silicates, sulfides and carbonates. The most abundant minerals in South African coals are clays, carbonates, sulphides, quartz ( $\text{SiO}_2$ ) and glauconite  $((\text{K,Na})(\text{Fe}^{3+},\text{Al,Mg})_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2)$ . Phosphate minerals like apatite  $(\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl}))$  are present as submicroscopic grains except in some coals where they occur as discrete microscopic grains. They sometimes occur together with rutile ( $\text{TiO}_2$ ) and zircon ( $\text{ZrSiO}_4$ ). Common minerals in the High-veld (South Africa) coals include pyrite, kaolinite  $(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)$ , quartz and dolomite  $(\text{CaMg}(\text{CO}_3)_2)$ . The different processes in which minerals occurring in coal can be formed by are reviewed:

#### **1.2.2.1 Detrital minerals**

These are some of the minerals washed as detrital (a geological term used to describe particles of rock derived from pre-existing rock through processes of weathering and erosion) fragments into the accumulating peat deposits. These minerals occur in several forms (Ward, 2002):

- A) Mineral of epiclastic origin may include silt to sand-sized fragments of quartz and sometimes feldspar (Na, Ca,  $KAlSi_3O_8$ ) (Ward, 2002). These are minerals found in peat as a result that peat acted as a filter preventing some sediments carried in rivers and other water bodies from penetrating beyond the margins of the peat bed. Some of the quartz is thought to have been transported by water flow from the swamp margin, and some introduced to the peat by mixing with sediment of the swamp floor. Mixing of peat and swamp floor sediment is thought to have arisen from a combination of bioturbation (the displacement and mixing of sediment particles by benthic fauna (animals) or flora (plants)) and contemporaneous clastic (made up of fragments of pre-existing rock; fragmental) deposition early in the history of peat accumulation.
- B) Tonsteins are defined as materials which often consist almost entirely of well ordered kaolinite. These include sediments blown by winds into swamp. It also includes thin but extensive bands of altered volcanic ash that are found in some coal seams.

#### **1.2.2.2 Biogenic minerals**

Many of the minerals in coal result directly from biological activity in the original peat swamp (Ward, 2002). These include skeletal fragments from diatoms and other organism, minerals formed within living plant tissues and possibly minerals deposited in the peat swamp as faecal pellets. Ward (2002), observed that the siliceous skeletons of diatoms and possibly siliceous sponge spicules are abundant in a number of modern-day peat deposits. These particles are relatively soluble in water and may be corroded and partly dissolved in older peat accumulations. Shell rich bands occurring in some seams may represent drowning of the original swamp environment, with replacement of the floral ecosystem by a deeper-water faunal accumulation. Many of the plant forming modern-day peats contain accumulations of inorganic silica, oxalates and possibly also a range of other compounds such as phytoliths within the vascular structure. These minerals accumulations may be preserved within the peat or they may be released in solution with plant decay and either lost from the depositional system or re-precipitated in other parts of the peat deposit (Ward, 2002).

### **1.2.2.3 Authigenic Mineral Precipitates**

This category includes the extrinsic or introduced forms of mineral matter. These minerals may either be primarily syngenetic, meaning they crystallised within the peat deposit during the time of peat formation, or be epigenetic, meaning they could have crystallised later in the process long after initial peat accumulation into the pores, cavities and fractures of the coal. Syngenetic precipitates include siderite nodules, microcrystalline aggregates of pyrite crystals and a range of cell and pore infillings. These infillings are typically kaolinite, quartz, phosphate minerals and pyrite. Epigenetic mineralisation commonly occurring as joint or fracture infillings can include calcite, dolomite, ankerite ( $\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$ ) and siderite ( $\text{FeCO}_3$ ), sometimes pyrite, marcasite ( $\text{FeS}_2$ ), apatite, dawsonite ( $\text{NaAlCO}_3(\text{OH})_2$ ), illite ( $(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_2, (\text{H}_2\text{O})]$ ) and chlorite ( $\text{ClO}_2^-$  ion).

Pyrite is a common mineral in many coal seams, especially those associated with sedimentary strata of marine origin. Much of the pyrite is intimately associated with the organic matter as it was clearly formed during or shortly after peat accumulation. Early-formed pyrite in coal is generally thought to have been precipitated by interaction of dissolved iron and  $\text{H}_2\text{S}$  within the peat bed. The  $\text{H}_2\text{S}$  was derived from bacterial reduction of sulphate ions in the reducing environment of the peat deposit with the sulphate introduction from water, especially sea water, infiltrating into the swamp or permeating through the peat bed (Ward, 2002).

### **1.2.2.4 Non-Mineral Inorganics**

There is also a significant amount of mineral matter intimately associated with organic constituents like macerals, sometimes referred to as inherent mineral matter. Non-mineral inorganics, which are also part of the mineral matter, may be concentrated in different parts of low-rank, water-filled coal seams by post-depositional ion migration effect (Ward, 2002). Some may be held in exchangeable relationships with particular organic compounds (for example in carboxylates) and inorganic elements forming chelates and other organometallic complexes within the organic matter. Post depositional effects control the distribution of these mineral in the coal seam. These include the movement of ground water through the coal seam.

### **1.3 Trace Elements Origin in Coal**

Trace elements in coals have been defined as those elements with concentrations below 1000 micrograms per gram and are generally reported in parts per million (ppm) (Richaud et al., 2000). Coal contains a variable assemblage of elements in trace amounts. They can originate either from the initial plant material or from mixtures of organic and inorganic compounds during the first stage of coalification process. They may represent either metallo-organic compounds in the coal structure, minor amounts of a mineral with an abundance of the particular element e.g. zinc in sphalerite or major amounts of a mineral in which the element itself occurs in trace proportions for example, manganese in ankerite (Ward, 1984). They can also be components of other minerals in the coal for example silver in galena, arsenic in pyrite or in clay minerals (Stach et al., 1982).

The modern investigations of trace elements in coal were pioneered by Goldschmidt, (1975) (Babu, 1975) who developed the technique of quantitative chemical analysis by optical emission spectroscopy and applied it to coal ash. In these earliest works, Goldschmidt, (1975) was concerned with the chemical combinations of the trace elements in coals. In addition to identifying trace elements in inorganic combinations with minerals in coal, he postulated the presence of metal organic complexes and attributed the observed concentration of vanadium, molybdenum and nickel to the presence of such complexes in coal. Goldschmidt, (1975) also introduced the concept of geochemical classification of elements in which the elements are classified on the basis of their affinities and tendencies to occur in minerals of a single group. The chalcophile elements are those which commonly form sulphides (Babu, 1975). In addition to sulphur they include Zn, Cd, Hg, Cu, Pb, As, Sb, Se, and others. When present in coal, these elements would be expected to occur at least in part, in sulphide minerals. Sulphides other than pyrite and marcasite have been noted in coals but, except in areas of local concentration, they occur in trace or minor amounts (Babu, 1975).

The lithophile elements are those that generally occur in silicate phases and include among others: Si, Al, Ti, K, Na, Zr, Be, and Y (Babu, 1975). These would be expected to occur in coals in combination with the silicate minerals: Kaolinite, illite, other clay minerals, quartz and stable heavy detrital minerals. The carbonates minerals in coal

occur primarily as epigenetic fracture filling (cleat filling). Magnesium, iron, and manganese are often associated with the sedimentary carbonate minerals and would reasonably be expected to be associated with the cleat fillings in coal.

A large number of silicate, sulphide and carbonate minerals have been identified from coal seams. The constituents of these minerals necessarily occur in coals in inorganic combination. There has been some difficulty in the past to quantify the mineral composition (Valkovic, 1983). It could not be ascertained that a particular mineral occurs in the inorganic or maybe it is also present in organic association. Up to now indirect methods for investigating information about the mode of occurrence of trace elements have been employed. These methods include the density separation and leaching of coal and coal ashes. They are inexpensive, but inaccurate and remain a speculation tool which could be substantiated by the direct spectroscopic methods. The indirect methods; leaching and density separation are accepted international and used by most researchers (Huggins, 2002) as a starting point in the investigation of mode of occurrence of trace elements in coal.

Some of the chalcophile elements (Hg, As and Se) have been reviewed extensively by Yudovich and Ketris (2005) and Diehl et al. (2004) in terms of their origin and occurrence in coal. According to Diehl et al. (2004), Laser ablation analysis showed that trace elements are hosted in pyrite. Diehl et al. (2004) concluded that the deformation events allowed the introduction of trace metal rich fluids along faults, veins and in directly adjacent coal. Tectonism (is a theory of geology that has been developed to explain the observed evidence for large scale motions of the Earth's lithosphere) resulted in mega- and microscopic scale cross cutting pyrite-filled veins with attendant As and Hg assemblages. Earlier cell-filling pyrite and As rich pyrite overgrowths were likewise associated with deformation events. On a macroscopic scale, Hg and As rich pyrite is associated with faults related to Alleghanian (Lower Middle Pennsylvanian geologic time) tectonism.

Coal with early pyrite generations that were Hg- and As-poor, reacted with hydrothermal metal-bearing fluids that were focused along a North West-South-East Guizhou Province, China trending normal faults formed after significant burial of the coal-bearing units (Diehl et al., 2004). On the microscopic scale, As-rich pyrite

postdates early framboidal pyrite as well as massive pyrite that fill woody cellular structures. Thus, framboidal and massive cell filling pyrite are likely early diagenetic (process of chemical and physical change in deposited sediment during its conversion to rock.) phases. In contrast, As- and Hg-rich pyrite commonly occurs as overgrowth on the earlier generations of pyrite and as a late-stage vein-filling mineral. Mercury and As were found to be most likely in solid solution with pyrite (Diehl et al., 2004).

Mercury could be occurring in both parts of the coal as observed by several researchers including Diehl et al. (2004) and Yudovic and Ketris (2005). Diehl et al. (2004) suggests that Hg has been added epigenetically (change in the mineral content of a rock because of outside influences) to the coal matrix. They found a positive correlation between Hg and non-pyritic S that is organic S. Therefore, as it has been demonstrated by other researchers Yudovic and Ketris (2005) that the mercury is in pyrite, some of it could be associated with the organic sulphur compounds present in coal as suggested by Diehl et al. (2004). The binding of Hg by organic S compounds is well documented (Diehl et al., 2004). Organic sulphur is a very common constituent of coal, particularly coal formed in a marginal marine setting. Diehl et al. (2004) suggest that organic S may have been an early diagenetic constituent of the coal and it acted to trap Hg which was added during later epigenesis. The mechanism of trapping Hg and other trace elements by Pyrite is complex (Diehl et al., 2004). It is stated that the fluids which introduced As to Black Warrior Basin (Alabama, USA) coals were likely H<sub>2</sub>S bearing. This is because complexation with bisulfide ion (HS<sup>-</sup>) is the dominant mechanism for the transportation of As and associated trace elements in hydrothermal fluids. To precipitate the As- and Hg –rich pyrite, one potential pathway is to add Fe to this H<sub>2</sub>S bearing fluid (Eq 1).



This mechanism for pyrite precipitation in coal from hydrothermal fluids is likely because siderite (FeCO<sub>3</sub>) is commonly associated with coal beds (Stach et al., 1982). A potential link between organic S and As-rich pyrite abundance has been suggested by Diehl et al. (2004).

Yudovic et al. (2005) observed that in low-sulphur coals, which are generally poor in Hg, only two Hg sites dominate: Hg<sub>org</sub> and Hg<sub>sulphide</sub>. High sulphur coals usually contain

higher amounts of Hg, which is typically in the  $Hg_{pyr}$  form. Hg is also found in sedimentary rocks and the highly dispersive materials, mainly clays are chiefly responsible for strong Hg sorption in these rocks. Other strong mercury scavengers include Fe-hydroxides and humic organic matter. Adsorption of Hg by Fe-hydroxides is efficient in the 7-8 pH range, where most Hg exists as  $Hg(OH)_2$ , (Yudovic et al., 2005). It has been shown in other experiments that more than 90% of Hg was firmly bound to humic matter (Yudovic et al., 2005). It has also been found that plants do not concentrate mercury relative to surrounding soils, except in areas with high mercury rich soils, where ordinary birch and some other plants can be enriched in mercury (Yudovic et al., 2005). It has been noted that peat contains an order of magnitude more mercury than the plants. This shows that a large part of the Hg in the peat originated from surface waters rather than from Hg accumulated by the peat-forming plants. Some mercury could have entered peat through volcanic activities (Yudovic et al., 2005). Finkelman (1994) concluded that there is strong evidence that a significant proportion of the Hg in coal is associated with pyrite, probably of secondary origin. The occurrence of Hg in sulfide forms is indicated either indirectly (by correlation between S and Hg contents) or directly (by means of sulfides analyses). This occurrence in coal pyrite may result from several processes.

- pyrite may contain micro-inclusions of cinnabar.
- Hg can be isomorphically introduced into pyrite during its formation in hydrothermal solutions.
- due to its special electrochemical and sorption properties, pyrite can scavenge Hg from its surroundings at 200°C and higher temperatures (Yudovic et al., 2005).

Arsenic present in coal belongs to marine elements; this means that arsenic, like sulphur, may be contributed into coastal peatbogs during marine transgressions. Such a process may account for arsenic enrichment in sulphur-rich upper benches of the coal beds (Yudovic et al., 2005). Arsenic enrichment is commonly related to sulphide mineralization, either syngenetic or epigenetic. In other cases, arsenic enrichment seems to have resulted from epigenetic hydrothermal fluids, related to burial metamorphism (Yudovic et al., 2005). Yudovic et al. (2005) reports some arsenic enrichment which resulted from the ground water as input from the overlying volcanogenic strata.

There are three dominant forms of arsenic present in coal: pyritic, organic and arsenate. There is a positive correlation of arsenic to pyritic sulphur or total sulphur. This indicates the pyritic association of arsenic in coal. Finkelman (1994) determined local arsenic concentrations in later cleats within pyrite. Therefore, direct evidence of epigenetic enrichment in arsenic in syngenetic pyrites was obtained. Arsenic associated with organic matter has also been observed (Yudovic et al., 2005).

### **1.3.1 Syngenetic processes**

Syngenetic means pertaining to a primary sedimentary structure formed contemporaneously with sediment deposition.

Two types of arsenic accumulation can be established: terrigenous (those derived from the erosion of rocks on land; that is, that are derived from terrestrial environments) and volcanogenic. Strong accumulation of arsenic in lignite may be related to the proximity of Paleogene (unit of geologic time that began  $65.5 \pm 0.3$  and ended  $23.03 \pm 0.05$  million years ago) Sb-As ores during peat accumulation. A study shows that arsenic seemed to be supplied to the coal forming peatbogs by aereol waters, due to an erosion of sulfide mineralization (arsenopyrite ( $\text{FeAsS}$ ), molybdenite ( $\text{MoS}_2$ ), galena ( $\text{PbS}$ ), sphalerite ( $\text{ZnS}$ )) or due to a thermal water discharge related to late volcanism and magmatism (Yudovic et al., 2005). A second important mechanism of syngenetic arsenic accumulation is volcanism, occurring simultaneously with peat accumulation.

### **1.3.2 Epigenetic Processes**

Two types of epigenetic (produced or formed at or near the surface of the earth) arsenic accumulation can be established: infiltration and hydrothermal accumulation. It was found that the highest arsenic concentration in the Upper Permian coals are spatially related to thrust faults which are sub parallel to a regional anticline axis. It is of note that in coal-host rocks, epigenetic As-Sb-Hg-Au mineralization in the form of conformable or cutting joints with orpiment and other specific ore and vein mineral are in direct proximity to the arsenic-bearing coals. The arsenic-bearing sulphides are epigenetic (Yudovic et al., 2005).

#### **1.4 Mode of occurrence of trace elements in coal**

The mode of occurrence of an element refers to whether the element forms a specific mineral, whether it is dispersed within a particular host mineral, or in the coal macerals. The association of the element with a particular coal fraction as well as the oxidation state the element occurs in the coal are all important in describing the mode of occurrence of an element (Huggins, 2002 and Finkelman, 1994). The comprehensive understanding of mode of occurrence of trace elements in coal is reached with the understanding of the coalification process in terms of enrichment of the elements as discussed in the coal origin section. Finkelman (1994) highlights the challenge in determining the mode of occurrence of trace elements in coal as each element is unique and it is likely that not all of a particular element in a coal will be in the mode or modes suggested, nor will the element even occur in the suggested mode in every coal.

There are several techniques available for the determination of mode of occurrence of trace elements in coal (Huggins, 2002). Indirect techniques in which the mode of occurrence can be inferred includes float-sink data, statistical correlations with other elements or with other coal characteristics such as ash yield, from elements geochemical characteristics or monitoring the behaviour of the element during heating or leaching of the coal (Finkelman, 1994, Spears et al., 1999 and Huggins, 2002). Direct methods such as X-ray absorption fine structure spectroscopy, scanning electron microscopy-energy dispersive X-ray analyser and X-ray diffraction are preferred (Finkelman, 1994 and Spears et al., 1999). The main problems noted with these analytical techniques are the low levels of the elements being analysed such that often elements fall below the detection limit of such techniques. They are also time consuming, expensive and tend to favour the detection of trace elements in discrete mineral forms rather than the dispersed occurrences of the element in macerals in the coal (Spears et al., 1999 and Huggins, 2002). The concern with leaching schemes is that there is not one preferred sequential leaching scheme, but rather variations in practise, making it difficult to compare data from different leaching methods, even on the same coal. Leaching schemes are also based on assumed limited set of elemental occurrences, which brings about considerable uncertainty regarding the validity of the data obtained in such test (Huggins, 2002). Leaching of coal has been used by other researchers including Benson et al., 1998, Babu, 1975, Spears, 2001, Wagner &

Hlatshwayo, 2005, Lu et al., 2004, Feng & Hong, 1999, Ren et al., 2004, Querol et al., 1996, Goodarzi, 2002, Ohki et al., 2004, Wang et al., 2003 and Khan et al., 2002. An ideal experimental set up to investigate the mode of occurrence of trace elements in coal would be to correlate results obtained using indirect methods to those obtained using direct methods of analysis.

#### **1.4.1 Mercury**

According to cited literature, mercury is mostly associated with pyrite. Recently published data by Goodarzi (2002) on the mode of occurrence of mercury for a suite of coals indicate that mercury is mostly associated with the organic fraction of coal followed by pyrite and carbonate. Benson (1998), Finkelman (1994) and Diehl et al. (2004) found mercury to be inorganically associated in coal. In a review article, Yudovich & Ketris (2005) concluded that mercury is a very coalphile element with a strong affinity for inorganic and organic coal matter. Feng & Hong (1999) found mercury to have a good correlation with sulphur in the inorganic matter, but determined a negative correlation between Hg and the organic matter present in coal. It can be concluded with no confidence from these conflicting literature findings that mercury in coal occurs in both organic and inorganic forms of the coal.

#### **1.4.2 Arsenic & Selenium**

Spears et al. (1999) indicated the possible association of arsenic and selenium with pyrite and that they could have been enriched with pyrite from seawater source. Diehl et al. (2004) suggest that As & Se are mostly likely in solid solution with pyrite and they could have occurred during a late stage metal bearing fluid migration event in coals from the Black Warrior field Basin. Goodarzi (2002) indicates that As in coal is generally thought to be associated with pyrite, most likely in a solid solution. However, a portion of As may be organically associated or in a chelated form. Finkelman (1994) pointed out, with a high level of confidence that there is association of As in coal with pyrite, although there may be very minor As associated organically in coal. The Se is suggested by Finkelman (1994) to be associated with organic constituents in most coal. Goodarzi (2002) suggests that selenium in coal is associated with minerals such as pyrite, ferroselite ( $\text{FeSe}_2$ ) and clausthalite ( $\text{PbSe}$ ) which are absorbed in galena ( $\text{PbS}$ ), possibly in clay, on coal and some organic association. Benson (1998) found Se to be associated with the organic matrix of coal. Based on more literature in Wagner &

Hlatshwayo (2005) arsenic and selenium is associated with mostly the mineral matter of coal although selenium may have many other associations including organic association. Therefore from most literature, As & Se appears to be inorganically associated in coal.

#### **1.4.3 Chromium**

It is possible that the Cr in Highveld coals could have originated from chromite ((Fe, Mg)Cr<sub>2</sub>O<sub>4</sub>) originally found in the Witwatersrand Basin (Wagner & Hlatshwayo, 2005). Goodarzi (2002) indicates that Cr is mostly associated with clay minerals in the organic fractions and possibly with pyrite and carbonate in high sulphur coals. Ren et al. (2004) and Finkelman (1994) found Cr to be associated with the organic part of the coal. The modes of occurrence of Cr in coal can be concluded to be multiple, based on the cited literature.

#### **1.4.4 Copper and Nickel**

Ren et al. (2004) found Cu and Ni to be organically associated in lignite coals. Cu was found by Diehl et al. (2004) to be associated with pyrite. Benson (1998) found Ni to be strongly associated with clay mineral found in coal. Chalcopyrite (CuFeS<sub>2</sub>) and millerite (NiS) are the minerals thought to be the sources of Cu and Ni respectively in coal, but organic association of Cu is possible (Goodarzi, 2002 and Orem & Finkelman, 2004). Literature clearly demonstrates Cu and Ni to be inorganically associated in coal.

#### **1.4.5 Other trace elements (Zn, Pb, V, Mn)**

Sphalerite (ZnS) is the likely mineral for Zn in coal and in most cases sphalerite is found to be associated with galena (Deer et al., 1992). Pb can replace the Zn in the mineral in some cases (Deer et al., 1992). Mn and Zn have been reported to have an inorganic association (Valkovic, 1983, Babu, 1975 and Querol et al., 1995). Pb is generally associated with mineral matter in coal, particularly sulfides such as galena (PbS) and pyrite (Goodarzi, 2002). Vanadium has a dual association and may occur both with clays and organic matter in coal (Goodarzi, 2002).

### **1.5 Trace element emission during coal utilization**

Trace elements in the atmosphere occur naturally as part of the biogeochemical cycling process. Most natural and man-made (anthropogenic) release are in the form of particulate material, but a portion of the more volatile species such as mercury may exist in the vapour phase, even under ambient conditions. Natural sources include the weathering of rocks, volcanism, sea spray, thermal springs, vegetation and forest fires. Anthropogenic inputs include mining, smelting, combustion, industrial processes, agriculture, tyre wear and incineration. Both anthropogenic and natural emissions can cause local enrichment around a source, but trace elements that are deposited slowly can show enrichment on both regional and global scales (Swaine, 1997).

Major, minor and trace elements associated with coal undergo a complex series of chemical and physical transformations during coal conversion. Heavy metals and other trace elements are mobilised during coal utilization in processes such as gasification and combustion, the more volatile elements exiting with the stack gases, the less volatile with the fine particles or residual solids (chars) (Richaud et al., 2000). Although the most volatile elements such as mercury, arsenic and selenium are often found in the vapor phase of process product, there is still a vast majority of trace elements retained within the ash. In the case of combustion processes, some of these trace elements are effectively removed by existing equipment such as electrostatic precipitators (ESP) (Richaud et al., 2000). Oxygen stoichiometrics, gas composition of the flame and subsequent flue gas temperatures, particle residence times and cooling rates for example, may influence the fate of inorganic species, as will the chemical and physical composition of the elements themselves and their inter-relationships (Richaud et al., 2000).

Coal combustion contributes significantly to the atmosphere emissions of trace elements; however, gasification has minimum contribution of trace elements to the atmosphere as some of the volatile elements re-condense in the gas stream during the gas clean up process due to lower temperature and high pressures. The concentrations of trace elements present in fossil fuels vary depending on the conditions of coal origin, its rank and geological history. The partitioning is influenced by many factors, but size of combustion particles plays a dominant role, as well as the residence time. In addition to these factors that influences the mechanical partitioning, there are other factors

influencing volatility of elements. Affinity of an element to the inorganic or organic matter of coal is considered to control element volatility. Boiling points of elements and related compounds present in coal or formed during coal utilisation all contributes to volatility of an element (Klika & Kolomaznik, 2000).

The volatility behaviour of some trace elements during gasification has been reported. It is reported that Co, Cr, Ni and V condense under gasifier conditions (940-980°C, 1.3MPa), Cu, Mo, Zn mostly condense on cooling the gas stream to 600°C; Mn, Pb, and Sn on cooling to 400°C and that As, Cd, Hg and Se still exist as vapours at 400°C (Richaud et al., 2000). Richaud et al. (2000) determined that all Hg was discharged into the gas stream, and the major destination of the other trace elements was into the primary fines stream. Arsenic, molybdenum, lead, tin and possibly zinc and selenium were found in the residue, with significant losses to the gas stream. In most processes, it is often difficult to measure accurately the content of the elements present in the gas phase. Therefore, calculation is by difference of the trace elements present in feed coal, slag and fly ash. The differences can indicate those elements lost as volatiles. A slag is considered as complete melt of the mineral matter; on cooling the melt becomes a slag. Fly ash is a pozzolan which contains fine siliceous and aluminous material which reacts with calcium hydroxide  $\text{Ca(OH)}_2$  at room temperature to form compounds with cementitious properties in the presence of moisture (ASTM, 1987)

One way of abatement of trace elements in the atmosphere is to capture them before they are emitted. As it has been mentioned that some of the trace elements are emitted with particulate matter, it has been observed that the capture of particulates is dependent upon the form of the material and mode of collection. Swaine (1997) reports that up to 80% of mineral matter in coal reports to fly ash after combustion, and 20% to bottom ash. Particles less than 10 micrometers in diameter may leave via stack gases. Various researchers including Swaine (1997) have noted that trace elements concentration has a linear correlation with decreasing particle size. Electrostatic precipitation is related to the resistivity of the ash particles, as well as to particle size. Ash collected in the baghouse is related to the size of the particles and the cohesive properties of the ash dust cake. (Swaine, 1997). Knowledge of the coal chemistry is

important prior to determining the most efficient mitigation procedures (beneficiation, modifications to combustion conditions, scrubbing).

According to Clarke (1993), trace elements can be classified into 3 broad groups relating to their partitioning behaviour during combustion and gasification. Group 1 elements concentrate in the coarse and fine residues; group 2 elements are volatilised and condense downstream, concentrating in very fine particles; group 3 elements are highly volatile and are depleted in all solid phases. Hg, Br, Cl and F are considered as group 3 elements, with B, Se and I considered as borderline between group 3 and 2 (see Figure 1.8).

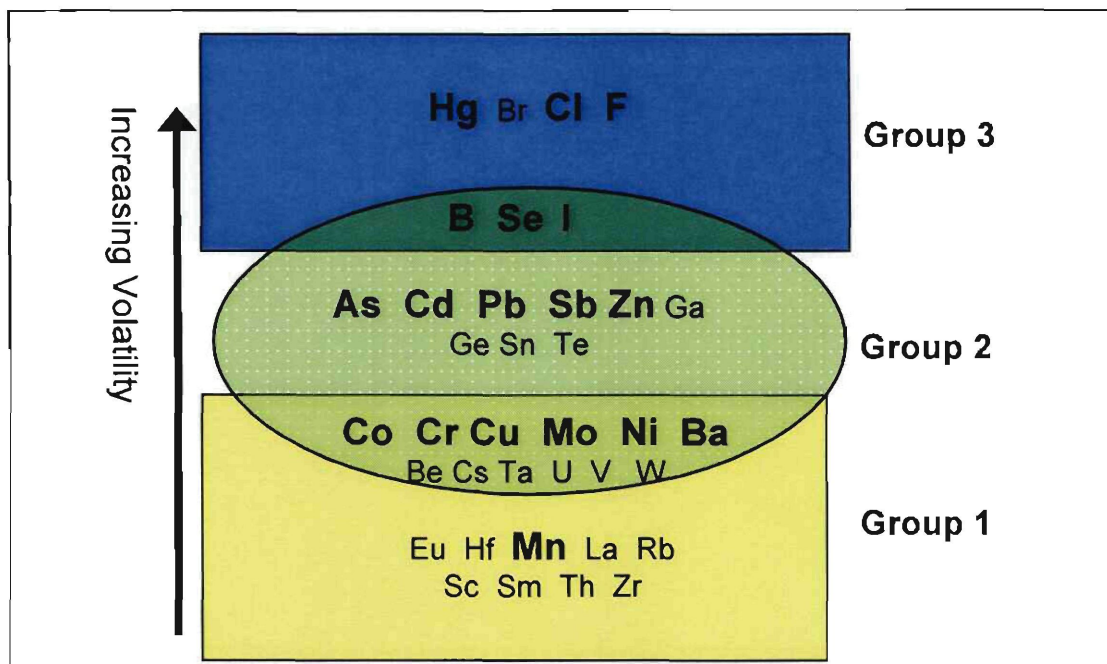


Figure 1.8: Trace elements categorization based on volatility behavior

### **1.6 Trace element emission during coal combustion**

According to the United Kingdom Department of Trade and Industry (DTI) technology status report (2004) coal combustion in utility boilers takes place at operating temperatures of over 1400°C. The coal is injected as a fine powder (less than 150µm) and ignited in suspension. As the particles are heated, volatile matter is released, char is formed and mineral matter is exposed to rapid heating and high temperatures. This exposure may result in thermal decomposition, fusion, disintegration and agglomeration of mineral matter. Any trace elements in the mineral matter may be released and dispersed among the fly ash, bottom ash and combustion flue gases

depending on the degree of volatilisation of their particular geochemical modes of occurrence. Those elements that are volatilised during combustion of the coal are carried through the high temperature regions of the furnace with the flue gases. Those elements that are not volatilised during combustion form a melt of a fairly uniform composition that comprises the matrix of both fly ash and furnace bottom ash. A portion (~20%) of this non-combustible mineral matter is retained within the furnace (United Kingdom Department of Trade and Industry technology status report, 2004).

Furnace bottom ash tends to be fairly coarse and can include massive fragments. This ash experiences extremely high temperatures (up to 1400°C from the top of the furnace) initially, but once it has fallen to the floor of the furnace it undergoes rapid cooling, remains in a fairly inert stagnant atmosphere, and is not in intimate contact with flue gas. This is important in explaining the generally low trace element content of this material. Only those elements that are completely involatile are retained in the bottom ash, the remainder is depleted to some extent. The remainder of the ash (~80%) is carried through the furnace along with the flue gases. This suspended ash is commonly known as fly ash or pulverised fuel ash (pfa). The partially and fully vaporized trace element species in the flue gas undergo further transformations and partitioning as the flue gas starts to cool in the post-combustion zone of the upper furnace and heat recovery sections of the combustion system (United Kingdom Department of Trade and Industry technology status report, 2004). As the flue gases containing vaporized trace elements and entrained ash leave the furnace and pass through to the convective section of the boiler, the temperature starts to fall. A number of physicochemical processes occur including coalescence, condensation, nucleation and agglomeration. Just prior to reaching the air heater, the flue gas temperature is approximately 400°C. After exchanging heat with the clean combustion air in the air heater, the flue gas temperature falls rapidly to approximately 130°C, resulting in further reaction and partitioning of the vapour phase species onto particulate material (United Kingdom Department of Trade and Industry (DTI) technology status report, 2004).

The volatilization behavior of trace elements based on their volatilization has been investigated and categorized, see Figure 1.8. The reality of the situation is not that simple; if elements remained completely involatile, the ash remaining after combustion

would contain the same elements as were contained in the coal, but enriched in the ash by a factor equal to:

$$100/(\text{ash yield in \%}), \text{ i.e. } [TE_{\text{ash}}] = [TE_{\text{coal}}] \times 100/(\% \text{ ash yield in coal})$$

where  $[TE]$  is the trace element concentration in the ash and coal respectively

Because specific surface area increases with decreasing particle size although not with fused particles of ash, elements that are vaporized at high temperatures and subsequently condense back onto the fly ash particles will tend to be more enriched on the smaller particles. Hence, as the emitted dust, i.e. that portion that is not collected in an electrostatic precipitator, is finer than the inlet dust, individual elements will be enriched to varying degrees, depending on their volatility. Only for B, Se and Hg is this phenomenon relatively unimportant (United Kingdom Department of Trade and Industry (DTI) technology status report, 2004).

Mercury shows extremely complex behavior on combustion and of all the trace elements, its behaviour has been studied in the great detail, United Kingdom (DTI) technology status report, 2004). The boiling point of mercury is 360°C and therefore, at typical combustion temperatures of around 1500°C, it is completely volatilised. Typical concentrations of mercury in flue gases from coal combustion range from 1 to 20µg/m<sup>3</sup>. However, the amount of mercury remaining in the vapour phase at the stack can vary widely, depending on flue gas temperatures, cooling rates, coal type, mineral association and non mineral elements and combustion conditions, particularly carbon-in ash levels. Whatever the form of mercury in the coal, elemental mercury (Hg<sup>0</sup>) is assumed to be formed immediately on combustion and until fairly recently, all was assumed to be released to the atmosphere in the vapour phase. Further investigation has shown this not to be the case and subsequent reactions with various flue gas species can result in some of the elemental mercury being oxidised to Hg<sup>2+</sup>. Both forms of mercury may also be adsorbed onto particulate matter and there is considerable evidence for affinity with carbonaceous material. The behaviour of Hg<sup>0</sup> and Hg<sup>2+</sup> in downstream flue gas cleaning equipment is quite different, and in order to develop effective control strategies, it is necessary to try to predict relative proportions of each (United Kingdom Department of Trade and Industry (DTI) technology status report, 2004).

Results obtained from the United States Environmental Protection Agency's Information Collection request Centre (EPA ICR) in 1999 indicated that coal containing low levels of chlorine results in flue gas where elemental mercury ( $\text{Hg}^0$ ) predominates. However, flue gases from coals containing high chlorine ( $>500\mu\text{g/g Cl}$ ) have a much higher proportion of oxidized mercury ( $\text{Hg}^{2+}$ ). Generally, combustion of bituminous coals gives an approximately 50:50 split of  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  in the emitted flue gas. Although the major reaction pathways for mercury during coal combustion are known with some degree of confidence, it is not yet possible to make quantitative predictions of the emission of specific mercury species from coal-fired power plant. The ultimate aim is to develop a predictive model so that emissions of total and specific mercury species can be formulated. During recent years, progress in this area has been rapid with mechanisms being developed for homogeneous oxidation reactions involving primarily chlorine species, followed by combination with heterogeneous oxidation reactions involving carbon-in-ash and transition metals, (United Kingdom DTI technology status report, 2004).

### ***1.7 Trace element release behaviour during coal pyrolysis***

As pyrolysis is one important step in coal utilization; the release behaviour of trace elements has been investigated during this process, (Zajusz-Zubek and Konieczynski, 2003, Sugawara et al., 2002 and Wang and Tomita, 2003). In a gasification process pyrolysis is believed to take place in an oxygen depleted atmosphere at a temperature of up to  $700^\circ\text{C}$  forming combustible compounds that are suitable for fuel gas (Slaghuis, 1993). Pyrolysis is one of many steps taking place during gasification, which contributes significantly to the transformation or behavior of trace elements. In literature it is understood that the behavior of trace elements during pyrolysis is affected by various chemical factors such as the mode of occurrence, the interactions with bulk ash and the affinity to chlorine, fluorine and sulphur (Wang, Sharma and Tomita, 2003). The studies conducted by different researchers (Zajusz-Zubek and Konieczynski, 2003, Sugawara et al., 2002, Wang and Tomita, 2003 and Guo et al., 2002 and 2004) cited below on behavior of trace elements during pyrolysis are discussed:

Zajusz-Zubek and Konieczynski, (2003) investigated the dynamics of trace element (As, Be, Cd, Mn, Ni, Pb, Hg and Se) release in a coal pyrolysis process. Samples of coal and solid carbonisation product obtained at four temperatures: 400, 600, 850 and 1000°C were tested on account of the contents of trace elements. The temperature levels correspond to the stages used in the coal coking theory. Dynamics of trace elements release was measured by comparing their concentrations in a coal sample and in the carbonisation product obtained at the temperature levels indicated. Approximately 1 g of crushed coal (below 0.2 mm) sample were placed in a crucible, covered with a lid and placed in a muffle furnace that has been preheated to the required temperature level. The samples were heated at this temperature without any air supply for 15 min. The end samples were then prepared for trace element analysis and ultimately verified by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

Results showed good repeatability for some elements at other temperature levels. The results showed an inverse relationship between the content of the element and the temperature in the solid carbonisation product. The release rate observed is highest for cadmium, mercury and lead mean for selenium and lowest for nickel, manganese, arsenic and Beryllium. It is interesting in this experiment to observe a discrepancy of the behaviour of arsenic as least volatile, yet literature cited (Wang and Tomita, 2003) indicate that arsenic is among the highly volatile elements. In this experiment it is still classed as the least volatile after 1000°C.

Sugawara et al. (2002) investigated the dynamic behaviour of trace elements during pyrolysis. Release behaviour of sodium and potassium was investigated during pyrolysis of coals in a nitrogen stream up to 1200°C. The coal samples were heated in a fixed bed reactor with infrared gold image furnace under nitrogen at 20°C/min up to 1200°C. Nitrogen gas flow rate was maintained at 600cm<sup>3</sup>/min. The extent of release for sodium was about 3%. Potassium release almost attained to the constant over 800°C.

Wang and Tomita, (2003) investigated the vaporisation behaviour of nine selected trace elements including (Be, V, Cr, Mn, Co, Ni, Zn, As and Pb) during coal combustion and pyrolysis below 1150°C in a laboratory experiment. The pyrolysis experiment was

conducted in two parts with a slow heating rate and a high heating rate. In the slow heating rate pyrolysis, 1.5 g of coal sample was loaded on an alumina boat and heated in a nitrogen flow of 1.5 dm<sup>3</sup>/min from room temperature to 950°C at 10°C/min and then to a higher temperature at 5°C/min and held at final temperature for 1 h. In the rapid heating experiment; the furnace was first heated to 1150°C and then the coal sample was pushed through and held at that temperature for 1 h while the nitrogen gas was flowing at 1.5 dm<sup>3</sup>/min.

The trace elements analysis in the samples; coal, char and ash were performed on an ICP-AES. In both experiment (slow and rapid heating rate), arsenic appeared to be retained in the char during pyrolysis. This behavior of arsenic matches the behaviour of arsenic observed by Zajusz-Zubek and Konieczynski (2003) which is in disagreement with the known volatility of arsenic. Zinc and lead in both experiments volatilised above 950°C. The other elements including Be, Mn and Ni showed nearly no volatilization during pyrolysis, which is in good agreement with the release behavior of trace elements observed by Zajusz-Zubek and Konieczynski (2003) for the same elements. The results in both slow and rapid heating rate experiment appears to not differ which indicate that heating rate has minimal influence on the volatility of trace elements. The holding time of the samples at a particular temperature also appears to have minimal effect after 15 min. This is observed when comparing release behaviors of trace elements in Zajusz-Zubek and Konieczynski (2003) and Wang and Tomita (2003). This point is in contrast with observation of Guo et al. (2003) where it is observed that holding time and atmosphere greatly influence the release behavior of trace elements during pyrolysis. The atmosphere of the experiments appears to have not influenced the release behaviour of trace elements. Zajusz-Zubek and Konieczynski (2003) conducted the pyrolysis experiment without air while Wang and Tomita (2003) conducted it under nitrogen atmosphere. The fact that Wang and Tomita (2003) experiment was at 150°C higher than Zajusz-Zubek and Konieczynski (2003) did not introduce any significant difference in the final result of release behavior.

Guo et al. (2002) investigated the transformation behaviour of trace elements (As, Pb, Cr and Cd) during pyrolysis of coal at temperatures up to 1000°C. Preparing the coal sample involved crushing and sieving through a 0.16 - 0.27mm, then drying under vacuum at 110°C with a nitrogen purge. Pyrolysis experiment was conducted in a fixed

bed quartz reactor under N<sub>2</sub> or H<sub>2</sub> stream at a heating rate of 20°C/min in the temperature range of 500 – 1000°C. Trace element analysis in the coal and char was conducted using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

The results by Guo et al. (2002) show arsenic to be released at temperatures below 500°C in both atmospheres. This is in sharp contrast to the non-release behavior of arsenic as observed by Zajusz-Zubek and Konieczynski (2003) and Wang and Tomita (2003) at much higher temperatures of about 1000°C. Elements such as Pb and Cr were released at much higher temperature in this experiment. Lead was among the highly volatile elements in Zajusz-Zubek and Konieczynski (2003) studies while it was released at above 950°C in Wang and Tomita (2003) studies. Cr showed nearly no volatilisation in Wang and Tomita's (2003) experiment.

According to Wiley in Ullmanns, 6<sup>th</sup> edition, (2002) the atmosphere appears to have significant effect on the release behavior of trace elements. The bleeding ratios of elements are higher in H<sub>2</sub> atmosphere than in N<sub>2</sub> atmosphere. The effect of the hydrogen atmosphere can be construed to the stabilisation of the breaking fragments with hydrogen, which gives rise to primary volatile products and favours a high yield of gases and liquids (Wiley in Ullmanns, 6<sup>th</sup> edition, 2002)

Guo et al. (2004) investigated the transformation behaviour of selected trace elements (Na, K, Pb and Mn) during thermal treatments under different temperatures, pressures and atmospheres. The experiments were conducted in a pressure reactor, which was placed in a muffle furnace for the period of the experiment. Pyrolysis experiments were carried out for 2 min on a 5 g coal sample at maximum 700°C. The content of the trace elements in the samples; raw coal and char was measured using ICP-AES. The results show that all the elements slightly decreased in the chars with increase in pyrolysis temperature. The observed behaviour of Na is in agreement with results obtained for this element by Sugawara et al. (2002). In Sugawara et al. (2002) studies, Potassium almost attained a non-release behaviour at temperatures above 800°C. Lead in this experiment show a very slight release behaviour. This is in agreement with observations by Wang and Tomita (2003) that it was released only at temperatures above 950°C, which is in contrast with observation by Zajusz-Zubek and Konieczynski,

(2003) that lead is among the most volatile element. Manganese has been found to be non-released in all experiments conducted.

The atmospheres appear to have influenced the released behavior of the trace elements. The H<sub>2</sub> atmosphere released more of the elements as compared to N<sub>2</sub> and CO<sub>2</sub> atmospheres, with CO<sub>2</sub> being the least to influence release behavior. As it was stated earlier in this chapter this finding compares well with results obtained by Guo et al. (2002).

Effect of pressure appears small on the release behavior of trace elements during pyrolysis. The important steps that may affect the release of the elements are breaking of chemical bonds and transfer of volatiles from coal pore to the gas phase.

### ***1.8 Trace element partitioning behaviour during gasification***

Gasification is the conversion of coal into a combustible gas that can be classified by pyrolysis and heterogeneous reactions (Slaghuis, 1993). Gasification can be considered to be a more amenable coal utilization process with regards to the environmental impact compared to combustion. Relatively poor quality coal is used for combustion and gasification applications in South Africa (Hlatshwayo and Wagner 2005). Coal as primary feedstock is gasified at a typical pressure of 30 bar in the presence of steam and oxygen (as gasification agents) to produce a gas suitable for a variety of applications.

Data regarding the behaviour of trace elements in gasification is limited, and most behaviour has been inferred by analogy with combustion studies and combined cycle processes. The significant difference between combustion and gasification is the reducing environment associated with gasification versus oxidising environment associated with combustion environment, which may result in different behaviour of volatile species. The particle size of coal fed in the gasifier is of multimodal distribution with a top size of about 75mm. The combustion plant in most cases is fed with fine material of less than 6mm. Some articles referring to trace element behaviour during gasification are summarized:

- Baker (1994) working on a Shell coal gasification combined-cycle power plant, concluded that, in general, trace elements were tightly bound in the inert slag and fly ash, with low levels of hazardous air pollutants (HAP's) in the syngas.
- Reed et al. (2001) working on a pilot plant gasifier, determined that Hg and Se were only detected in the fuel gas, whilst Cd and Pb were concentrated in the fine dust removed by the hot gas filter.
- Helbe et al. (1996) working on a laboratory-scale entrained flow gasifier, indicated that considerable trace element volatilisation occurs during coal gasification.
- Richaud et al. (2000) reported that Co, Cr, Ni and V condense under gasifier conditions (940-980°C, 1.3MPa), Cu, Mo, Zn mostly condense on cooling the gas stream to 600°C; Mn, Pb, and Sn on cooling to 400°C and that As, Cd, Hg and Se still exist as vapours at 400°C. It was determined that all Hg was discharged into the gas stream, and the major destination of the other trace elements was into the primary fines stream. As, Mo, Pb, Sn and possibly Zn and Se were found in the residue, with significant losses to the gas stream. If the trace elements in feed coal, slag and fly ash are determined, the differences can indicate those elements lost as volatiles.

### 1.9 Trace element content comparison in Lignite and sub-bituminous coal

Table 1.1: Trace element analysis in Lignite coal compared with sub-bituminous coal (Sasol internal report on gasifier digout for lignite coal, 2007)

Trace metals	Method	Sub-bituminous coal (Coal B)	Lignite coal
		mg/kg	mg/kg
Hg	CVAA	0.20	0.08
As	AES	4.41	
Se	AES	0.75	
Ba	AES	461.5	15
Cd	AES	1.06	<1
Co	AES	8.50	3.0
Cr	AES	33.29	9
Cu	AES	13.99	13
Mn	AES	101.5	107
Mo	AES	0	<1
Ni	AES	17.23	3
Pb	AES	6.45	<1
V	AES	30.77	6
Zn	AES	9.82	4

### 1.10 Modeling of trace elements during coal processing

Experimental measurement of the behaviour and distribution of trace elements during coal utilization either during gasification, combustion or pyrolysis proves to be a difficult task. This is because of the very low levels in which they exist in the coal as explained earlier. Methods of computational thermodynamics have been used for the investigation of various processes and the development of new technologies for many years. Now there is no need to prove the practical value of calculation of equilibrium composition and properties of thermodynamic systems. There is a wide range of field of science where thermodynamics calculations have proven to work best:

- development of the new high-temperature technological processes;
- the optimization of chemical processes, including synthesis of refractory materials and materials of microelectronics;
- examination of stability of materials at high temperatures and in various media;
- investigation of the chemical processes occurring in power-generating facilities, including the nuclear plants;

- the study of the emissions of burning products and industrial exhaust gases into the atmosphere;
- development of the processes preventing environmental pollution;

In all the processes the thermodynamics calculation has yielded results, which are close to reality at a very short time. The cost of experimental work, which in most cases is very expensive, is exponentially reduced by performing calculations. It should be noted that although predictions of this type can be performed cheaply, they serve as a guide because in some cases it is difficult to attain equilibrium. Kinetic influence has to be considered in some occasions.

The basic concept of thermodynamics is thermodynamic equilibrium. Thermodynamic equilibrium is some final state of a thermodynamic system insulated from the external medium, where  $\Delta G=0$ , when  $\Delta H - T\Delta S = 0$ , that is, there exists thermal, mechanical and chemical equilibrium in each point of the system and there are no flows. In practice, the requirement of isolation means that the processes leading to equilibrium occurs faster than the changes on the system's boundaries (external change of pressure, temperature and chemical composition, etc.) take place. In an equilibrium model it is assumed that the system being modeled has infinite time to reach equilibrium. The result of modeling depends on many parameters of which the software for the model is usually supplied with a database on thermodynamic properties of substances. A thermodynamic model may include the following components:

- two thermodynamic parameters with their values that specify thermodynamic equilibrium;
- list of chemical elements and their amount in the system;
- list of substances that form the system examined;
- thermodynamic properties of substances;
- equations of state of the phases, and, first of all, the equation of state of the gas phase;
- distribution of substances among possible phases, possible existence of condensed solutions;
- assumptions concerning the behavior of the condensed solutions if there is any

To validate the results of a model, it is necessary to obtain experimental data where possible and compare these results with the results of calculation. Key questions to address when performing a model are

- is there thermodynamic equilibrium in the system examined?
- are the components of the model used valid?

Based on the knowledge of the system being model, exclusion of some substances in the result generated may be applied provided there is supporting evidence that such substances cannot form in the real system. There is also a possibility of assigning concentrations for one or several substances if there are some grounds to do that. This is all done when the specific behaviour of the system caused by the chemical kinetics of the system is taken into account. There exists the need to understand the system one is working on. Several researchers including Reed et al. (2001), Thompson and Argent (2002) and Yan et al. (2001) have applied thermodynamic modeling in coal gasification and coal combustion processes:

A modeling package consists of:

1. user interface for inputting initial species and conditions and introducing user induced changes.
2. database of thermodynamic properties for a large number of species
3. methods of data storage and data exchange formats;
4. methods of data access in the databases, which provide the possibility of data import and export, and presentation of thermodynamic information in table and graphical forms
5. calculator module using proprietary algorithms
6. creation of new thermodynamic models and perfection of existing ones
7. methods of analysis of the results of thermodynamic calculations;
8. methods of evaluation of model parameters' uncertainties upon the results of calculation of equilibrium composition;
9. methods of thermodynamic and thermochemical class libraries to facilitate the execution of such routine procedures as data storage, calculation of thermodynamic functions of a substance or thermodynamic properties of chemical reaction for assigned pressure and temperature, etc.

Modeling packages often cannot incorporate reaction rates or surface effects. They can handle non-ideal conditions. The quality of the results is dependent on the quality of the thermodynamic data and the number of species available.

Reed et al. (2001) predicted the speciation of trace elements in the fuel gas from a gasifier comparing result with experimental findings from a 2 Mt (metric tones) gasifier pilot plant. The thermodynamic equilibrium model used in the work was a MTDATA (software package) version 4.60. This model applies an ideal gas-phase model and a pure substance model for each condensed phase (assumes no mixing of condensed phases). The systems modeled were selected to represent the hot gas filter test conditions used in the experimental work conducted by Reed et al. (2001). The experimental conditions were such that the gasifier bed temperature was at maximum 960°C, pressure of maximum 13 bar with the hot gas filter temperature at maximum 580°C. The trace elements composition was taken as the total of the amounts measured in the hot gas filter fines and fuel gas. During modeling global equilibrium of all the components in the system was assumed. Thermodynamic predictions were generated for the speciation of As, B, Be, Cd, Co, Cu, Pb, Sb, Sn, V and Zn. The non-volatility of Be, Co, Cu, V and Zn under gasification conditions was predicted by equilibrium modeling calculations and confirmed by experimental data. The elements As, B, Cd, Pb, Sb and Sn were all predicted to form larger amounts of gaseous species than measured experimentally.

Thompson and Argent (2002) predicted the equilibrium distribution of major, minor and trace elements in Pittsburgh No 8 coal for gasification under conditions of the Prenflo gasifier using the FACT and MTDATA predictive programs. The observed experimental results were compared with the predicted distribution in which general agreement was found with regard to the trace elements. The modeling conditions are such that the gasifier is modeled as two regions: in the first the temperature is 1127 - 2027°C and the reacting mixture consists of the coal, carrier added steam and oxygen. The second region equilibrium mixture from the first is quenched by addition of an equal amount of the cooled, dried product gas then cooled in -263°C steps from 800°C to 200°C. The final result was to group the elements into those which are virtually immobile (Cr, Ni, Ba, Mn, V), somewhat mobile (Mo, Cu, Be), mobile (Sb, B) and almost totally mobilized

(As, Cd, Pb, Tl, Sn, Zn). Such grouping from prediction was also found to be consistent with experimental findings from relative abundances in slag and fly ash.

In an underground coal gasification process, a thermodynamic equilibrium study of trace elements (As, Se, Pb, Ni, Cd, Cr, Sb) was conducted (Liu et al., 2006). The agent inputs were air, oxygen and steam in varying proportions as based on technical parameters during underground coal gasification. Temperatures selected for the system ranged from 0 - 1600°C and the pressure was up to 150bar. Ni and Cr were found to be hardly volatile. As, Pb, Cd, Sb totally or partially occur in the gas phase in the underground gas cleaning system. Se present in gas phase in the form of  $H_2Se_{(g)}$ . As appears difficult to volatilise in the presence of potassium due the formation of  $K_3AsO_4$ , which is less volatile. For some of the elements, pressure played a role in their volatilization behaviour.

The volatility behaviour of some elements like mercury has been found to be the same in both gasification and combustion models. Yan et al. (2001) found mercury to volatilize 100% in a model of a coal combustor.

### ***1.11 South Africa's coal geological setting and typical coal properties***

South Africa has approximately 75% of the coal resources in Africa (Figure 1.9). Of the nineteen coalfields in South Africa (Figure 1.10), the Highveld coalfield (number 12 in Figure 1.10) is one of the nine currently producing, and is second largest in terms of production. The Highveld coalfield in South Africa is located in the province of Mpumalanga approximately 200km south-east of Pretoria, due south of the Witbank coalfield. The Vryheid Formation of the mid Permian (Ecca Group) of the Karoo Supergroup hosts the sedimentary succession in which the coal deposits of the Highveld coalfield occur (Falcon, 1986). Coals in this sequence were deposited in the Karoo Basin in a cool to warm deltaic environment with run-off water originating from the retreating glaciated highlands to the north (Figure 1.11). The coals from the Highveld coalfield are typically low rank bituminous (mean %RoV around 0.58 to 0.65). Permian coals of the southern hemisphere are generally considered to contain lower sulphides, chlorine and trace elements and have higher ash and inert organic matter than carboniferous coals of the northern hemisphere (Falcon, 1986). It has been in the

South African coal fields that generally the rank or carbon content of the coals increases eastwards while the number of seams and their thickness decrease. Thus, Mpumalanga and Northern Province coals are usually classified as bituminous, occurring in seams up to several meters thick, while KwaZulu-Natal coals are often anthracitic and are found in relatively thin seams. Most of South African coals are of a bituminous thermal grade; only two per cent is anthracite, and 1,6 per cent coal of metallurgical quality (Chamber of mines South Africa, in Department of energy and minerals, 2007).

The composition of South Africa coals reflect changing palaeo environments, from glacial to deep marine, deltaic, fluvial and aeolian during the Permian (Falcon, 1986). The fluctuating water levels and salinity levels, varying temperatures, humidity, rainfall and differing plant communities affected the geochemical environment during coalification, influencing the organic and inorganic affinities of trace elements in coal (Cairncross et al., 1990). Ion exchange between mineral matter and macerals following coalification gives added complexity to establishing the distribution of trace elements in coals (Bushell & Williamson, 1996). Penetration of the South African coal-bearing sequences by igneous intrusions after coalification may have also influenced the geochemistry of the coals.

The Highveld coal seams have a similar nomenclature to those of the Witbank Coals, the seams being numbered from the base upwards in chronological order from seam 1 to 5 (seam 6 rarely occurs). The number 4 lower seam (No 4L) is the main pay zone, and is reasonably well developed throughout the Highveld area, ranging in thickness from 1 to 11m. High ash content typifies the upper sections of the seam. Generally the in-situ coal qualities of the Highveld coals are lower than those of the Witbank coals, and export coals are not typically generated in this basin (although 2 mines are currently exporting a washed product). Dolerite intrusions (sills and dykes) have disturbed the region and have caused localized devolatilisation of the coal, resulting in mine planning and development problems. The No 4L Seam is characterized by ubiquitous laminae and thin mudstone beds which are mined (Pinheiro, 2000). Kaolinite dominates the mineral matter composition of the No 4L seam (43.7%), followed by quartz (24.7%), pyrite (8.5%), calcite (7.82%) and dolomite (7.1%) (Buhmann, 1991) based on 100% crystalline phases in the coal.

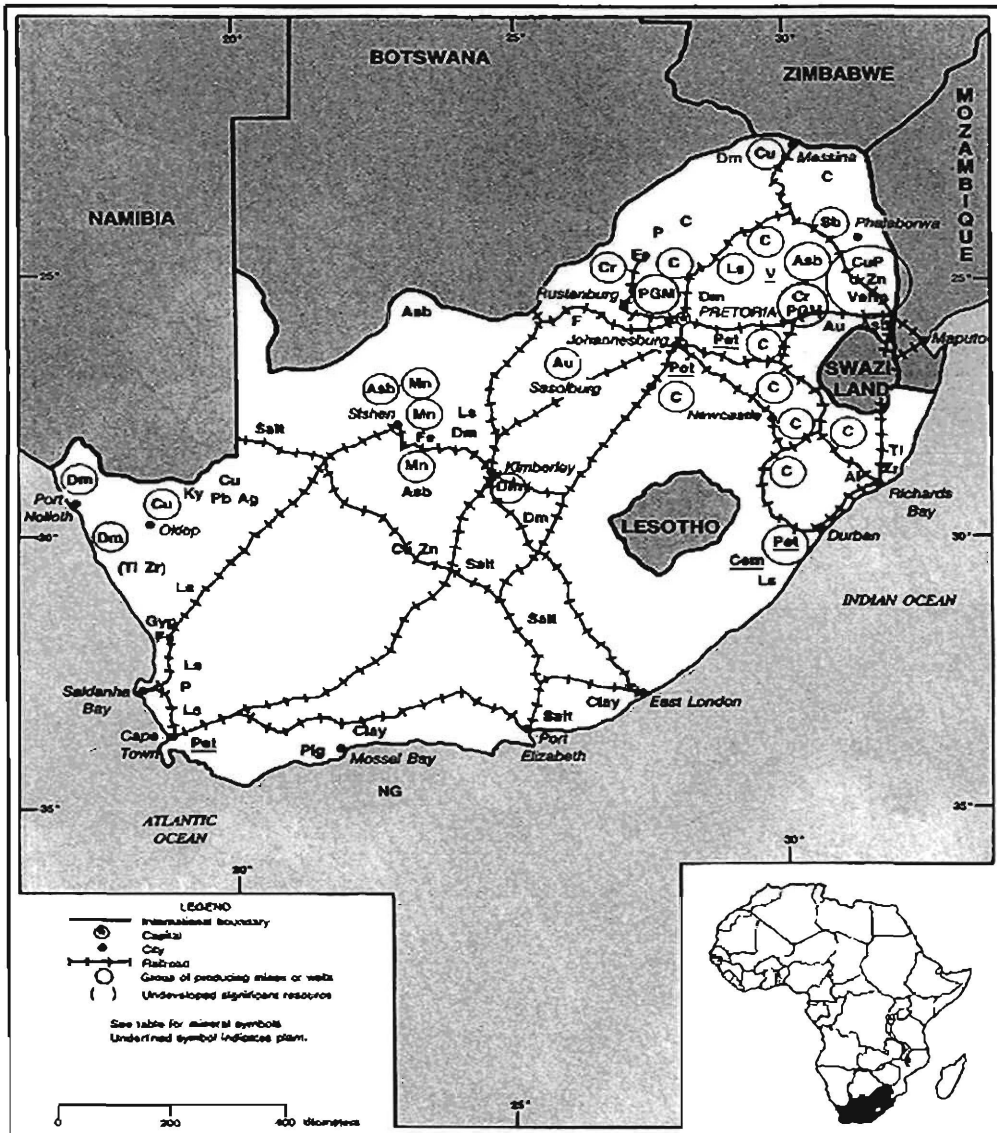


Figure 1.9: Location of mineral deposits in South Africa

© = coal

Source: <http://minerals.usgs.gov/minerals/pubs/country/maps/92359.gif>

Downloaded 04/01/2005 (Wagner and Hlatshwayo, 2005)

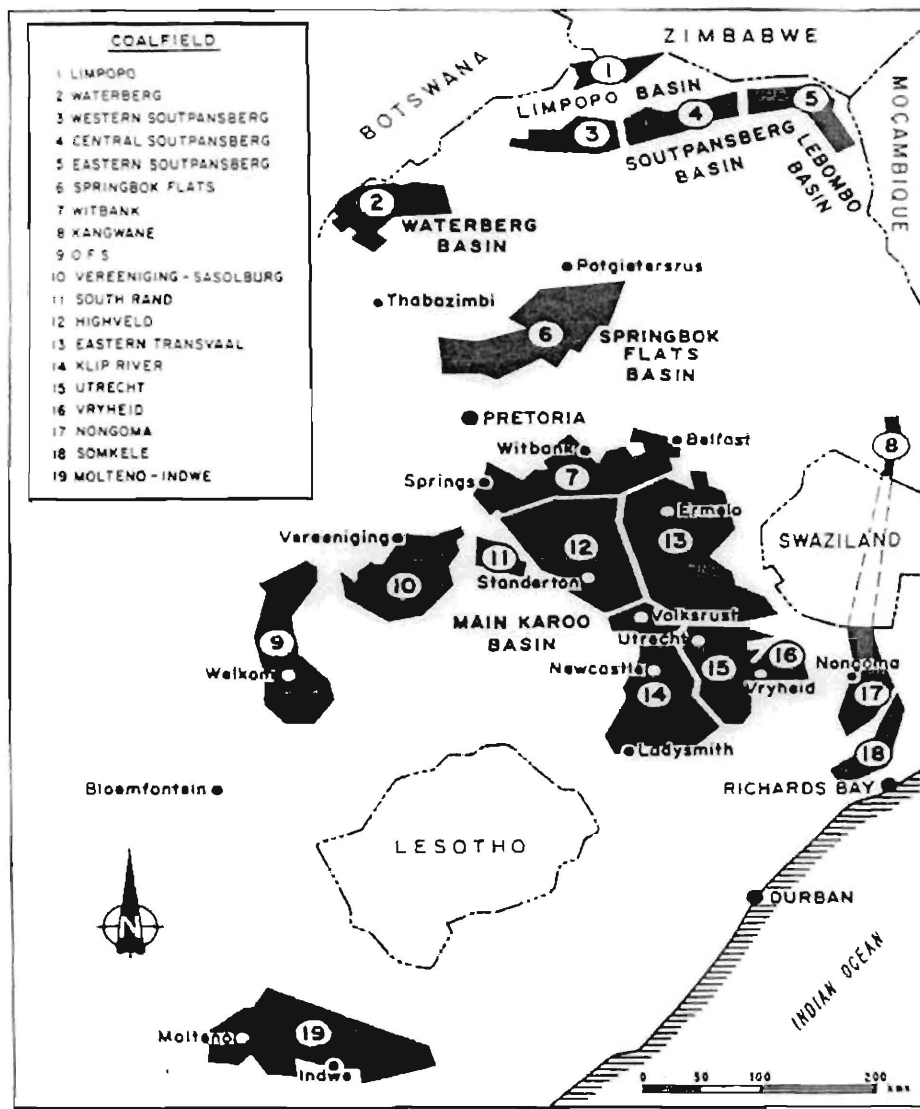


Figure 1.10: Coalfields of South Africa (Wagner and Hlatshwayo 2005)

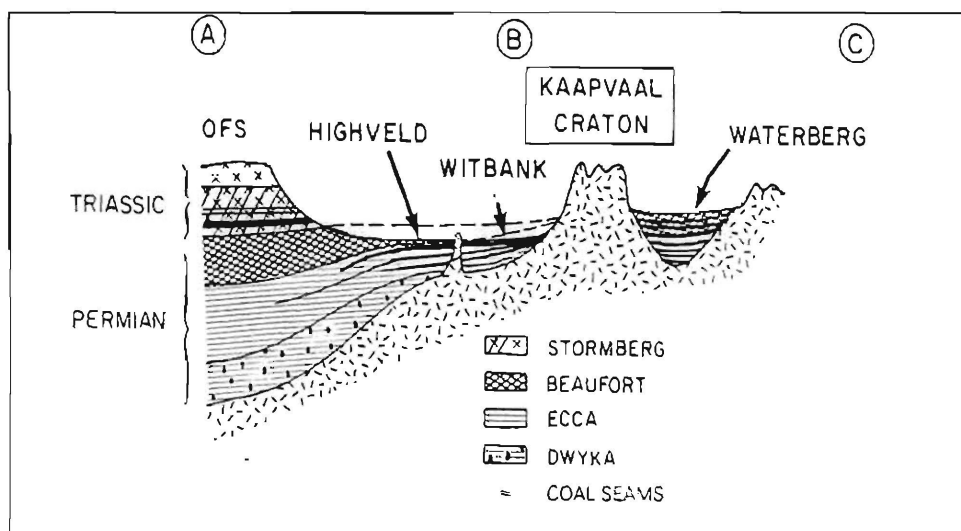


Figure 1.11: Sedimentary succession Witbank-Highveld Coal field (Source: Falcon, 1986)

Coal is the primary fuel produced and consumed in South Africa. Only one-third of coal produced in South Africa is exported, primarily to the European Union (EU) and East Asia. South African collieries range in size from small operations with output limited to a few thousand tons of coal per year to the Highveld coal field, the world's largest underground coal mining complex, which has an annual production of about 35 million tons. Almost 90 per cent of the country's saleable coal is mined in the Mpumalanga (Chamber of mines South Africa, in Department of minerals and energy, 2007).

According to the Department of Minerals and Energy (2006) around 40 per cent of coal comes from opencast operations, some of which have recovery rates approaching 90 per cent. The South African coal mining industry is also supported by a large domestic market as well as having a strong international position.

- About 40% of all bituminous coal produced in South Africa is used in the generation of electricity (mainly Eskom), making this industry the largest single user of coal in the country, using about 61% of country's coal used local.
- The second major coal user is Sasol Lurgi Fixed Bed Dry Bottom gasification process, in which low grade coal (ash of about 20 – 30%) is used accounting for 23% of the county's coal used local (Department of Minerals and Energy, 2006).
- Other significant domestic users are Iscor's metallurgical plants (the steel industry requires coking coal to be prepared in coke ovens to provide metallurgical coke capable of reducing and melting iron ore to liquid iron in blast furnaces), accounting for 4% of the country's coal used local.
- 8% for general industry
- 4% is purchased by merchants and sold locally or exported

Environmental concerns pose the main challenge to coal as energy source. Particulate and trace elements emissions from household and industry utilising coal and the mining activities to extract coal impact negatively on the environment. (Department of Minerals and Energy, (DME), 2006)

### **1.12 Synopsis**

This chapter provides understanding of the geological formation of coal in terms of the depositional environment required including the South African context of coal formation

in the Karoo region. The chemical structure of coal appears to have not been altered with major changes when compared to earlier investigations. There has been an addition to the number of aromatic rings and heteroatoms. The difficulty of coming up with the true structure of coal still exists, because none of the structures observed shows the exact location of the trace elements.

Based on coal origin information, trace elements appear to be associated with the mineral matter of coal. According to mode of occurrence of trace elements research, most trace elements are associated with the mineral matter especially the pyrite, but some are found to also exist in the organic matter of the coal. It should be highlighted that results of mode of occurrence of trace elements are specific only for that coal being investigated. Therefore the need arise to look into the occurrence of trace elements in South African coals. Some disagreement in this area of investigation can be due to the different analytical methods, like the different leaching schemes being used makes it difficult to compare results even for the same coal. A universal analytical method needs to be developed.

There has been good agreement in the volatility behaviour of some trace elements during coal utilisation. Mercury appears to be the most volatile element during most coal utilisation process. There is still some speculation with regard to the species emitted for these trace elements; which the use of the impinger/ scrubbers (Ontario Hydro Sampling train) method maybe able to address. The use of modeling packages also gives a better speculation of the form and partitioning behaviour of trace elements. The volatility behaviour of trace elements during pyrolysis appears to be a challenging task. As observed in the literature, there are contrasting results with regard to the influence of the heating rate, holding time and atmosphere. Such arguments, again provides good bases for more research especially modeling the pyrolysis system. Again direct comparison of results is not always possible as the experiments are not conducted on the very same coal and the experimental setup is not the same. Although much research has been reported the point of convergence is that:

- For environmental impact assessment, the trace elements released must be known in both their quantity and chemical form.
- Reports send a confusing message with regard to the release behaviour of trace elements during coal utilization.

- The low content level of the trace elements in the coal and in the resulting streams makes the experiments or analytical techniques unreliable.
- Equilibrium modeling might be a useful tool in addressing some of the disagreement as it will employ universal data for the calculations.

# CHAPTER 2

## Experimental

### Chapter Summary

This chapter is divided into two sections. The first section outlines the general analytical methods used for coal characterisation and trace elements analysis in coal. Comparison of these analytical methods is presented discussing their advantages and disadvantages. The second section focuses specifically on methods employed in this work citing reasons behind their selection. The general information on the coal used in this project is also provided. The modeling experiment is also presented.

### ***2.1 Analytical Techniques for Identifying Trace Elements in Coal & its Products***

It has been observed that there are no international standard methods for the determination of trace elements in coal (Dale and Riley, 1995). Therefore there is a need for developing accurate and reliable methods for determining trace elements of environmental concern in coal and its products. Such methods should be sophisticated and based on modern techniques and have the necessary sensitivity to reliably and accurately specify the levels of all key environmental trace elements (Dale and Riley, 1995). It has been observed that a major consideration in the determination of trace elements concentration in coal and other materials is the sample preparation technique (Wagner and Hlatshwayo, 2005). Further, it should be acknowledged that there is a huge difficulty in obtaining results especially repeatable results of trace elements in coal due to the nature of their occurrence as well as the low level of the order of parts per million in which they occur. The heterogeneity of coal also complicates matters even more as it is often difficult to repeat an experiment with similar coal that has the same concentration of trace elements.

Huggins (2002) has compiled a review of analytical methods that can be used to identify inorganic constituents in coal. According to Huggins (2002), analytical methods for analysis of inorganic components in coal can be divided into the following categories (Figure 2.1):

- (i) Methods that measure elemental concentrations in the coal (or ash)
- (ii) Methods that determine mineralogical components

(iii) Methods that determine elemental modes of occurrence

It is worth mentioning that each of these three types of analyses provides different information about inorganic components in coal and that, to understand fully the behaviour of a specific entity in coal utilization may require data from each type of analysis as there are limitations associated with each instrument. As observed in Figure 2.1, a variety of methods for determination of trace elements in coal and its by-products are available.

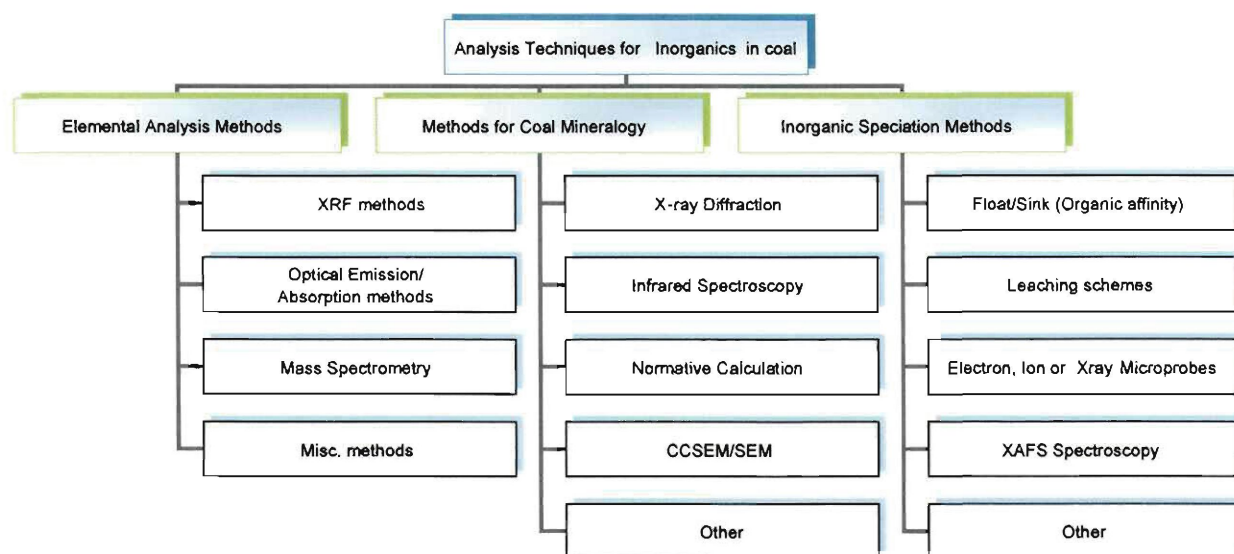


Figure: 2.1 Subdivision of analytical techniques for inorganics in coal (*modified schematic representation from Huggins, 2002*)

In the reviewed literature, several combinations of instrumental techniques for trace elemental determination have been noted; a common selection being the combination of X-Ray Fluorescence Spectroscopy (XRF), X-Ray Diffraction (XRD) and ICP-AES/MS techniques (Huggins 2002 and Querol et al., 1996, 1995).

The sample analytical techniques reviewed and used in this work are:

- Inductively Coupled Plasma Atomic Emission Spectroscopy or Mass Spectrometry (ICP-AES/MS)
- Cold Vapour Atomic Absorption Spectrometry

The sample preparation (solution preparation) techniques reviewed and some used in this work are:

- Microwave oven digestion

- Conventional Ashing and digestion methods

## **2.1.1 Sample Analysis Techniques**

### **2.1.1.1 Inductively Coupled Plasma Atomic Emission Spectroscopy or Mass Spectrometry (ICP-AES/ MS)**

ICP-AES/ MS are regarded as the preferred analytical techniques for the determination of trace elements concentration in solution. As ICP typically require solutions for analysis, the trace elements in solid samples require extraction via destructive digestion or dissolution techniques. These solution preparations are a major concern in trace element assessments.

The ICP-AES is a multi–element analysis technique that dissociate a sample into its constituent atoms and ions. The atoms are excited to a higher energy level and when they return to ground state, they emit photons of a characteristic wavelength. The radiation is detected and converted into electronic signals that are further converted into concentration information. There are several **advantages** of ICP–AES including other methods based on plasma source:

- Lower inter-element interference, which is as a results of their high temperature.
- Good spectra can be obtained for most elements under a single set of excitation conditions; therefore multi element analysis is possible.
- They permit the determination of low concentration of elements.
- Permit the determination of non-metals.

ICP-AES single notable **disadvantage** when compared to other complimentary techniques like atomic absorption is the high cost of the instrument as well as operational cost associated with it. Figure 2.2 is a schematic representation of the major components and layout of a typical ICP-AES instrument. Most of technical information associated with the detail operation of ICP-AES can be found in ICP-AES handbooks.

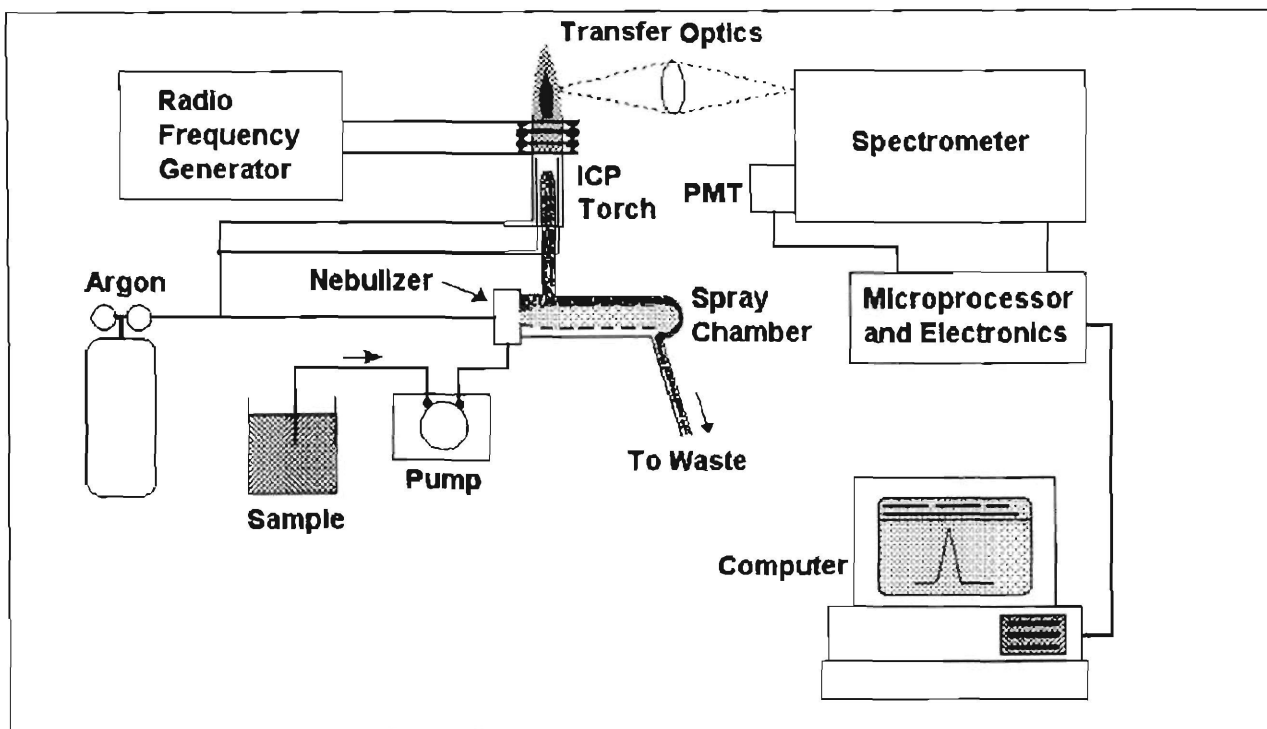


Figure: 2.2 Major components and layout of typical ICP-AES instrument (Boss and Fredeen, 1997).

As coal contains low levels of most of the trace elements of environmental concern, the ICP-AES has found wide application due to its sensitivity and ability to detect at low levels compared to other traditional techniques. Typical detection limits for some elements in an ICP-AES are presented in Figure 2.3. The other advantage of using ICP-AES is that as a multi-element analysis technique it serves a great deal of time in analysis while giving accurate and reliable results. Although the basics of sample preparation into solution may differ, it is observed through literature review (Atkin, et al., 1995) that ICP techniques are chosen by a number of workers in the field of determination of trace elements in coal and its products. A brief review of researchers (Atkin, et al., 1995, Crock et al., 1983, Lachas et al., 2000, Booth et al., 1999, Richaud et al., 2000, Dale and Riley, 1995, Ebdon and Wilkison, 1987) that have applied ICP-AES in their work is presented;

Booth et al. (1999) prepared pellets from a South African Reference Material (SARM 18, 19 & 20) which were introduced into an ICP-MS using a laser system which generated particulate aerosols from the solid material by pulsing a laser beam onto the target surface. Results obtained for the reference materials were in excellent agreement between reported and observed concentrations with a standard deviation of

between 10-20% for elements such as As, Cd, Se, Mo, Sn and Sb. Accurate determination of As was achieved mainly because of the absence of polyatomic ions within the plasma due to the elimination of acid dissolution and the presence of low Cl in the coals. It has been reported previously that As suffers polyatomic ion interference from the  $\text{ArCl}^+$  in the plasma (Booth et al., 1999). Hg was also analysed successfully in the coals using this technique. It is noted that improved or confirmatory results can be easily obtained by using XRF techniques as the pellets are prepared in a similar fashion suitable for XRF analyses.

Fadda et al. (1995) used an open microwave digestion technique as a sample preparation technique for the analysis of trace elements in ICP-MS. SARM 18, 19 & 20 and National Bureau Standards (NBS), standard reference material (SRM) NBS SRM 1632b coal standards were employed in this work. Generally good (2-7%) to excellent (0-2%) agreement with certified values was observed with most elements falling within the specified uncertainties or ranges. It was noted that determination of As was successful because the sample dried twice to remove Cl, which causes the polyatomic ion interference.

Atkin, et al. (1995), Crock et al. (1983), Lachas et al. (2000), Booth et al. (1999), Richaud et al. (2000), Dale and Riley (1995), Ebdon and Wilkison (1987) have all employed ICP techniques to analyse the content of trace elements in coal and other cases biomass. It should be noted that different sample preparation techniques were used to prepare the samples for analyses.

It is often difficult to directly compare results obtained by different parties as the sample preparation methods differ while this contributes significantly to the end results. This is observed in the arsenic results as it has been mentioned that a high Cl content can affect the determination of As. The acid used in sample preparation can introduce the presence of Cl in the solution.



The signal is then amplified and measured electronically. A schematic representation of an atomic absorption cell (AAS) unit is presented in Figure 2.4.

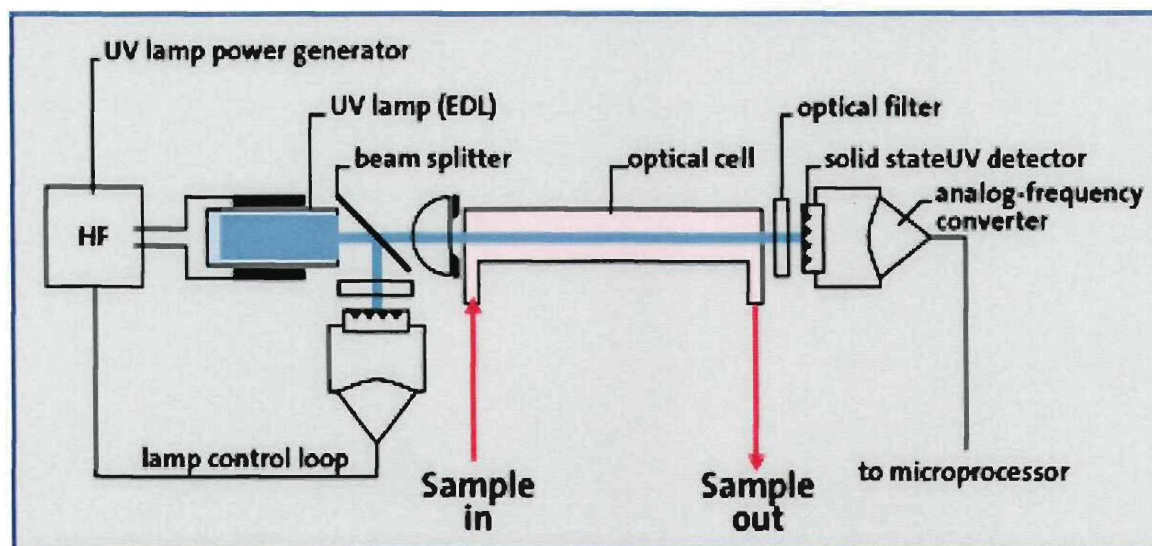


Figure: 2.4 Schematic diagram of the AAS measuring-cell unit. *The mercury concentration is measured in a 230 nm optical cell entirely made of fused silica at a wavelength of 253.7 nm (mercury instruments)*

CVAAS is the most common technique used for mercury determinations, due to its simplicity, high sensitivity and relative freedom from interferences with regard to this element. During its inception, tin (II) salts solutions were used to generate the mercury vapour. More recently, reduction with sodium tetrahydroborate (III) instead of tin (II) chloride has been widely used, because of its strong reducing ability and being able to reduce mercury in most of its compounds in contrast to the tin (II). It has been argued in literature that the sodium tetrahydroborate (III) reduction is more rapid and may give better precision than the tin (II) method (Martinez-Garcia et al., 1998).

In this technique, Hg is separated from the coal by combustion or oxidising acid digestion into the  $\text{Hg}^{2+}$  state in solution. The mercury is then reduced to metallic Hg by either stannous chloride or sodium tetra-hydroborate (III), producing free mercury atoms, which are captured in silver or gold amalgamation, process (Huggins, 2002). Mercury is then thermally released from the amalgamated silver or gold as atomic vapour and analysed in a CVAAS cell (Figure 2.4). It is suggested that many elements such as Ag, Au, Pt, Pd, Cu, Ni, Pb and Se, significantly affect the mercury analytical

signals. This is in sharp contrast to the non-interference of elements in mercury analysis in this technique (Huggins, 2002). Other techniques like ICP-AES/MS have an even poorer detection limit and suffer from greater interferences. In ICP-AES, the atomic hydrogen generated in the hydride generation, directly influences Hg, Sb, As, Bi, Ge, Pb, Se, Te and Ti in forming volatile hydrides of these elements, therefore resulting in possible interferences (Huggins, 2002).

Major **advantages** of AAS methods appear to be:

- the relative simplicity, availability and speed of the technique
- the suitability for major and trace element species
- the detection limits and precision for some trace element determinations being far better, depending on the AAS technique employed
- sufficient variations existing so that many elements in the periodic table can be determined by this technique

No major **disadvantages** of this technique have been noted. Several workers have accepted CVAAS as an accurate, reliable technique for the analysis of mercury in coal (Bushell and Williamson, 1996 and Zajusz – Zubek and Konieczynski, 2003).

### ***2.1.2 Sample Preparation Techniques***

As it has been highlighted with regard to the techniques reviewed (ICP-AES, CVAAS), that the sample needs to be in a solution form in order for it to be transferred to the unit; therefore sample dissolution is a critical step in preparation for analysis. There are several standard methods available for sample dissolution. Some involve the traditional methods of dissolution in some potentially harmful acid in a beaker, over a hot plate for several hours, running into days in some cases. In most cases these methods do not dissolve the solid sample completely into solution. Newly developed methods are able to digest the solid sample rapidly and completely into solution. Such methods are even less harmful, as they require the use of closed vessels under high pressure and temperature. In the following section the different sample preparation procedures for analysis by ICP-AES or CVAAS are explored.

### **2.1.2.1 Microwave digestion**

Microwave techniques are rapid, require fewer reagents and lessen possibilities of contamination when closed vessels are used. The microwave digestion is a relatively new technique, substituting digestion by using beakers on a hot plate in a fume hood. In both techniques the coal particles are broken down by acids with the addition of heat to ensure that all the elements requiring detection are in solution. The Microwave digestion involves high-pressure build-up in the tough teflon vessel and rapid increase in temperature to be able to obtain optimum digestion.

The **advantages** of microwave digestion are:

- It reduces sample preparation time by more than 90%, while improving precision and repeatability of results.
- In a good microwave instrument, the temperature and pressure are monitored continuously; this increases the safety of the equipment at the same time being able to record correctly the conditions at which digestion of a material occurred.
- It also requires minimum supervision, compared to conventional methods of hot plates.
- Very little sample is required for this technique, the maximum being 0.5 g for organic samples like coal and even less for inorganic samples.
- It retains semi-volatile elements like mercury, which tends to volatiles at about 140°C.
- It also eliminates cross-contamination between samples, reduces acid trace impurities for lower detection limits and eliminates worker exposure to toxic and hazardous fumes that could be obtained when conventional methods are employed.

The digestion method basically depends on the nature of the sample. It can be a single or multi-step method, with an addition of other reagents in each step. Digestion of a coal sample requires the coal to be pulverised (passing through a 250µm screen), addition of a small amount of HNO<sub>3</sub> acid, approximately 5 cm<sup>3</sup> per step to maximum of 15 cm<sup>3</sup>. An aqua regia mixture (HCl:HNO<sub>3</sub>, ratio of 1:3 ) can also be used to digest coal. Coal contains silicates, which cannot be digested by either HNO<sub>3</sub> or HCl acid. Therefore, if 100% digestion of coal material is to be obtained, an addition of HF acid is

necessary to dissolve the silicates. If HF acid is introduced then it needs to be neutralised by addition of boric acid once the digestion is complete. In most cases, addition of boric acid introduces the problem of a high dilution factor. Then the trace elements of interest tend to be below the detection limit of the ICP-AES instrument. A possible solution to this problem would be to filter out any remains, assuming that no trace elements of concern are in the solid filtered material. Cooling of vessels before opening is a critical step, as some of the more volatile elements like mercury, may be volatilised from the hot solution.

The sample preparation technique of using microwave digestion and ultimately ICP-AES for analyses has been investigated by a number of researchers. A discussion of some of the investigations is presented below.

Atkin et al. (1995) has investigated the microwave digestion technique, which is based upon the sequential attack of coal sample by acids in a sealed microwave digestion system. The first digestion stage utilises a mixture of HCl and HF, mainly attacking the non-pyritic mineral matter followed by addition of HNO<sub>3</sub> in the second step. The HNO<sub>3</sub> attacks the pyritic phase and the final digestion stage utilises a mixture of HCl/HF/HNO<sub>3</sub> and attacking the organic phase and any remaining mineral grains. The coal sample is crushed to less than 40µm and approximately 0.5 g is used in the digestion vessel. After addition of 5 mol dm<sup>-3</sup> HCl and 20 mol dm<sup>-3</sup> HF acid, the vessels are heated in the microwave for 10 minutes in total.

The vessels are cooled by partially immersing in water, before opening them. Residues from this first step are removed with the assistance of a centrifuge to allow them to settle at the bottom. The clear solution is transferred into an appropriate volumetric flask. This residue is then washed with a mixture of HCl and H<sub>3</sub>BO<sub>4</sub>, centrifuged again and the clear solution is transferred into the same appropriate flask, which is then made up to the mark by a solution of HCl and H<sub>3</sub>BO<sub>4</sub>. The residue is then washed with deionised water, transferred to the microwave vessel and the second digestion step is performed by addition of HNO<sub>3</sub>. The residue remaining after this step is treated in a similar fashion as the residue in step one, except that HNO<sub>3</sub> is used when washing. The clear solution and the acid washing are transferred to a second volumetric flask. The last digestion step of the residue is performed by adding a mixture of HCl/HF/HNO<sub>3</sub>

and complete digestion is obtained at this stage. The solutions are then analysed by ICP-AES. To be noted in this method, is the use of HF in the first step of digestion, which is of a harsher acid when compared to HCl and HNO<sub>3</sub>. Also to be noted is that complete digestion was obtained with this method.

Fadda et al. (1995) employed a single stage digestion procedure in a mixture of HF/aqua regia and HClO<sub>4</sub>. Complete digestion was not obtained with this procedure; the residue was therefore further treated on a hot plate with addition of HNO<sub>3</sub>. The final solution was a combination of the two solutions (from microwave digestion and hot-plate dissolution), which was then analysed using ICP-MS for 45 elements.

Lachas et al. (1999) and Richaud et al. (2000) used a three-stage microwave digestion procedure, which does not require addition of acid between the stages. HNO<sub>3</sub> was added in the initial stage, after the final stage the vessels were cooled to -18°C to prevent the loss of volatile elements. Remaining residues were filtered out. Solutions were made to uniform volume and analysed in ICP-MS. In this work the microwave digestion was compared to the wet ashing (open vessel acid) digestion method.

#### ***2.1.2.2 American Society for Testing and Materials standard test methods (ASTM)***

ASTM's are approved methods, which are then adopted internationally for the analysis of a particular material. ASTM methods are reviewed every five years by the responsible ASTM technical committee and if not revised, they are either re-approved or withdrawn. The methods are also accessible through the ASTM website.

#### ***2.1.2.3 Mercury Determination (D6414–99)***

The standard test method for total mercury in coal and coal combustion residues by acid extraction or wet oxidation or cold vapour atomic absorption (D 6414–99), covers procedures to determine the total mercury content in a sample of coal or coal combustion residue. Mercury in the sample is solubilized by heating the test sample at a specified temperature in a mixture of HNO<sub>3</sub> and HCl. The acid solutions produced are transferred into a vessel and further treated, such that the mercury is reduced to

elemental mercury. The mercury vapor is determined by flameless cold-vapour atomic absorption spectroscopy.

#### **2.1.2.4 Arsenic and Selenium Determination (D6414–99)**

ASTM D4606–95 (re-approved 2000) is a standard test method for the determination of arsenic and selenium in coal, using the hydride generation or atomic absorption method. Arsenic and selenium are determined by mixing a weighed coal sample with Eschka mixture (2 part MgO + 1 part Na<sub>2</sub>CO<sub>3</sub>) and igniting it at 750°C. The mixture is dissolved in HCl, acid, the gaseous hydride of each element is generated from the appropriate oxidation state and determined by atomic absorption spectrophotometry.

#### **2.1.2.5 Trace Elements Determination (D6357–00a)**

ASTM D 6357–00a is a standard test method for the determination of trace elements in coal, coke and combustion residues from coal utilization processes by ICP–AES/MS and graphite furnace atomic absorption spectrometry (GFAA). Trace elements determined by this method include antimony, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, vanadium and zinc in coal and coke. It can also be used in the determination of other trace elements not mentioned in this list. The coal or residue to be analysed is ashed under controlled conditions, digested by a mixture of aqua regia (HNO<sub>3</sub> and HCl) and HF acid and finally dissolved in 0.16 mol dm<sup>-3</sup> HNO<sub>3</sub> acid. The concentration of individual trace elements is determined by either ICP–AES or ICP–MS. Selected elements that tend to be below the detection limits of the ICP can be quantitatively analysed by GFAA.

Controlled ashing (dry ashing) is understandably used for samples containing a significant amount of combustible material as the matrix. It is performed by placing the sample in an open inert vessel to destroy the combustible portion of the sample by thermal decomposition using a muffle furnace. The ashing temperature range is 450–550°C, at some point the temperature can be increased to 750°C, depending on the chemical nature of the sample as well as the volatility of the elements to be analysed. Ash prepared at this temperature range is called high temperature, ash (HTA). Typical elements that could be analysed on samples that have been prepared at a temperature of 750°C, without being affected by temperature include Si, Al, Ti, Ca, Fe, Mg, K, Na

and P. The loss of the volatile species such as H<sub>2</sub>O, CO<sub>2</sub> and sulphur as SO<sub>2</sub> is as a result of transformation of the minerals at high temperature (Huggins, 2002).

For the more volatile elements, typically As, Se, Hg and halogens, a much lower temperature (maximum 200°C) needs to be applied to the original coal sample to ensure minimum volatilisation of these elements. A muffle furnace is not capable of producing the required ash at this temperature (200°C). Normally ash obtained at this low temperature is called low temperature ashing (LTA), which is prepared by oxidizing away the carbonaceous matter under an oxygen plasma (Huggins, 2002). Whether to use HTA or LTA is really dependent on the elements one is interested in analysing. Gaines, (2006) detailed some advantages and disadvantages of ashing:

#### **Advantages of Ashing**

- the ability to decompose large sample sizes
- the need for little or no reagents
- the technique is relatively safe
- The ability to prepare samples containing volatile combustion elements such as sulphur, fluorine and chlorine
- the technique lends itself to mass production

#### **Disadvantages of Ashing**

- losses due to retention in the ashing container
- losses due to volatilisation
- contamination from the muffle furnace
- physical loss of low-density ashes when the muffle door is opened (air currents)
- difficulty in dissolving certain metal oxides
- formation of toxic gases in poorly ventilated areas

Huggins (2002) highlights that ashing has the advantage of increasing the concentration of an element by a factor of about 5 -10 and thereby significantly improving the sensitivity and precision of the determination of the trace element. Generally working on the raw coal is much easier and quicker, eliminating some of the problems associated with ashing. There has been increasing use of the recent

techniques, which permits the dissolution of coal into solution. Such techniques like microwave-oven digestion of coal have produced good repeatable results for some researchers (Fadda et al., 1995).

These ASTM methods have been applied internationally as standard methods for the determination of trace elements in coal. In some cases they have been slightly modified and adapted for that laboratory. Examples of an ashing procedure for the determination of trace elements are described below:

Richaud et al. (2000) and Lachas et al. (1999) successfully conducted wet ashing in which a 10 mg sample of NBS SRM 1632b was heated in a platinum crucible on a hot plate at 150°C, in the presence of 100µL of concentrated H<sub>2</sub>SO<sub>4</sub> (0.5 mol dm<sup>-3</sup>), before being ashed at 520°C in a muffle furnace. The HTA was then heated with 300µL HClO<sub>4</sub> acid and 500µL of HF acid to dryness at 200°C and dissolved in a 0.63 mol dm<sup>-3</sup> HNO<sub>3</sub> solution, then ultimately analysed by ICP-MS. A microwave-oven digestion was conducted for the same coal samples, for comparison of the results obtained through both techniques. Results obtained through wet ashing were found to agree within 20%, with certified values of SRM 1632b.

Doughten and Gillison (1990) prepared ash from Eight Argonne Premium coal samples. The coal samples were first ashed by weighing 70 g of coal into a weighed porcelain crucible. The crucible was placed in a muffle furnace, which was slowly heated to 200°C. After 1.5 hours at 200°C the temperature was increased to 350°C and was held at that temperature for 2 hours. The temperature was then increased to 525°C and maintained for about 36 hours and after cooling the weight of the ash was determined. The ash was then weighed into a screw-cap bomb with an addition of HNO<sub>3</sub> acid. The bomb was then capped and heated on a hot plate overnight at 200°C. After cooling, HNO<sub>3</sub>, HClO<sub>4</sub> and HF acid were added and the bomb recapped, then heated further on a hot plate at 200°C for 4 hours. The solution was then evaporated for dryness with an addition of HCl and gently heated until it was clear. The determination of trace elements was conducted on this final solution by using ICP-AES.

This dry ashing procedure is time consuming, when compared to other reported ashing procedures (Richaud et al., 2000 and Lachas et al., 1999).

## **2.2 Analytical Methods Selected for this Project**

The focus of this section is mainly on the analytical techniques that were ultimately employed in this investigation of trace elements in coal and its products. Coal obtained before the preparation process is called run of mine (ROM). Preparation of a representative sample from the ROM coal will not be discussed in this chapter, as it is outside the scope of this work. Standard dry coal crushing, milling and screening were employed to obtain particle sizes less than 250 $\mu\text{m}$  in all samples. Several methods were attempted during this study to determine the most appropriate preparation technique, but the discussion will focus only on the methods that were ultimately selected to pursue the investigation and behavior of trace elements in coal during coal utilization. Certified reference materials (South African Reference Material (SARM) 18, 19 and 20) were used as controls in every method.

The methods discussed are:

- Microwave-oven digestion (for sample preparation)
- Coal Ashing, using the ASTM standard method
- Float or sink density separation methods (determination of the mode of occurrence of trace elements in coal)
- Methods for the determination of mercury in gas streams (Gold tube and activated carbon tube)
- DMA 80 Mercury Analyzer as a confirmation tool
- Pyrolysis experiment

### **2.2.1 Chemicals used in this Project**

All chemicals used in this project were pure analytical grade materials purchased from reputable chemical suppliers (SIGMA-ALDRICH and MERCK). Water used during experimental refers to double distilled water. All apparatus used during experimental work was treated in 1.6 mol dm<sup>-3</sup> HNO<sub>3</sub> and rinsed with double distilled water to eliminate possible sources of contamination.

### **2.2.2 Information on the Coal used in this Work**

During coal mining, heavy machinery called a 'continuous miner' is used to break the coal seam. The coal is transferred to a crusher where it is crushed and screened. Two

ROM samples were collected from two different mines in the Highveld region. For proprietary reasons the coal will be referred as Highveld coal A and Highveld coal B respectively. 5 kg of well mixed samples were prepared from each of the two runoff mine samples and subsequently crushed and screened to obtain particle sizes of less than 250  $\mu\text{m}$ , as described in detail in the experimental section in Chapter 2. These coals are low rank bituminous coals, as explained in Chapter 1. The geological location of the two mines is the same and the mines are adjacent to each other, with a separation distance of a few kilometres. The ash content and trace elements content is also generally comparable between the two coals, hence the two coals are not significantly different from each other. The Coal A mine supplies a percentage of feed coal to gasification and combustion. There are basically six mines around the same region, with minimum differences in terms of ash content, all contributing to the feed coal of the two plants. All the coals from the mines are converged to two central places, where a blend is prepared based on availability of coal. A plan is underway to prepare the blend coal in terms of its properties.

The coal B mine mainly produces coal for the export market, therefore coal contributed to the feed coal could be as a result of surplus, but the discard after beneficiation is mainly sent for inclusion in the blend. For the purpose of this study coal B was chosen to better understand the coal being exported in terms of trace elements and also remain abreast with an environmental footing in the international community.

Coal A is mainly representative of the coals found in the Mpumalanga region. The information obtained from coal A in terms of trace element content can be translated to other coals.

### **2.2.3 Microwave-oven Digestion**

Several microwave digestion methods were investigated in order to develop a suitable method. In this exercise, several parameters that could lead to uncertain results were investigated in detail; thereby a suitable method for digestion was developed.

The initial approach taken was to successfully digest two coal reference materials (SARM 18 & 20), followed by a Highveld coal samples. Two digestion methods were

applied: these were multi-stage methods, one using only HNO<sub>3</sub> acid and the other using a mixture of HNO<sub>3</sub>, HCl and HF acid. The microwave-oven used in this work was a CEM MARS 5, which takes up to 12 teflon digestion vessels, including the control vessel and allows temperature and pressure variations.

### **2.2.3.1 Methods**

Sample type: coal with particle size less than 250µm.

Sample weight: 0.3 g

Reagents used in all microwave methods:

HNO<sub>3</sub> (5.92 mol dm<sup>-3</sup>, 1.41 g cm<sup>-3</sup>), HF (20 mol dm<sup>-3</sup>, 1.13 g cm<sup>-3</sup>) and

HCl (8.9 mol dm<sup>-3</sup>, 1.16 g cm<sup>-3</sup>)

### **MICROWAVE COAL DIGESTION: METHOD 1**

#### **STEP 1**

0.3 g of coal sample was accurately weighed into the teflon liner of the digestion vessel and 10 cm<sup>3</sup> HNO<sub>3</sub> (5.92 mol dm<sup>-3</sup>) was added. A blank sample was prepared in the same manner, without the addition of a coal sample. The vessels were closed and placed into the carousel. The heating programme (ramp to temperature) was followed as indicated below. The heating cycle was carried out twice without opening the vessels, to ensure maximum possible digestion.

Heating programme: Ramp to Temperature

Stage	Max. Power (watts)	Ramp (min.)	Pressure (bar)	Temperature (°C)	Hold (min.)
1	1200	15:00	24.13	210	15:00

The vessels were allowed to cool to below 50°C and 3.45 bar, before opening for step 2. Most of the material was already digested at this stage.

## STEP 2

5 cm<sup>3</sup> HF (20 mol dm<sup>-3</sup>) using a plastic pipette and 1 cm<sup>3</sup> HCl (8.9 mol dm<sup>-3</sup>) were added to each of the samples, including the blank one. The vessels were re-sealed and heated as indicated below (standard control).

Heating programme: Standard control

Stage	Max. Power	Ramp (Min.)	Pressure (bar)	Temperature (°C)	Hold (Min.)
1	1200*	10:00	10.34	200	15:00

## STEP 3

The vessels were allowed to cool slowly, to about room temperature, before being opened. The pressure was released slowly to minimize any possible loss of analyte. The contents of the vessels were individually transferred into 25 ml polyethylene volumetric flasks. Each vessel was rinsed well with small amounts of double distilled water and the washing liquid was also added to the volumetric flask, which was ultimately made up to the mark with the distilled water. The sample was at this stage ready for analysis using ICP-AES.

### MICROWAVE COAL DIGESTION: METHOD 2

Method 2 is similar to Method 1 with regard to the number of steps. The exception was that in step 2 of Method 2, only HNO<sub>3</sub> (5.92 mol dm<sup>-3</sup>) was added to the samples and the heating programmes were running at standard control only.

## STEP 1 & 2

Heating programme: standard control

STEP	Max. Power	Ramp (Min.)	Pressure (bar)	Temperature (°C)	Hold (Min.)
1	1200*	25:00	11.03	210	15:00
2	1200*	25:00	11.03	210	15:00

## STEP 3

The vessels were allowed to cool slowly to about room temperature, before being opened. The pressure was released slowly to minimize any possible loss of analyte. The contents of the vessel were individually filtered, into 25 ml volumetric flasks

through a No 42 Whatman filter paper placed in a plastic funnel. The purpose of the filter paper was to remove any undigested material which was observed after digestion. The vessels were then rinsed with double distilled water and the resulting washing liquid transferred through the filter paper into the volumetric flasks, which were ultimately made up to the mark with distilled water. The sample was at this stage ready for analysis of trace elements using ICP-AES.

## **2.2.4 American Society for Testing and Materials standard test methods (ASTM)**

### **2.2.4.1 ASTM method for trace elements determination (D6357–00a)**

**List of acid used in all ASTM methods:** HClO<sub>4</sub> (0.6 mol dm<sup>-3</sup>, 1.54 g cm<sup>-3</sup>) HNO<sub>3</sub> (5.92 mol dm<sup>-3</sup>, 1.41 g cm<sup>-3</sup>), HF (20 mol dm<sup>-3</sup>, 1.13 g cm<sup>-3</sup>) and HCl (8.9 mol dm<sup>-3</sup>, 1.16 g cm<sup>-3</sup>).

ASTM D6357 was followed for sample preparation of trace element analysis, excluding Hg, As & Se. A 5 g coal sample of particle size 250 µm was ashed in a porcelain crucible by heating at 300°C for 1 hour in a muffle furnace; then at 500°C for a minimum of 3 hours until ashing of constant weight was obtained. The ash was weighed and dissolved in a mixture of HClO<sub>4</sub> (0.6 mol dm<sup>-3</sup>) and HF (20 mol dm<sup>-3</sup>) in a teflon beaker at low heat using a hot plate. The acid composition of HClO<sub>4</sub> and HF give complete dissolution of the ash. The liquid was made up to 100 cm<sup>3</sup> in a volumetric flask with double distilled water. The sample was at this stage ready for ICP-AES analysis.

Such a method may be exposed to contaminations. However, with good care, reliable results were obtained in this work. It was also a much shorter method when compared to the method used by the United States Geological Survey laboratories for analysis of the same elements in coal. During a benchmarking exercise, it was found that results obtained by the United States Geological Survey were on par with results obtained at Sasol laboratories using the method described above.

It was noted that in the method used by the United States Geological Survey (Doughten and Gillison, 1990), the final solution was evaporated for dryness with an

addition of HCl ( $8.9 \text{ mol dm}^{-3}$ ) and gently heated until it was clear. This heating stage is of concern in that some of the volatile elements that may have been retained in the sealed bomb during extraction, may ultimately be lost in this heating stage, since it is conducted in an open vessel.

#### **2.2.4.2 ASTM Method for Arsenic and Selenium Determination (D4606–95)**

ASTM method D4606-95 (2000) was followed in preparing a coal sample for As and Se determination. The 1 g coal sample was mixed and also covered with 1.5 g of an Eschka mixture (magnesium oxide and sodium carbonate in a ratio of 2:1 respectively) in a porcelain crucible. The sample was then ashed in a muffle furnace from room temperature to  $500^{\circ}\text{C}$  for 1 hour, then to  $700^{\circ}\text{C}$  where it was kept for 3 hours. The sample was allowed to cool in the muffle furnace to room temperature. Once the sample was cool, it was then dissolved in boiling distilled water with an addition of  $20 \text{ cm}^3$  concentrated HCl ( $8.9 \text{ mol dm}^{-3}$ ) acid in  $5 \text{ cm}^3$  portions. This acidic solution was transferred to a  $100 \text{ cm}^3$  plastic volumetric flask which was then made up to mark with double distilled water. The solution at this stage was ready for ICP-AES analysis. The only notable difference to the actual ASTM standard method, was that in this project Hydride Generation (HG-ICP-AES) was used for analysis of As and Se, instead of atomic absorption methods. This was due to the availability of the ICP-AES at Sasol laboratories.

#### **2.2.4.3 ASTM Method for Mercury Determination (D6414–99)**

ASTM D6414-99 was followed for the determination of mercury in coal samples. In this method 1 g of coal sample was weighed into a screw cap glass bottle, then  $2 \text{ cm}^3$  of  $\text{HNO}_3$  ( $5.92 \text{ mol dm}^{-3}$ ) acid and  $6 \text{ cm}^3$  of HCl ( $8.9 \text{ mol dm}^{-3}$ ) acid were added. The bottle was then sealed, after some chemical reaction of the coal with the acid had ceased. It was then placed in a water bath, which had previously been heated to  $80^{\circ}\text{C}$  for 1 hour. In the laboratory the mixture was further treated with tin (II) chloride salts and potassium permanganate and analyzed using a Cold Vapor Atomic Absorption Spectrometry as described in detail earlier.

## **2.2.5 Methods for determining the Mode of Occurrence of Trace Elements in Coal**

### **2.2.5.1 Sequential leaching**

Leaching of the coal sample, using specified solutions in a sequence, was conducted using two methods;

- Column method: the coal was packed in a column and the solutions were introduced into the column, extracting specific elements.
- Slurry method: the coal and the solutions were placed in a slurry phase in a beaker and stirred to ensure good extraction of the specific elements with affinity to that solution.

### **2.2.5.2 Column method**

The experimental set-up for the column method is represented in Figure 2.1, in which 5 g of a coal sample of particle size less than 250  $\mu\text{m}$  was packed into a 60  $\text{cm}^3$  plastic column of 30 cm length fitted with cotton-wool at both ends of the bed. The coal sample was sequentially leached at room temperature, using 35  $\text{cm}^3$  each of the following solutions:

1. double distilled water removes the elements which are water soluble loosely on the surface of the coal;
2. 2  $\text{mol dm}^{-3}$   $\text{CH}_3\text{COONH}_4$  removes exchangeable cations and a portion of the carbonate-hosted cations;
3. 2  $\text{mol dm}^{-3}$   $\text{HCl}$  removes cations associated with carbonates and monosulfides (sphalerite, galena and chalcopyrite);
4. 2  $\text{mol dm}^{-3}$   $\text{HNO}_3$  removes elements associated with disulfides (pyrite and marcasite); and
5. 20  $\text{mol dm}^{-3}$   $\text{HF}$  destroys silicates and liberates elements present in silicates.

All solutions were controlled to run through the column in a 45 minutes period, to ensure equal residence time. 70  $\text{cm}^3$  double distilled water was used between each step to ensure that the sample was free from the previous solution used and that leachate was added to the 50  $\text{cm}^3$  plastic volumetric flask used for collecting the previous solution. The volumetric flask was made up to the mark by the addition of the solution used in the leaching process. The liquid sample in the volumetric flask was

ready for ICP-AES analysis at this stage. The above procedure was carried out several times for a coal sample from the same source, to determine reproducibility of results.

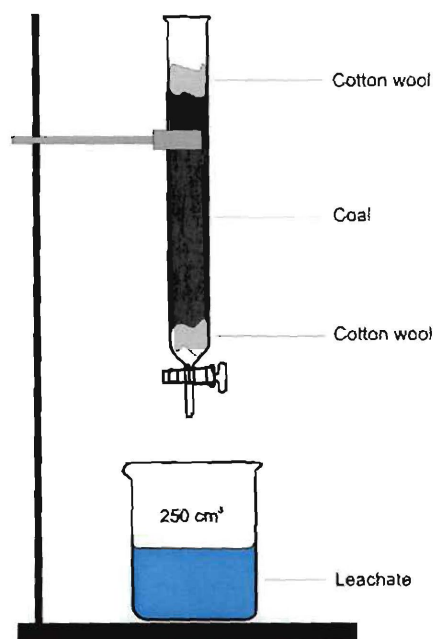


Figure 2.1: Experimental set-up of the column method

### 2.2.5.3 Slurry Method

This procedure was a three step procedure, using the solutions and sequence described in the column method:

1. 20 g of the coal sample of particle size less than 250  $\mu\text{m}$  was vigorously leached (stirring with a plastic coated stirrer bar) in a beaker with 70  $\text{cm}^3$  of each solution at room temperature for a 1 hour period.
2. The sample (coal and solution) was then separated by centrifuging with the liquid fraction decanted into a 100  $\text{cm}^3$  volumetric flask. The residue was then dried in an oven at 50°C to remove excess solvent.
3. The residue from step 2 was then leached with 2  $\text{mol dm}^{-3}$  HCl as described in step 1. The resulting residue was dried.
4. The residue from step 3 was leached with 2  $\text{mol dm}^{-3}$  HNO<sub>3</sub> as described in the above steps.

After the leaching process, each solution obtained was made up to the mark of the 100  $\text{cm}^3$  volumetric flask with the parent solution and sent for ICP-AES analysis at Sasol laboratories. Elements remaining in the solid residue after the leaching protocol has

been completed, may be hosted in insoluble minerals like clays that require strong reagents like HF to dissolve them.

#### **2.2.5.4 Float and Sink Density Separation Method**

The coal sample (100 g) of particle size less than 250  $\mu\text{m}$  was physically separated in a mixture of bromoform ( $\rho = 2.887 \text{ g/cm}^3$ ) and toluene ( $\rho = 0.8669 \text{ g/cm}^3$ ) which was prepared (thoroughly mixing (by weight) in a 1  $\text{dm}^3$  glass measuring cylinder placed on a proper calibrated balance) to obtain required densities (1.5, 1.6, 1.7, & 1.8  $\text{g cm}^{-3}$ ) as seen in Figure 2.2. The coal was allowed to separate fully overnight into float and sink fractions. The resulting fractions were then dried in an oven, set at 40°C under nitrogen atmosphere, for six hours to remove the residual of bromoform and toluene from the coal sample. The samples obtained were weighed to calculate percentage yield in each fraction. Each float or sink coal fraction obtained was then prepared for trace element analysis using the procedures described above.

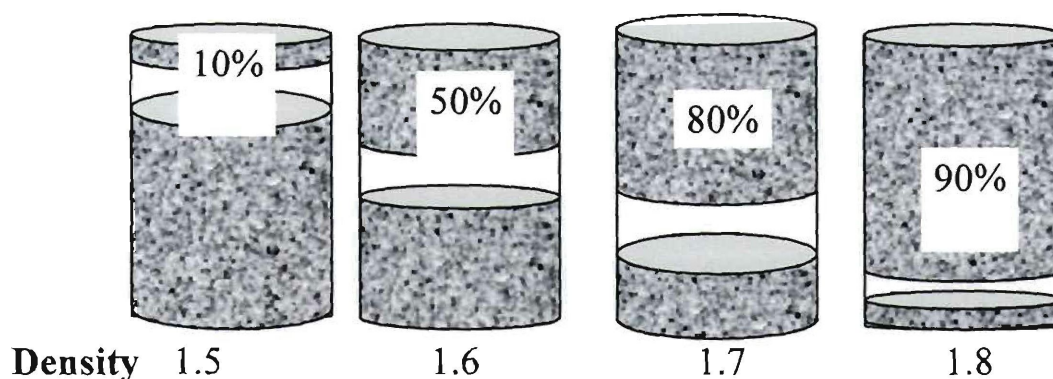


Figure 2.2: Coal separated in different densities of a mixture of bromoform and toluene

### **2.3 Pyrolysis Process**

In this section the details of the pyrolysis process are discussed to provide an understanding of the process. The experimental will then be discussed.

Coal pyrolysis is the thermal treatment of coal to produce gases, liquids and solid residue (char or coke) (Wiley in Ullmanns 6<sup>th</sup> edition, 2002). Pyrolysis occurs in all coal utilization processes, i.e. combustion, gasification, liquefaction and carbonization. The nature of pyrolysis and of the products is intimately related to the operating conditions

and to the composition and properties of the coal. Therefore, control of pyrolysis is important in the coal utilisation processes (Wiley in Ullmann's 6<sup>th</sup> edition, 2002).

Wiser's model of the thermal decomposition of coal is represented in Figure 2.3. Pyrolytic rupture of functional groups attached to aromatic and hydroaromatic units of the coal structure leads to the formation of gases (CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, etc). The overall yield and distribution of the products is controlled by the break and release of the reactive fragments indicated by arrows in Figure 2.3. Stabilisation of the fragments with hydrogen gives primary volatile products and favours a high yield of gases and liquids (Figure 2.4). Some primary products are also obtained by release of low molecular mass species, which are believed to be trapped within the coal network. However, if the fragments undergo secondary cracking, polymerisation or condensation reactions, part of the primary product is converted to char.

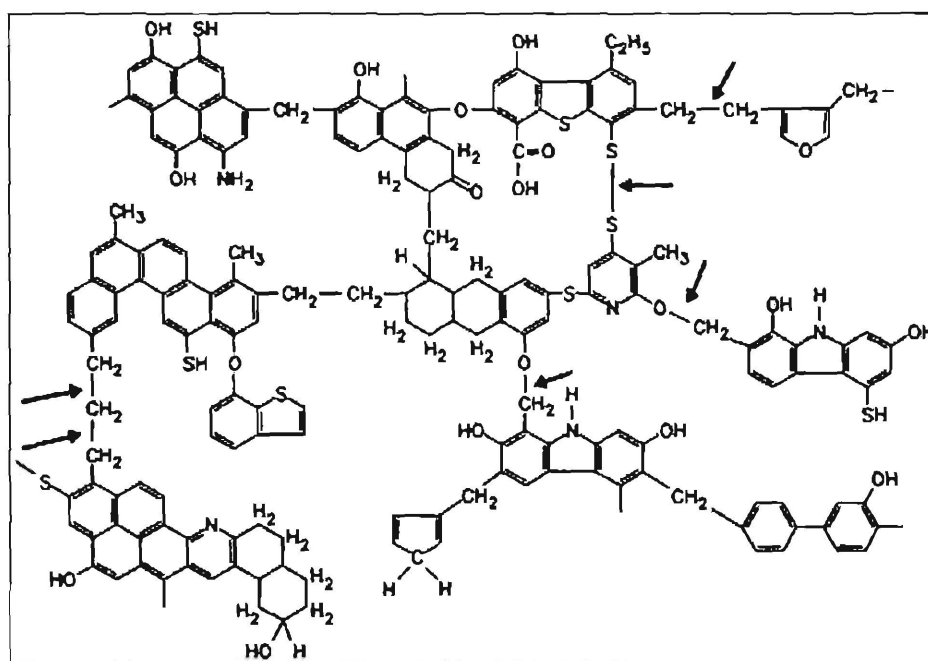


Figure 2.3: Wiser's model of coal structure (Wiley in Ullmann's 6<sup>th</sup> edition, 2002)

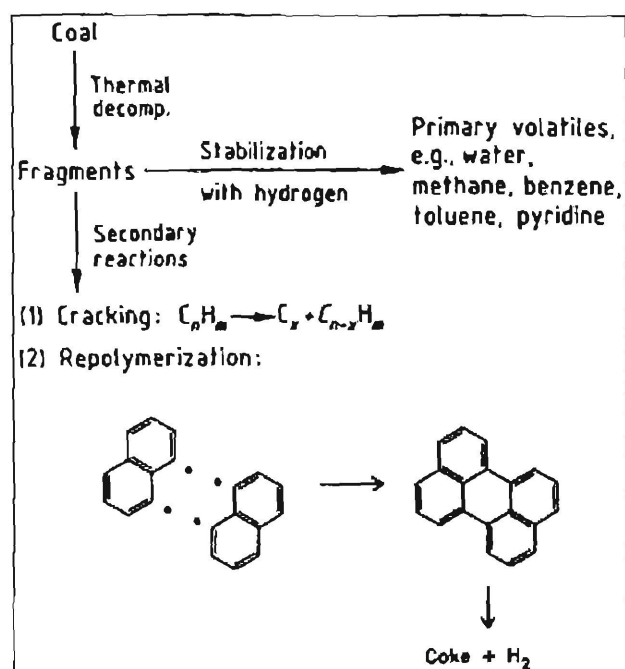


Figure 2.4: Primary and secondary reactions in coal pyrolysis (Wiley Ullmanns 6<sup>th</sup> edition 2002)

### 2.3.1 Pyrolysis Experimental Set-up

The experimental set-up (Figure 2.5) consisted of a high-pressure reactor vessel with a capacity of 1.2 kg of coarse coal. The reactor was placed in vertical heating elements that can reach temperatures of about 800°C; and the reactor can reach a pressure of 24 bar. The top part of the reactor was removable for sample loading and had three flanges attached to it. On one flange, a thermocouple was inserted to monitor the internal temperature of the reactor. The second flange has a pressure regulator connected to monitor and control the pressure inside the vessel by releasing the pressure release valve. The third flange allowed the exit of all gases and volatiles and was further connected to a series of cold traps to allow condensation and collection of the material. In this exit pipe a pressure reducer was also installed to reduce the pressure of the gas from the reactor pressure of 24 bar to atmospheric pressure. There was an inlet at the bottom of the reactor vessel to allow the carrier gas into the vessel, which also contributed in creating and maintaining the 24 bar pressure required in the vessel.

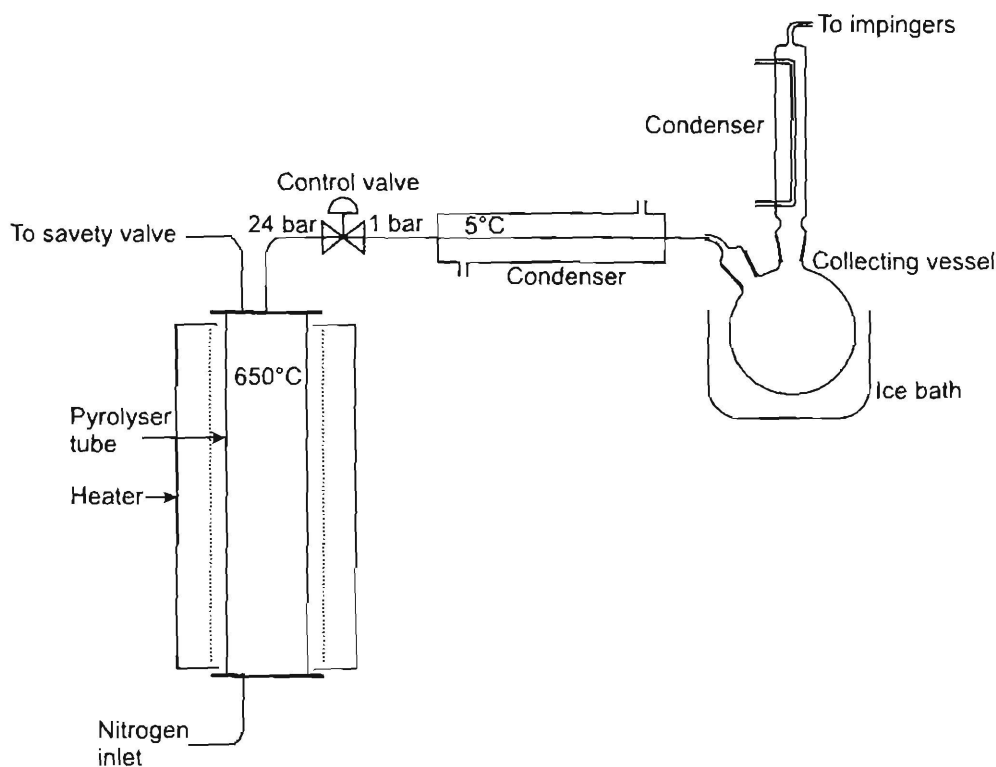


Figure 2.5: Schematic representation of the pyrolysis set-up experiment

Coal samples were prepared with varying particle sizes, as detailed in Table 2.1. A total of about 1.2 Kg of each coal sample was then placed into the pyrolyser unit reactor.

Table 2.1: Particle size and weight of coal fed in the pyrolyser

Particle size (mm)	Weight (g)
>13.2	0
9.5 -13.2	350
6.7 - 9.5	320
4.75 - 6.7	290
3.35 - 4.75	150
2.36 - 3.35	70
< 2.36	20

### 2.3.1 Pyrolyser Set-up

The pyrolyser was operated to a maximum temperature of between 530 and 570°C and pressure of 24 bar. Nitrogen gas was used as a carrier gas. The pipe connected to the exit flange of the reactor was continuously cooled down to about 10°C, with a condenser circulating water from a cold-water bath maintained at 5°C (see Figure 2.6).

In the first and second cold trap, condensate was produced as a result of the gas condensing at temperatures of 5°C into two round bottomed flasks, which were connected in series and fitted with condensers on top. The trace elements that may be further present in the gas stream were captured using a series of solution (0.1 mol dm<sup>-3</sup> KCl, HNO<sub>3</sub> (0.8 mol dm<sup>-3</sup>) in H<sub>2</sub>O<sub>2</sub> (0.3 mol dm<sup>-3</sup>) and KMnO<sub>4</sub> (4 g dm<sup>-3</sup>) in H<sub>2</sub>SO<sub>4</sub> (0.1 mol dm<sup>-3</sup>) in an impinger sampling train system, as shown in schematic representation Figure 2.7. Although most of the heavy condensate had been removed in the preceding round bottomed flask, there was still some lighter condensate condensing in the impinger train, especially in the first impinger that was observed. The outlet of the impinger train was connected to a wet gas flow meter to determine the amount of gas released. Flow rate of the inlet gas was maintained with the use of a mass flow controller.

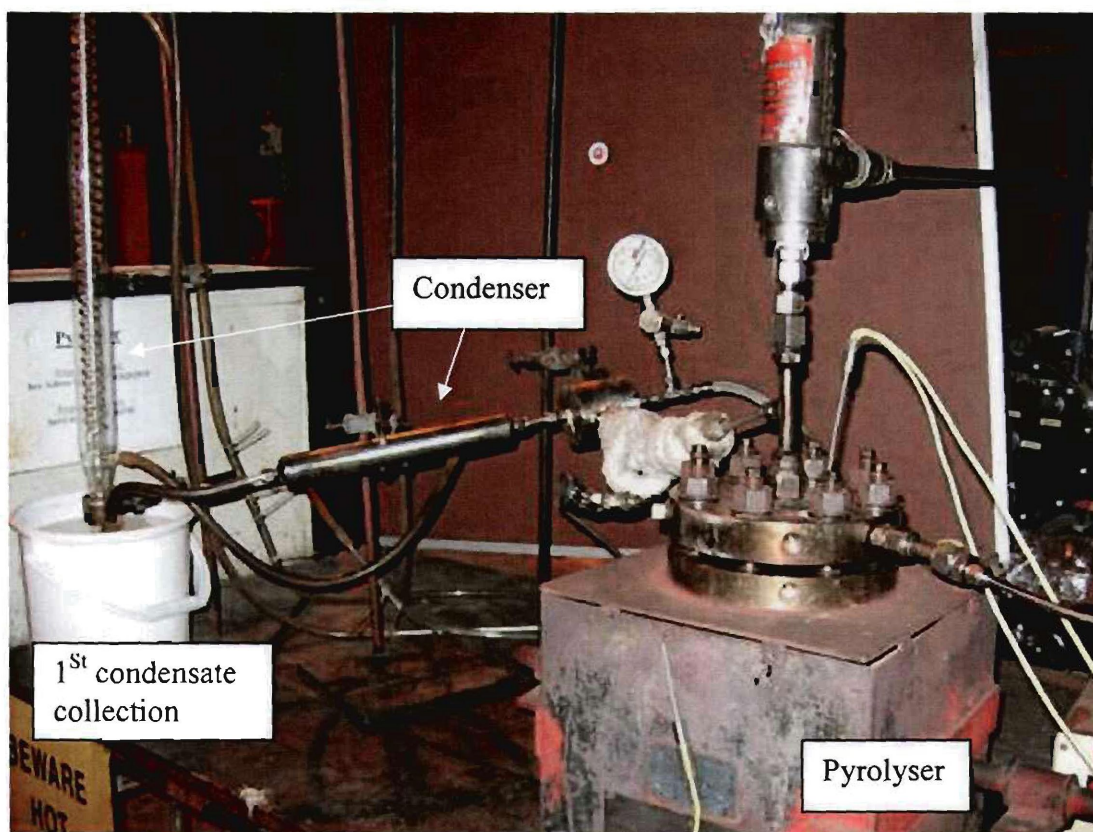


Figure: 2.6 a picture of the pyrolyser unit set up. Visible in this picture is the closed pyrolyser vessel (bolts and nuts removable to open the top for sample loading). The steel condenser circulating water, as well as the glass condenser also circulating water, are visible in this picture.

### **2.3.2 Pyrolyser Programme**

Temperature:	From room temperature to 530°C in 3 hours (held for 2 hours at this temperature)
Pressure:	Inlet pressure of the system was 24 bar therefore the reactor was maintained at 24 bar
Coal volume:	1.2 kg (as described in Table 2.1)
Carrier gas:	Inert nitrogen gas at a flow rate of 1 dm <sup>3</sup> /min
Gas cooling:	The water bath and cooling traps were maintained at about 5°C

### **2.3.3 Impinger Train**

The impinger train system is part of a well-established Environmental Protection Agency (EPA) method 29 for the determination of metal emissions from stationary sources. The complete method (Ontario Hydro Sampling Train Method) was intended for sampling flue gases and the determination of elemental, oxidized, particle-bound and total mercury emissions. Otero-Rey et al. (2003) have applied this method with success to the determination of As, Hg and Se in flue gases emitted from a coal-fired power plant. As and Se were trapped in the KCl solution. Oxidized Hg was collected in impingers containing a chilled aqueous KCl (1 mol dm<sup>-3</sup>) solution. Elemental Hg was collected in subsequent impingers (one impinger containing a chilled solution of HNO<sub>3</sub> (0.8 mol dm<sup>-3</sup>) in H<sub>2</sub>O<sub>2</sub> (0.3 mol dm<sup>-3</sup>) and three impingers containing chilled solutions of KMnO<sub>4</sub> (4 g dm<sup>-3</sup>) in H<sub>2</sub>SO<sub>4</sub> (0.1 mol dm<sup>-3</sup>). Therefore the method was adapted for the determination of trace elements in the pyrolysis gas after it has been through the two cooling stages of the stream.

### **2.3.4 Samples obtained during Pyrolysis**

Hydrocarbon rich and aqueous samples were taken as condensate from the gas stream and prepared for trace element analysis as per ASTM method described earlier in this chapter. There was no standard method for analysing the aqueous phase, so methods developed in Sasol laboratories (confidential) were used for the determination of trace elements in gas liquor. Char is the solid remain in the reactor (coal after it has lost most of its volatiles) after pyrolysis has been completed. The char was prepared as per ASTM procedure for preparing coal for trace element analysis. The solutions from the impinger train were recovered, made up to constant volume in a 250 cm<sup>3</sup> volumetric flask with corresponding blank solutions and transferred to sealable bottles

for the determination of trace elements by ICP-AES and cold vapour atomic absorption (for Hg analysis only).

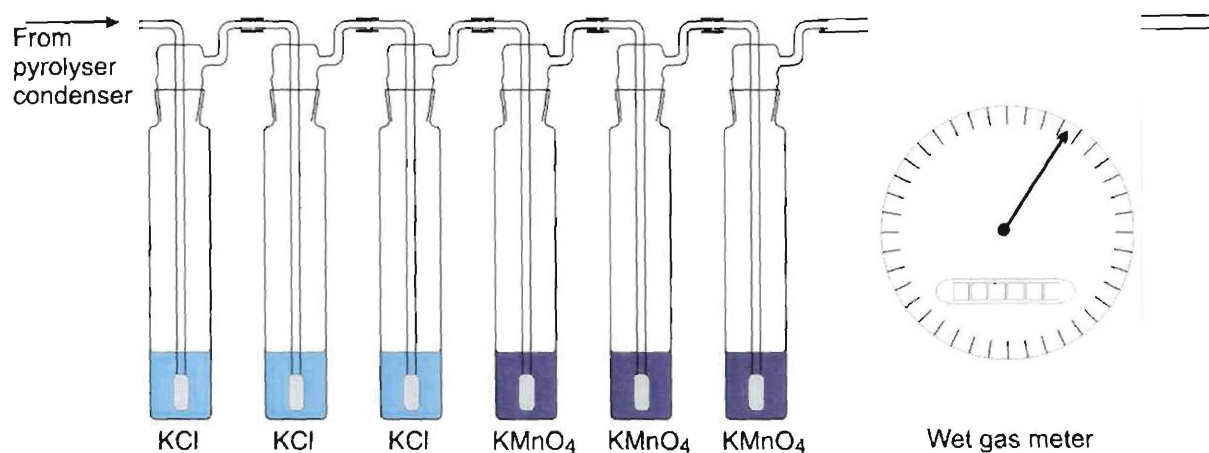


Figure 2.7: The schematic representation of the impinger sampling train system

#### **2.4 Methods for determination of Mercury in Gas Streams (Gold tube and activated carbon tube)**

The objective of this experiment was to validate the analytical technique employed in capturing mercury in gas stream, by spiking the gas stream with a known amount of mercury. The mercury was trapped in tubes containing activated carbon or gold. The gold tubes were ultimately analysed using the SIR GALAHAD mercury analyser. The safety hazards associated with all mercury compounds used in this exercise were considered and detailed information with regard to the safety hazards is attached in Appendix A.

The adsorption of mercury by activated carbon at atmospheric pressure occurs through two distinct mechanisms: Physisorption with heat of adsorption of 97 KJ/mol at low ambient temperatures (<75°C) and chemisorption with heat of adsorption 579 KJ/mol at higher ambient temperatures (>75°C), Kwon, Borquet and Vidic (2003). Thus the activated carbon packed in small glass tube employed in this investigation adsorbs mercury at ambient temperature. In another study it has been demonstrated that varying the physical and chemical properties of activated carbons has an influence on the adsorption of elemental mercury ( $Hg^0$ ) Kwon, Borquet and Vidic (2003). The silica coated with gold is assumed to be trapping only elemental mercury. Therefore the gas

stream in this investigation was spiked with mercury vapour generated from pure mercury, thus highly concentrated with elemental mercury vapours.

#### 2.4.1 Experimental Set-up for Mercury Trapping

The experimental arrangement was separated into setups A and B. The first setup (A) consisted of a laboratory-made mercury vapour generator (Figure 2.8). A small vessel with volume of  $100\text{cm}^3$  was filled with some copper metal strips or 'wool' to have the mercury suspended for even mercury vapour generation. The copper was first cleaned using dilute HCl ( $0.01\text{ mol dm}^{-3}$ ), then dilute  $\text{HNO}_3$  ( $0.01\text{ mol dm}^{-3}$ ). A few drops of mercury and dilute  $\text{HNO}_3$  ( $0.01\text{ mol dm}^{-3}$ ) were then introduced into the vessel. After vigorous shaking the vessel set-up, the mercury managed to stick to the surface of the copper metal.

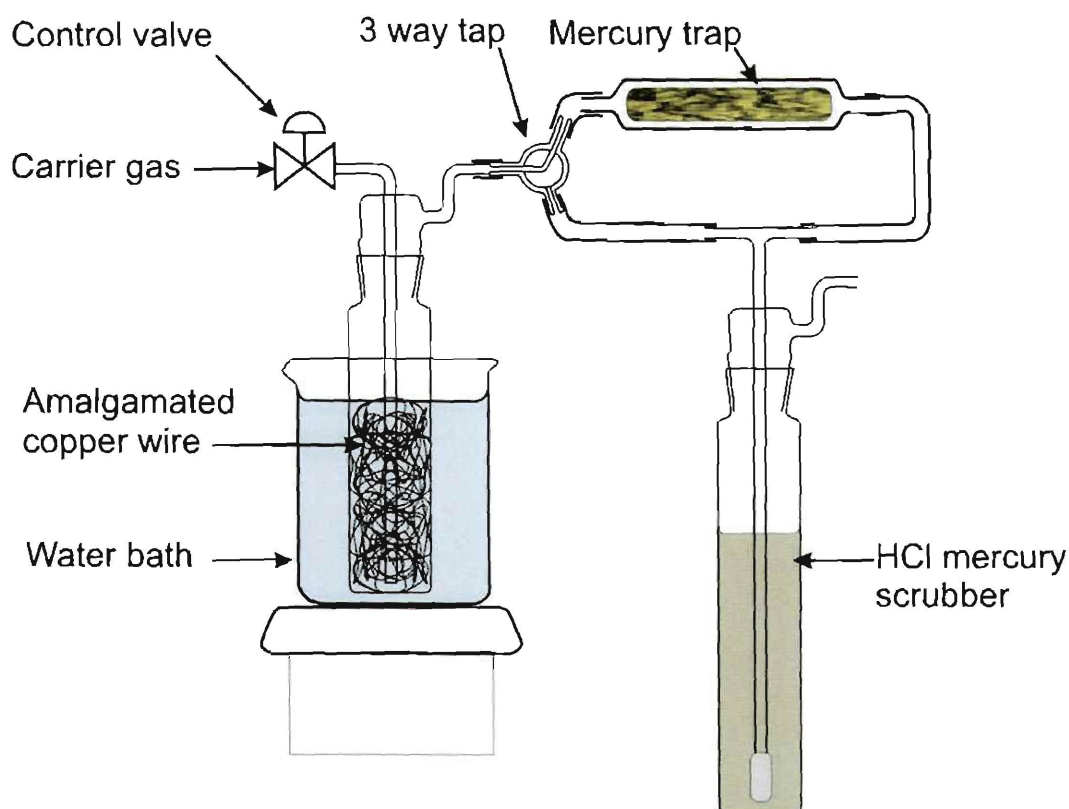


Figure 2.8: Schematic representation of experimental set-up for mercury vapour generation

The cap of the vessel had three air-tight openings for a temperature monitor, an inlet and an outlet gas flow. The temperature was controlled by the water bath. The amount of mercury vapour that could be generated was dependent on the temperature and

pressure of the set-up. The information for the calculation was obtained from the table of vapour pressures of mercury, Lide, (1998-1999) in CRC Handbook of Chemistry and Physics. The three-way valve allowed the gas to by-pass the gold trap, while optimizing the experimental conditions. Unused gas was dissolved in the dilute HCl ( $0.01 \text{ mol dm}^{-3}$ ) solution, which was discarded as per requirement of mercury waste. The flow rate of the inert argon gas used as a carrier gas was controlled through a mass flow controller.

In set-up B, the vessel used in set-up A was adapted with the cap having only one septum, to allow syringing out of a known amount of the mercury gas, instead of flushing a carrier gas to carry the mercury vapour to the collector. The mercury vapour gas was then injected into an inert gas stream, to the gold or activated carbon trap for collection.

In another experiment the method of heating up some mercury salts to generate mercury vapour in a horizontal furnace was briefly investigated by using the gold tubes for mercury vapour trapping. The method proved to be a health hazard, due to the uncontrolled mercury fumes; it was therefore discontinued.

#### **2.4.2 DMA 80 Mercury Analyzer as a Tool for Comparison**

The DMA 80 is a direct mercury analyzer instrument for Hg analysis of liquid and solid samples, which requires very limited sample preparation. The solid samples need to be crushed to at least less than  $150 \mu\text{m}$ . Samples are weighed and introduced into the sample boat. The sample is initially dried and then thermally decomposed in a continuous flow of oxygen. Combustion products are carried off and further decomposed in a hot catalyst bed. Mercury vapours are trapped on a gold amalgamator and subsequently desorbed for quantification. The mercury content is determined using an Atomic Absorption Spectrophotometer at  $253 \text{ nm}$  wavelength. The results generated are presented in both absolute amount of mercury and in concentration.

The DMA 80 used in this investigation was obtained on loan from the instrument supplier, Apollo Scientific cc. This DMA was used to analyze the content of mercury in activated carbon tubes, which were used to trap mercury in gas streams. It was also used as a comparison tool in analyzing liquid samples obtained from impingers during

pyrolysis experiments, therefore also investigating its compatibility with different types of samples. The main objective from the suppliers of this instrument was to evaluate the instrument in terms of reliability and reproducibility of results.

#### **2.4.2.1 Comparison of DMA 80 mercury analyzer and the SIR GALAHAD mercury analyzer**

##### **SIR GALAHAD**

- designed for analysis of the gold tubes as it desorbs the mercury by a thermal process in the evaporation chamber
- carrier gas used is argon
- analyzer used is the atomic absorption spectrophotometer
- mercury detection range up to 22 nanograms with a detection limit of 0.001  $\mu\text{g}/\text{m}^3\text{Hg}$
- gold tubes are re-usable
- analysis time for one gold tube could be up to 10 min

##### **DMA 80 Mercury Analyzer**

- designed for analysis of both solids and liquids with no sample preparation required
- carrier gas used is oxygen, which also supports combustion in the combustion chamber, where complete combustion of the sample takes place in the presence of a catalyst bed which will convert all mercury to elemental mercury
- gold amalgamator exists for trapping the mercury in the oxygen gas stream
- once mercury is desorbed from the amalgamator it is transferred to a reading cell, where the mercury content is determined using atomic absorption spectrophotometry at 253 nm
- analysis time is 5 min per sample, while the loading stage can take up to 40 samples
- large detection range, maximum 600 nanograms Hg, with detection limit of 0.01 nanograms Hg

From this comparison the DMA 80 instrument appears to outweigh the SIR GALAHAD instrument, in that it is compatible with a range of samples and it has a larger detection

range. The gold tubes cannot be analysed in the DMA 80, as it requires complete combustion of the sample that has been introduced, which is not possible with the gold tubes. Activated carbon tubes can also not be analysed in the SIR GALAHAD, as desorption of mercury from the activated carbon is conducted in two parts to determine penetration.

### ***General Observations***

- Mercury on gold absorption is limited and the absorber will be saturated easily in a 1.2 kg coal pyrolysis experiment.
- The operation of the Sir Galahad mercury analyser is not stable enough and unreliable results can easily be obtained.
- The DMA 80 Mercury Analyser is more acceptable in terms of measuring range and ease of operation.
- There were indications of a memory effect with the DMA 80 that would manifest as an over-sampling of mercury.

The solvent trapping of mercury with impingers is still competitive to the use of absorbing tubes, only when a good instrument is used for the actual analysis.

## ***2.5 Modeling of Trace Elements during Coal Processing***

In this section FACTSAGE thermodynamic modeling package is presented with SimuSage used as the interface in performing thermodynamic calculations for coal pyrolysis.

### ***2.5.1 FACTSAGE Thermodynamic Modeling Package***

Factsage is a thermo-chemical software with databases, which is as a result of fusion of two well established thermo-chemical packages (FACT-Win and ChemSage) founded some years ago. The FACTSAGE package runs on a PC operating under Microsoft Windows and consists of a series of information, database, calculation and manipulation modules that enable one to access and manipulate pure substances and solution databases. The modeler can perform a wide range of thermo-chemical calculations and generate tables, graphs and figures of interest to chemical engineers, chemists, etc. It should be noted that the use of FACTSAGE has been made more convenient and is no longer limited to use by only professional modelers, but anyone with enough chemical and thermodynamic knowledge of chemical species can employ

it to solve problems by calculation. A paper by Bale et al. (2002) describes this package in detail discussion of which will not be included in this work.

### **2.5.2 *SimuSage***

SimuSage is a library of components for process modeling and simulation. The system is based on the Borland Delphi's component technology. It enables the developer to assemble a network of "streams" and "unit operations" into a flowsheet in an interactive manner. At the same time it allows for the use of all Delphi-related language and programming features to customise the flowsheet. SimuSage is based on GTT-Technologies' ChemApp Programmer's Library. Thermodynamic data are provided in the form of using ChemSage or ChemApp compatible data-files. The ChemApp equilibrium calculation process is implemented primarily as a unit operation (TPbGttBalance) in SimuSage. More information on the usage of SimuSage is provided in its supporting manual.

### **2.6 *Coal Pyrolysis Modeling***

The FACTSAGE modeling package was used in this project to predict trace element volatility behavior, transformation behavior, partition behavior and speciation behavior during coal pyrolysis in a high pressure reactor in a laboratory. The model allows one to trace the specific temperature and pressure at which a certain species is formed or diminished, as well as the physical state of that component.

### 2.6.1 Comparison of the Actual and Modeled Pyrolysis Experiment

Table 2.2: Comparison of the actual and modeled pyrolysis experiment

Actual pyrolysis	Modeled pyrolysis
<p>Dynamic conditions:</p> <ul style="list-style-type: none"> <li>• Continuous flow of carrier gas</li> <li>• Temperature increases gradually</li> </ul>	<p>Static conditions</p> <ul style="list-style-type: none"> <li>• Constant volume for all reactions taking place</li> <li>• Reactants are reacting at one temperature until they reach equilibrium</li> </ul>
<p>Non-equilibrium</p> <ul style="list-style-type: none"> <li>• Products are continuously removed from reaction vessel</li> <li>• Reaction is conducted for specified period of time</li> </ul>	<p>Thermodynamic equilibrium</p> <ul style="list-style-type: none"> <li>• Products and reactants are enclosed in the isolated system until reaction reaches equilibrium</li> </ul>
<p>Heterogeneous coal with mineral inclusions.</p> <ul style="list-style-type: none"> <li>• Coal is a complex material with a lot of inclusions</li> </ul>	<p>Homogeneous mixture of pure elements and compounds.</p> <ul style="list-style-type: none"> <li>• Only pure components with known thermodynamic values are used to represent coal, omitting other minor coal inclusions</li> </ul>
<p>Uneven temperature distribution</p> <ul style="list-style-type: none"> <li>• In the reactor the temperature is not distributed evenly throughout the coal material</li> <li>• Residence time of the gas in the condensers and absorbers is uneven</li> </ul>	<p>Homogeneous temperatures</p> <ul style="list-style-type: none"> <li>• Temperature is perfect for all reacting materials throughout the reaction</li> <li>• Isolated system with no external influence</li> </ul>
<p>Restricted mass flow between coal components and different regions in the experimental set-up.</p> <ul style="list-style-type: none"> <li>• A distribution of particle size of coal fed into reactor can affect some reactions, inhibiting volatiles escaping</li> </ul>	<p>No mass flow restrictions</p> <ul style="list-style-type: none"> <li>• All components react with no restrictions</li> </ul>
<p>Possible interaction of the reactor material, tubing and other construction material with the coal and reaction products</p>	<p>Apparatus perfectly inert</p>
<p>Erratic trace element trapping due to slow reaction rates and gas-liquid transport problems</p>	<p>Perfect trapping</p>
<p>Large mass balance errors</p>	<p>Perfect mass balance</p>

## 2.7 Calculation

The chemical reactions were not modeled and no knowledge about the chemical processes was needed to calculate thermo-chemical equilibria in the various temperatures. The complete information on how the thermodynamic calculation is performed is reported in the documentation of the package. In brief, the model uses Gibbs energy minimization for fixed values of temperature and pressure varying the amounts of the possible products under the constraint that the element balances must be kept constant. The reaction programme attempts several possibilities of a reaction to take place and ultimately present as output the reaction which has the most negative Gibbs energy change. Hence, according to thermodynamic laws, it is the most likely chemical change at equilibrium.

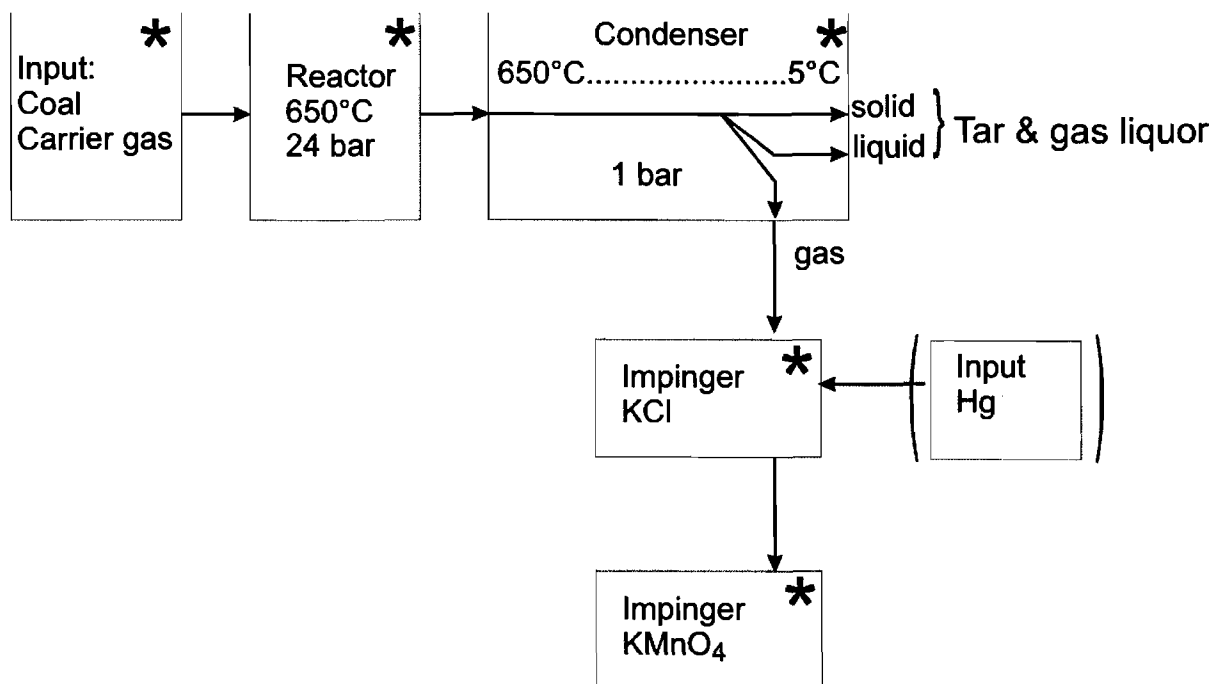


Figure 2.9: Schematic representation of the simulation

\* represents points at which the calculations were conducted

# CHAPTER 3

## Results

### Chapter summary

In this chapter the results obtained using the different sample preparation techniques are presented, followed by a brief discussion of the observed trends and comparison with some certified values. The results obtained for coal reference material using these different analytical techniques, are presented with the certificate values and details of how they were obtained in the reference laboratory as attached in Appendix B. The modeling results are also presented with comparison of the actual experimental results.

### 3.1 Coal Characterisation

Table: 3.1 Mineralogical composition, proximate, ultimate and trace element analysis of the parent coals

	Method	Coal B	Coal A
<b>Minerals:</b>		<b>g/100g</b>	<b>g/100g</b>
<b>Kaolinite</b> $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	XRD	14.1	8.2
<b>Alpha Quartz</b> $\text{SiO}_2$	XRD	4.9	5.6
<b>Calcite</b> $\text{CaCO}_3$	XRD	0.8	0.8
<b>Aragonite</b> $\text{CaCO}_3$	XRD	0.1	1.8
<b>Dolomite</b> $\text{CaMg}(\text{CO}_3)_2$	XRD	1.8	3.9
<b>Gypsum</b>	XRD	1.6	0.0
<b>Pyrite</b> $\text{FeS}_2$	XRD	0.1	0.3
<b>Pyrrhotite</b> $\text{Fe}_{1-x}\text{S}$	XRD	0.0	0.0
<b>Greigite</b> $\text{Fe}_3\text{S}_4$	XRD	0.0	0.0
<b>Muscovite</b> $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{F})_2$	XRD	0.6	1.2
<b>Rutile</b> $\text{TiO}_2$	XRD	0.0	0.1
<b>Gorceixite</b> $\text{BaAl}_3(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6$	XRD	0.5	0.4
<b>Main constituents:</b>		<b>g/100g</b>	<b>g/100g</b>
<b>Moisture</b>		4.96	4.76
<b>Volatiles</b>		22.83	22.34
<b>Fixed Carbon</b>		47.49	49.30
<b>Ash</b>		24.72	23.60
<b>C</b>		53.68	55.38
<b>H</b>		2.85	2.84
<b>N</b>		1.35	1.37
<b>S</b>		1	0.84
<b>Trace metals:</b>		<b>mg/kg</b>	<b>mg/kg</b>
<b>Hg</b>	CVAA	0.20	0.17
<b>As</b>	AES	4.41	2.84
<b>Se</b>	AES	0.75	1.32
<b>Ba</b>	AES	461.5	448.33
<b>Cd</b>	AES	1.06	0.71
<b>Co</b>	AES	8.50	6.17
<b>Cr</b>	AES	33.29	38.07
<b>Cu</b>	AES	13.99	11.17
<b>Mn</b>	AES	101.5	89.47
<b>Mo</b>	AES	0	0.60
<b>Ni</b>	AES	17.23	14.27
<b>Pb</b>	AES	6.45	6.77
<b>V</b>	AES	30.77	28.40
<b>Zn</b>	AES	9.82	11.53

### 3.2 Microwave-oven Digestion (method evaluation)

#### 3.2.1 Microwave Coal Digestion Method 1 and 2

The results obtained from the microwave digestion of coal following Method 1 (acid mixture) and Method 2 (HNO<sub>3</sub> acid only), using ICP-AES for analysis of trace elements are presented in Table 3.2, Table 3.3 and Table 3.4.

Table 3.2: Concentration of trace elements in SARM 18 coal (South African Reference Material 18) prepared using Method 1 (HNO<sub>3</sub>/HCl/HF) of the microwave oven digestion and ICP-AES for analysis.

	Co	Ni	Mn	Cr	V	Zn	Cu	Pb	Cd	Mo	Ba
Sample	mg/kg										
obtained	6.5	7.1	19	14	21	3.1	6	<9.5	<0.56	<2.40	82
	<b>6.7</b>	<b>10.8</b>	<b>22</b>	<b>16</b>	<b>23</b>	<b>5.5</b>	<b>5.9</b>		<b>0.032</b>		<b>78</b>
certificate values	(5.5-7.2)	(10.1-11.5)	(21-23)	(14-18)	(21-25)	(5.2-6.8)	(5.2-6.4)	5	(+/-0.002)	1	(71-82)

**Bold figures are certified values with the acceptable ranges in brackets**

\* unct. = uncertified

Table 3.3: Concentration of trace elements in SARM 20 coal prepared using Method 1 (HNO<sub>3</sub>/HCl/HF) of the microwave-oven digestion and ICP-AES for analysis.

	Co	Ni	Mn	Cr	V	Zn	Cu	Pb	Cd	Mo	Ba
Replicate no.	mg/kg										
1	9.3	13	57	50	40	12	19	19	0.77	3.4	227
2	9.4	13	55	52	39	12	19	20	0.77	3.7	250
3	8.7	14	52	50	39	12	20	21	0.84	4	260
4	8.3	12	54	50	40	12	21	19	0.85	3.6	264
5	10	13	59	53	42	317*	20	26	1.1*	3.9	>417*
Std Dev	0.66	0.71	2.7	1.4	1.22	0.0	0.8	2.9	0.04	0.2	16.5
Certified values	<b>8.3</b>	<b>25</b>	<b>80</b>	<b>67</b>	<b>47</b>	<b>17</b>	<b>18</b>	<b>26</b>	<b>0.1</b>	<b>1.4</b>	<b>372</b>
	(7.6-9.0)	(23-26)	(77-82)		(45-50)	(14-18)	(15-19)	(20-29)			(363-384)

**Bold figures are certified values with the acceptable ranges in brackets.**

\* excluded from calculation as outliers

### 3.2.2 Microwave Coal Digestion Method 2

Table 3.4: Concentration of trace elements in SARM 20 coal prepared using method 2 (HNO<sub>3</sub> only) of the microwave-oven digestion and ICP-AES for analysis.

Sample	Co	Ni	Mn	Cr	V	Zn	Cu	Pb	Cd	Mo	Ba
Replicate no	mg/kg										
1	7.7	20	69	61	35	31*	17	<23	<1.4	7.7	Blank contamination
2	7.6	22	64	56	32	18*	16	<23	1.6	6.2	Blank contamination
3	7.8	19	65	57	33	18*	16	<23	<1.4	6.3	Blank contamination
4	7.6	18	67	57	33	41*	18	<23	<1.4	6.4	Blank contamination
5	8.1	17	67	55	32	29*	20	<23	<1.4	5.9	Blank contamination
6	7.0	16	62	50	30	1*	16	<23	<1.1	<4.8	314
7	6.8	17	61	52	31	109*	19	<23	<1.1	<4.8	321
8	7.1	16	62	51	31	6.3*	17	<23	<1.1	<4.8	330
9	7.4	17	61	51	31	57*	17	<23	<1.1	<4.8	326
10	6.8	17	60	52	31	1*	17	<23	<1.1	<4.8	324
Std Dev	0.4	1.9	3.1	3.6	1.4	/	1.3	/	/	0.7	6.0
	<b>8.3</b>	<b>25</b>	<b>80</b>		<b>47</b>	<b>17</b>	<b>18</b>	<b>26</b>			<b>372</b>
Certified values	(7.6-9.0)	(23-26)	(77-82)	<b>67</b>	(45-50)	(14-18)	(15-19)	(20-29)	<b>0.1</b>	<b>1.4</b>	<b>372</b> (363-384)

**Bold** figures are certified values with the acceptable ranges in brackets

\* excluded from calculation as outliers

### 3.2.3 Discussion

The initial investigations centred on the comparison of HNO<sub>3</sub> and a mixture of acids, namely HNO<sub>3</sub>, HCl and HF to achieve complete digestion of the coal. The advantage of using only HNO<sub>3</sub> acid is that it is a simpler procedure with all the elements requiring detection being soluble; it does not require the addition of boric acid to the final solution to neutralise the HF, thus minimising the dilution factor. The latter is necessary if the ICP set-up is not compatible with HF. When using HNO<sub>3</sub> only, complete digestion is

not achieved and a small amount of residual material (mineral matter such as silicates that did not dissolve in hot HNO<sub>3</sub>) needs to be filtered off (Lachas et al., 1999). This did not appear to adversely affect the results. The use of a mixture of acid was also investigated by Atkin et al. (1995), which is based on the sequential attack of coal sample by the acids. The results of the analysis of SARM 18 prepared using Method 1 are presented in Table 3.2. The results of the analysis of SARM 20 using HNO<sub>3</sub>/HCl/HF method and HNO<sub>3</sub> only method are presented in Table 3.3 and 3.4 respectively. For comparison purposes the certificate values are included. While the recoveries of some of the elements were below that expected, relatively good repeatability and reproducibility were observed for both methods in both samples.

In general from the results it is evident that the HNO<sub>3</sub> acid digestion gave higher recoveries (although not always in line with the certificate value) than the mixture of acids. The lower recoveries observed, compared to the certificate values, were first thought to be due to loss of analyte as a result of volatility of the elements and subsequent loss of the elements on opening of the digestion vessel. This was tested by opening the vessels at an elevated temperature (100°C) as opposed to ambient temperature. No significant difference in the results was observed between the vessels opened at room temperature and at elevated temperature. An experiment was also conducted where the digestion vessels were cooled to 4°C for 60 minutes in a cold room. Once again, no difference in the results between the cooled vessels and the vessels opened at ambient temperature was observed. It is noted that Atkin et al. (1995) cooled the vessels before opening by immersing them in water. Lachas et al. (1999) also cooled the vessels after the final digestion step to -18°C before opening, to prevent loss of volatile elements.

The above investigation highlighted a few areas that required special attention. The first was contamination; this was particularly evident in the zinc and barium results. In the case of the latter, blank contamination was also a problem and highlighted the need for careful washing of all apparatus and the use of very pure reagents. The second was that the dilution factor should be kept to a minimum, to avoid obtaining results below the limit of detection (LOD) of the ICP. This was particularly evident for Pb (LOD 23 mg/kg), Cd (LOD 1.4 mg/kg) and Mo (LOD 4.8 mg/kg). Keeping the dilution factor to a minimum is difficult, as there are limitations to the sample size that one can use

and the amount of acid necessary for successful digestion. To improve the detection limit, the samples were diluted to 25 cm<sup>3</sup> (Samples 1 - 5, Table 3.3) instead of 50 cm<sup>3</sup> as for Samples 1 -10, Table 3.4.

The use of HNO<sub>3</sub> acid was not successful for the digestion of SARM 18 and poor recoveries were obtained, which was most likely attributed to the very poor digestion observed. The analysis results obtained using the HNO<sub>3</sub> acid method for SARM 18 are not presented due to the poor digestion. A large amount of undigested material remained in the digestion vessel (much more than SARM 20) and attempts to digest the sample completely, by the addition of more acid and by increasing the duration of microwave programme, were unsuccessful. In Lachas et al. (1999) remaining material after digestion with HNO<sub>3</sub> acid were filtered off. Although elements to be detected are soluble in HNO<sub>3</sub> acid, filtering off of remains introduces some uncertainty in the results. Some elements could still be trapped in the material that could not be accessed by HNO<sub>3</sub> acid. It is also noted that Lachas et al. (1999) suggests that the success of the sample preparation is dependent on the nature of the sample or the mode of occurrence of the trace elements.

It was observed again, when digesting the Highveld coal samples, that complete digestion was not possible with only HNO<sub>3</sub> acid. Lachas et al. (1999) has documented the inability of the HNO<sub>3</sub> acid to completely destroy the inorganic species (particularly silicates) and liberate the trace elements in ash. Gaines and Brolin (2003) highlight that HNO<sub>3</sub> acid is a very useful component in the destruction of organics but cannot by itself completely decompose organic matrices. In view of this and the difficulties experienced in digesting coal from different sources, it was decided to concentrate efforts on the use of HNO<sub>3</sub>/HCl/HF as the digestion mixture, since this was less problematic in terms of the sample preparation, i.e. complete digestion occurred, using a smaller amount of acid and no filtering was required, thereby reducing the possible sources of contamination and inaccuracies. As the ICP set-up at Sasol Infrachem laboratories is capable of withstanding HF, the addition of boric acid was not necessary, enabling the preparation of more concentrated samples, hence reducing the dilution factor.

Dissolution of SARM 18 was achieved using HNO<sub>3</sub>, HCl and HF. The results are presented in Table 3.2. Most of the elements analysed compare well with the certified

values and are close to the specified limits. In the case of Pb, Cd and Mo, these elements are below the limit of detection and can thus not be determined accurately. To overcome this, an even smaller dilution is necessary or analysis by ICP-MS could be necessary. ICP-MS was not accessible during the course of this project.

The microwave digestion of SARM 20, using HNO<sub>3</sub>, HCl and HF, was repeated several times in an attempt to optimize the conditions and improve the recoveries of the elements to be in line with the certified values, but this could not be achieved. In all instances good repeatability and reproducibility were observed, but the certified values could not be obtained for all elements, which led to explore other sample preparation methods.

### 3.3 American Society for Testing and Materials standard test methods (ASTM)

The results of trace element concentration in coal obtained using the different ASTM methods are presented below:

#### 3.3.1 ASTM method for trace elements determination (D6357-00a)

Table 3.5: Concentration of trace elements in SARM 19 & 20 coal prepared using ASTM method D6357-00a and ICP-AES for analysis.

Sample:	Co	Ni	Mn	Cr	V	Zn	Cu	Pb	Cd	Mo	Ba
SARM 20	mg/kg										
Replicate 1	11	17	61	42	38	14	17	11	0.44	0.94	469
Replicate 2	16	18	61	47	40	14	16	16	0.36	1.0	337
Certified values	<b>8.3</b> (7.6-9.0)	<b>25</b> (23-26)	<b>80</b> (77-82)	<b>67</b>	<b>47</b> (45-50)	<b>17</b> (14-18)	<b>18</b> (15-19)	<b>26</b> (20-29)	<b>0.1</b>	<b>1.4</b>	<b>372</b> (363-384)
SARM 19											
obtained	8.2	11.9	127.7	33.5	33.5	10.4	16.2	21	<0.06	2	310.5
Certified values	<b>5.6</b> (5-6.6)	<b>16</b> (13-20)	<b>157</b> (143-168)	<b>50</b> (47-58)	<b>35</b> (33-37)	<b>12</b> (12-16)	<b>13</b> (11-14)	<b>20</b> (17-23)		<b>2</b>	<b>304</b> (295-318)

**Bold figures are certified values with the acceptable ranges in bracket.**

The obtained results (Table 3.5) for the reference material appear to be within the stipulated range for most of the elements. SARM 20 has more of the elements

analysed and certified in the reference laboratory and therefore it is the material of choice for benchmarking in this work.

### 3.3.2 Results Comparison

Comparison of results obtained using ASTM method to those obtained using microwave digestion method is presented in Table 3.6

Table 3.6: Comparison of trace element concentration for SARM 20 as obtained using ASTM method D6357-00a and microwave digestion Method 1 as sample preparation techniques.

Sample	Co	Ni	Mn	Cr	V	Zn	Cu	Pb	Cd	Mo	Ba
SARM 20	mg/kg										
Replicate 1 (microwave method 1)	5.1	7	89	30	30	7	48	<10	<0.56	3.6	347
Replicate 2	4.9	7	91	30	30	6	54	<10	<0.56	3.8	*na
Replicate 1 ASTM method	11	17	61	42	38	14	17	11	0.44	0.94	469
Replicate 2	11	18	61	47	40	14	16	16	0.36	1.0	337
Certified values	<b>8.3</b> (7.6- 9.0)	<b>25</b> (23- 26)	<b>80</b> (77- 82)	<b>67</b>	<b>47</b> (45- 50)	<b>17</b> (14- 18)	<b>18</b> (15- 19)	<b>26</b> (20- 29)	<b>0.1</b>	<b>1.4</b>	<b>372</b> (363- 384)

**Bold figures are certified values with the acceptable ranges in brackets**

\*na = not analyzed

Both methods tend to show substantial deviations from the certified trace metal concentrations for SARM coal. The ASTM method seems to be slightly better for most trace elements.

### 3.4 Arsenic, Selenium determination (D4606–95) and Mercury determination (D6414–99)

Concentration of the selected trace elements in coal, as obtained using ASTM methods is presented in Table 3.7. ICP-AES was used for determination of As and Se, while cold vapour atomic absorption spectrometry was used for determination of mercury.

Table 3.7 Trace elements (Hg, As and Se) concentration results obtained for coal reference materials SARM 19 & 20, using ASTM method as sample preparation method.

<b>Sample</b>	<b>As</b>	<b>Se</b>	<b>Hg</b>
SARM 20	mg/kg		
Replicate 1	0.91 (outlier)	5.3	0.3
Replicate 2	5.8	0.9	0.2
Replicate 3	4.9	0.8	0.2
Certified values	<b>4.7 (4.6-6)</b>	<b>0.8 (0.7-1)</b>	<b>0.25 (0.2-0.3)</b>
SARM 19	7.5	1.2	0.2
Certified values	<b>7</b>	<b>1 *uncert.</b>	<b>0.2 *uncert.</b>

**Bold figures are certified values with the acceptable ranges in brackets**

\*uncert. = uncertified certificate value

The results obtained for the selected elements show a good agreement with the respective certificate values provided for these reference materials. Where the certified value was not obtained, the value obtained was within the acceptable range.

### 3.5 Methods for determining the mode of occurrence of trace elements in coal

#### 3.5.1 Sequential leaching

##### 3.5.1.1 Column method

In Table 3.8 the amount of trace elements recovered by sequential column leaching from Highveld coals is given. The amounts leached are reported as mg trace metal leached from 1 kg coal. The solvents were used in the sequence given in the table. ICP-AES was used for the actual analysis.

Sample	Parent (feed)	H <sub>2</sub> O	NH <sub>4</sub> OAc	HCl	HNO <sub>3</sub>	HF	cumulative % leached	
								mg/kg
Co	coal B	7.5	0.013	0.0085	0.027	0.0031	0.088	2
	coal A	6.2	0.012	0.0031	0.01	0.0031	0.0031	0.5
Ni	coal B	23	0.37	0.43	0.2	0.024	0.64	6
	coal A	15.5	0.4	0.076	0.084	0.019	0.46	5
Mn	coal B	107	0.68	0.51	6.7	0.45	0.72	9
	coal A	90	1.18	0.47	5.3	0.27	0.45	8
Cr	coal B	55.5	0.029	0.0073	0.85	0.041	0.3	0.8
	coal A	36	0.036	0.0073	0.14	0.04	0.25	1
V	coal B	33.5	0.013	0.0034	0.027	0.0052	0.61	2
	coal A	32.5	0.014	0.0034	0.05	0.0071	0.3	1
Zn	coal B	11.9	0.08	0.16	1.67	0.27	2.75	41
	coal A	10.05	0.27	0.082	0.22	0.055	0.50	10
Pb	coal B	8	0.88	0.047	0.047	0.047	0.335	8
	coal A	6.85	0.188	0.047	0.079	0.064	6.85	6
Cd	coal B	0.52	0.021	0.01	0.0082	0.007	0.047	18
	coal A	0.26	0.026	0.009	0.0067	0.0069	0.047	34
Mo	coal B	1.45	0.048	0.03	0.022	0.014	0.0028	8
	coal A	2.3	0.062	0.033	0.0125	0.014	0.0028	5
Ba	coal B	491	0.26	4.4	3.6	1.1	0.0028	3
	coal A	476	2.5	4.2	5.3	0.6	0.02	3
Cu	coal B	13	0.038	0.027	0.12	0.053	1.5	13
	coal A	14	0.16	0.017	0.07	0.064	3.3	25
Hg	coal B	0.14	0.012	0.003	0.003	0.003	0.039	40
	coal A	0.16	0.058	0.038	0.28	0.034	0.002	66

### **3.5.1.2 Results Discussion**

The amount of elements leached from coal A and coal B using the column method is reported in Table 3.8. There are only a few elements (Hg, Cd and Zn) that were cumulatively leached to a significant amount. As and Se were not analysed in this method. Mercury was leached to about 50% of the content present in the parent coals and a larger portion was leached by water. This suggests that the mercury is present in an exchangeable form in coal and not tightly bound in the coal matrix. A noticeable portion of mercury was also detected in HCl solution for the coal A, indicating that some of the mercury could be present in the mineral matter, especially the part containing monosulphides. HCl is able to react with pyrite, thus removing the mercury associated with pyrite.

Manganese was found in large amounts in the HCl solution, compared to the other solutions. As it has been mentioned HCl has an affinity for the monosulphide minerals, therefore the presence of Mn in HCl indicates the presence of Mn in monosulphide minerals. Pb, Cu and Zn report high levels in HF acid. HF destroys mainly silicates, therefore elements with high concentration in this acid solution could be bound in the silicate matrix of the coal. The concentration of most of the trace elements is just higher in HF than in the other solutions, indicating the low presence of trace elements in the silicate matrix. It was noted during the experiment that there was difficulty in controlling the residence time of the solution in the sample, this could contribute to poor repeatability of the analytical results. It has been mentioned that leaching methods cannot be used on their own to determine mode of occurrence of trace elements, but it should be coupled with direct measurement methods.

### 3.5.2 Slurry Method

In Table 3.9 the amount of trace elements recovered by sequential slurry leaching from coal B is given. The amounts leached are reported as mg trace metal leached from 1 kg coal. The solvents were used in the sequence given in the table. ICP-AES was used for the actual analysis.

	parent	NH <sub>4</sub> OAc	HCl	HNO <sub>3</sub>	cumulative % leached
mg/kg					
Hg	0.14	* na	na	na	na
As		na	na	na	na
Se		na	na	na	na
Ba	491	1.3	7.8	14.8	4.9
Cd	0.52	< dl	< dl	< dl	0
Co	7.5	0.0304	0.19	0.46	9.1
Cr	55.5	< dl	0.54	12.5	23.5
Cu	13	0.013	0.091	0.71	6.3
Mn	107	0.76	14.1	4.2	17.8
Mo	1.45	< dl	< dl	< dl	0
Ni	23	0.15	0.56	5.99	29.1
Pb	8	< dl	0.54	0.29	10.4
V	33.5	< dl	0.21	0.24	1.3
Zn	11.9	< dl	0.21	0.55	6.4

\*na = not analysed for that element

< dl = below detection limit of instrument

There is poor agreement between results obtained using column leaching method and slurry leaching method. The residence time of the solutions in the column could be contributing to this observed difference in results. It has been mentioned as well in literature that comparing results from one leaching technique to the other is a difficult task (Huggins, 2002).

### 3.5.3 Float and Sink Density Separation Method

The ASTM method (D6357-00a) was used for the trace element analysis and the bulk components (sulphur, volatile matter, fixed carbon and ash) were analysed by a Sasol

proprietary method. Cold vapour atomic absorption was used for mercury analysis, whilst ICP-AES was used for analysis of the rest of the trace elements.

Table 3.10 Trace element concentration obtained in the density separated samples for coal B.

Density / g/cm <sup>3</sup>	Float 1.5	Float 1.7	Float 1.8	Sink 1.5	Sink 1.7	Sink 1.8
mg/kg						
Hg	1.1	0.34	0.57	0.17	0.56	1.3
As	0	3	4.1	3.8	5.6	8.7
Se	0.47	0.53	1	0.89	1.1	2
Ba	253.4	329.1	380.3	401.6	130.5	123.5
Cd	0	0	0	0	0	0
Co	7.6	6.2	6.7	7.8	6.7	6.3
Cr	28	31.9	29.7	29.9	45.6	43.7
Cu	12.2	16.8	14.6	11.9	13.8	14
Mn	36.7	75.2	83.4	100.8	232.1	277.5
Mo	0.47	0	0	0	0.98	1.31
Ni	10.6	15.3	14.5	16.7	20.9	21.8
Pb	0	8.2	7.1	6.6	6.1	9.8
V	30.9	22.3	22.1	22.6	26.3	25
Zn	2.8	4.3	4.3	7.4	18	21.7
Mass fraction g/100g	14.8	85.8	88	85.2	13.6	12
g/100 g coal fraction						
Sulphur	0.6	0.7	0.61	1	3	4
Volatiles	31	29	27	24	24	24
Fixed C	60	54	50	16	30	30
Ash	10	17	22	60	46	45

Table 3.11: Trace element analysis in the density fractions and in the sequential leaching solutions for coal A.

							coal leaching			
	Float 1.5	Float 1.7	Float 1.8	Sink 1.5	Sink 1.7	Sink 1.8	NH <sub>4</sub> OAc	HCl	HNO <sub>3</sub>	
	mg/kg									
Hg	0.09	0.65	0.46	0.29	0.9	0.85	na	na	na	
As	* na	na	na	na	na	na	0.14	35.32	32.98	
Se	na	na	na	na	na	na	0	0	0	
Ba	380	430	481	499	531	613	5.7	7.5	5.1	
Cd	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl	
Co	4.4	3.7	4.8	5.3	8.8	12	0.0058	0.086	0.13	
Cr	34	34	38	37	33	36	0	0.104	2.2	
Cu	7	6	6	8	6	2	0.0096	0.12	0.41	
Mn	51	88	100	124	193	232	0.81	7.4	0.5	
Mo	1	1.6	1.7	1.7	4.2	4.1	0.074	0.028	0.061	
Ni	36	16	20	17	29	22	0.029	0.104	1.2	
Pb	3	3	7	9	13	12	0	0.35	0.17	
V	26	25	28	28	34	36	0	0.22	0.2	
Zn	9.4	10	17	17	32	39	0.015	0.22	0.45	
Mass fraction g/100g	10.01	84.67	91.12	88.22	14.41	7.41				
	g/100g coal fraction									
Sulphur	0.54	0.56	0.6	0.95	2.19	2.18				
Volatiles	27.5	26.8	25.2	23.6	22.6	22.1				
Fixed C	62.0	54.0	50.2	47.7	28.9	15.4				
Ash	10.5	19.2	24.6	28.7	48.5	62.5				

\*na = not analysed for that element

<dl = less detection limit of instrument

### 3.5.4 Results discussion

#### 3.5.4.1 Carbon and Ash Content

The carbon and ash content in the samples reported in Table 3.10 and 3.11 was used to indicate the success of the separation between the density separated fractions. The sink fractions, as expected, are richer in ash content (mineral matter) than their corresponding float fractions. The carbon content is depleted in the sink fractions,

therefore clean coal is the float fractions. Elements associated with the mineral matter would report higher concentrations in the sink fractions, whereas those elements associated with the organic matter would report higher concentration of the corresponding float fractions. In these samples there was good separation between the fractions since the sink fraction at 1.8 had 45% ash compared to float fraction at 1.5 that had 10% ash, for both samples.

As expected, the high density components in the float increased as the density of the separating fluid was increased. As a result, the lowest ash fraction was only obtained in the float of the lowest density separating fluid and the highest ash content was only obtained in the sink of the highest density separating liquid.

#### **3.5.4.2 Sulphur**

The content of sulphur present in the coal could be linked to sulphur-containing minerals present in the coal. From literature (Huggins, 2002) pyrite is known to be the main sulphur-bearing mineral in coal, therefore it would be logical to suggest that the increase in sulphur content in the sink fractions indicates the presence of pyrite. Although no Fe analysis was conducted, but based on the above information, it could be assumed that trace elements associated with pyrite would show a correlation to the sulphur content present in coal.

#### **3.6 Mode of Occurrence of Trace Elements in the Investigated Coal**

It has been mentioned earlier in Chapter 1 that the mode of occurrence of trace elements in coal influences the behavior of that element during coal utilization. The behavior of mercury during pyrolysis could have been influenced by its occurrence in the coal. In Chapter 3 the association of trace elements with known minerals in coal was briefly presented. In this section more detailed information on the mode of occurrence of trace elements in coal is presented, in order to fully understand their behavior during coal pyrolysis. The discussion will centre around the three important elements Hg, As and Se in the two coals (coal A and coal B). The coal B results are used as an example for the calculation and it has been mentioned that the two coals are not significantly different from each other in terms of trace elements.

Table: 3.12: Calculated concentrations of trace elements (based on density separation data) and the percentages of elements having affinity for the organic (OEA) and inorganic (IEA) matter in coal.

Element	Parent coal	Calculated average mg/kg	IEA (%)	OEA (%)
Hg	0.2033	0.45	47.06	52.94
As	4.41	3.59	100	0
Se	0.755	0.86	91.64	8.36
Ba	461.5	343.75	90.12	9.88
Cd	1.06	0.00		
Co	8.505	6.90	85.51	14.49
Cr	33.295	31.59	86.00	14.00
Cu	13.995	14.29	84.87	15.13
Mn	101.5	98.17	94.05	5.95
Mo	0	0.12	0	100
Ni	17.235	15.74	90.06	9.94
Pb	6.45	6.99	100	0
V	30.77	23.04	80.80	19.20
Zn	9.825	6.42	93.83	6.17

In Table 3.12, the method developed by Klika and Kolomaznik in Querol et al. (2001) has been used for the calculation of quantitative element distribution between inorganic parts of coal. This method is based on the following data input from sink-float experiments (as adapted for this calculation):

1. Mass of coal fraction
2. Concentrations of the elements for the distributions to be calculated

Generally, total concentration of the *i*th element ( $c_{C,i}$ ) in coal can be expressed using the following equation:

$$c_{C,i} = CI,i \frac{mI}{mC} + cO,i \left( 1 - \frac{mI}{mC} \right) \quad (2)$$

where  $CI,i$  is the concentration of the *i*th element in the inorganic and  $cO,i$  in organic parts of coal,  $mI$ ,  $mO$  and  $mC$  are the mass of inorganic and organic parts and total coal mass respectively. Eq. (2) is valid for each of the coal fractions. Then the percentage of the *i*th inorganic element affinity (IEA) of coal is defined as the percent of the element

in the inorganic components of coal in comparison to the total amount of the element present. In the same manner the organic element affinity is defined so that (IEA + OEA = 100).

$$IEA = \frac{cO,i.mI}{cC,i.mC} \cdot 100 \quad (3)$$

***Example of calculation based on data in Table 3.10, using a total coal of 100g in each density separation experiment***

Calculated total element concentration in coal = concentration of element in sink 1.5 (mass fraction of sink 1.5/ 100) + Float 1.5 (1- (mass fraction at sink 1.5/ 100))

Therefore: Calculated total Hg concentration in the coal = 0.17(14.8/100)+1.1(1-(85.2/100))

The above calculation gives a calculated Hg value from using only the density separated fractions at 1.5gcm<sup>-3</sup>. The calculation is then performed for the other float fractions at 1.7 and 1.8 and an average value is obtained, which is then compared to the parent coal measured values.

*Inorganic element association* = (concentration of element (Hg) in sink 1.5 x mass fraction of sink 1.5)/ (calculated concentration (Hg) at float 1.5 x total mass) x 100

Therefore: IEA = (1.7 x 85.2/0.31 x 100) x 100

From these results (Table 3.12), it is observed that for most of the elements, there is good agreement between the calculated values when compared to the parent coal measured values. This good agreement in the mass balance between total coal and density fractions validates the density fractionation and analytical methodologies. The calculated distribution of the elements between the organic and inorganic part of the coal is calculated, only based on the density fractions at 1.5 g cm<sup>-3</sup>.

### **3.6.1 Mercury**

According to literature (Goodarzi, 2002), mercury is mostly associated with pyrite. Results reported for float and sink data in Chapter 3 (for both coals) indicate mercury to be present in both organic and inorganic parts of the coal. According to calculated results in Table 3.12, mercury appears to be distributed equally between the organic matter of the coal (52%) and the inorganic matter 47%. Goodarzi (2002) indicated that

from recent data on the mode of occurrence of mercury for a suite of coals, mercury is mostly associated with the organic fraction of coal, followed by pyrite and carbonate. Pyrite in this case is linked to the content of sulphur in the coal, as mentioned earlier. Therefore, the calculated results are contradictory to the observed results presented in Chapter 3 (float and sink density data for coal B, section 3.4.3), because there is more sulphur or pyrite (4%) in sink fraction of 1.8 than there is (0.6%) in float fraction of 1.5 g/cm<sup>-3</sup>. Benson (1998), Finkleman (1994) and Diehl et al. (2004) found mercury to be inorganically associated in coal. In a review article, Yudovich & Ketris (2005) concluded that mercury is a very coalphile element, with a strong affinity for inorganic and organic coal matter. Leaching of coal B, using the column method, indicated mercury to be present in some silicate minerals as it was found in significant concentration in HF solution. A significant portion of the mercury was found in the water, indicating that part of the mercury could be occurring in the organic part of the coal. According to leaching protocol, if mercury was in the mineral matter it should have reported a high concentration in the HNO<sub>3</sub> solution since HNO<sub>3</sub> dissolves pyrite at ambient temperatures. It was expected that there would be high concentration of mercury in the sink 1.8 fraction, as sulphur is found to be enriched in this fraction. Feng & Hong (1999) found mercury to have a good correlation with sulphur, but determined a negative correlation between Hg and organic matter present in coal. It can be concluded with some uncertainty, from these conflicting results that mercury in coal B occurs in both the organic and the inorganic form of the coal.

### **3.6.2 Arsenic and Selenium**

The content of As and Se is high in the sink fractions, especially so in the sink 1.8 fraction (Chapter 3, float and sink density data for coal B, section 3.4.3) compared to the corresponding float fractions. This is a good indication that the two elements could be associated with the mineral matter in coal. The calculation in Table 3.12 further confirms the association of As and Se with the mineral matter as 100% and 91% respectively to be in the inorganic part of the coal. Spears et al. (1999) indicated the possible association of these elements with pyrite and that they could have been enriched in pyrite from a seawater source. Diehl et al. (2004) suggest that As and Se are mostly likely in solid solution with pyrite and they could have occurred during a late stage metal-bearing fluid migration event in coals from the warrior field. Goodarzi (2002) indicates that As in coal is generally thought to be associated with pyrite, most

likely in a solid solution; however, a portion of As may be organically associated or in a chelated form. Finkelman (1994) pointed out, with a high level of confidence, the association of As in coal with pyrite although there may be very minor As associated organically in coal. It is suggested by Finkelman (1994) that Se is associated in organic constituents with most coal, which is contradictory to the findings of this work. Benson (1998) found Se to be associated with the organic matrix of coal. Based on Wagner and Hlatshwayo (2005) As and Se is associated with mostly the mineral matter of coal, although selenium may have many other associations including organic association. It should be noted that in the leaching method As or Se were not detected in the solutions (due to detection limit), but overwhelming evidence of mineral association based on leaching has been cited in literature presented (Wagner and Hlatshwayo, 2005, Goodarzi, 2002 and Finkelman, 1994). Therefore from the results of this work and with comparison with most literature reported on lignite coal As & Se appear to be inorganically associated in the Highveld coal.

### ***3.7 Methods for determination of Mercury in Gas Streams (Gold tube and activated carbon tube)***

It appears that gaseous mercury in a gas stream can be more conveniently recovered by absorption tubes than by the well established method of a set of wash bottles with impingers. Both gold and activated carbon traps were tested to determine the suitability of these methods to collect mercury from the pyrolyser gas stream.

#### ***3.7.1 Validation of the Gold and Carbon Trap in Trapping Mercury in a Gas Stream***

Presented in this chapter are the results obtained from the two different experimental methods A and B, as described in Experimental in Chapter 2. Both methods of introducing mercury depend on the vapour pressure of mercury at a controlled temperature.

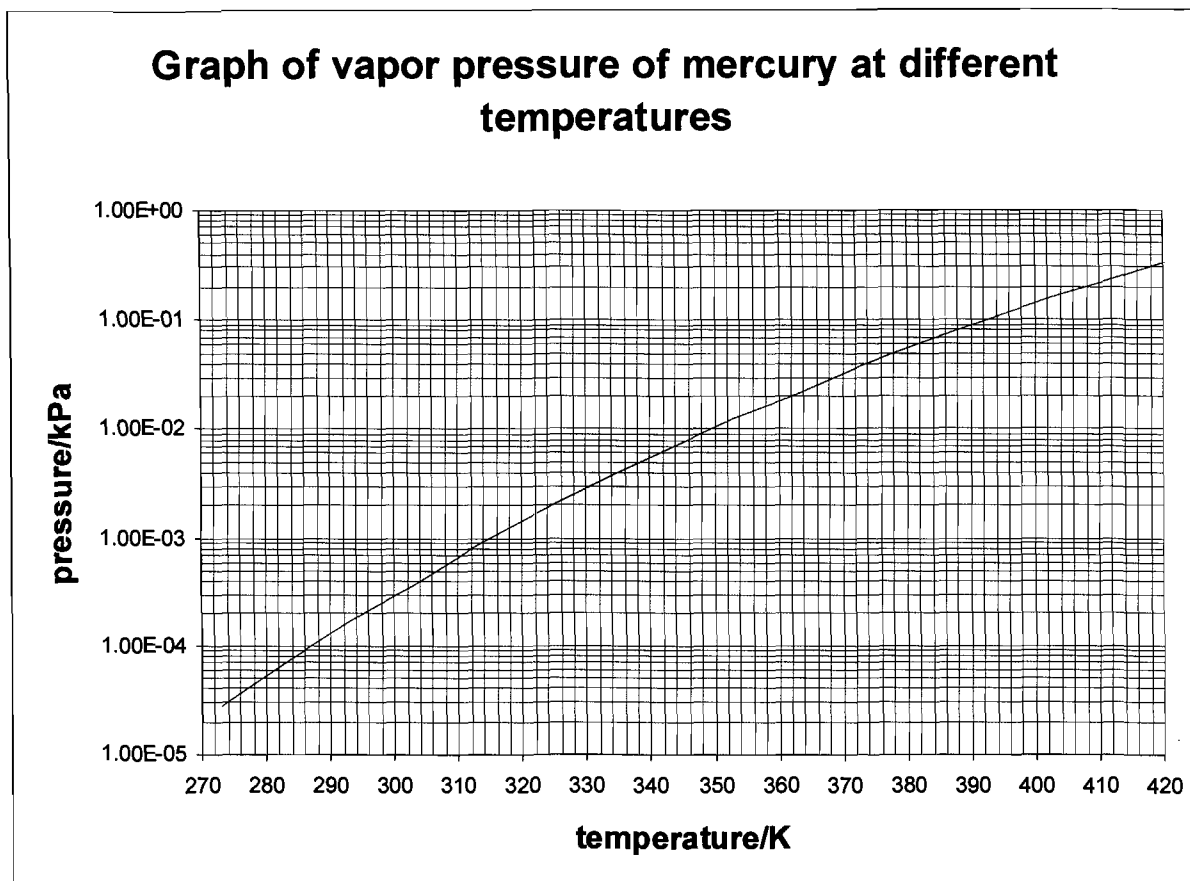


Figure 3.1: A graph of vapour of mercury at different temperatures is presented. The data for the graph was obtained from the table of vapour pressures of mercury (CRC Handbook of Chemistry and Physics).

It should be noted that the maximum detection range of the SIR GALAHAD mercury analyser (for gold tube analysis) is 22ng of mercury.  $n = PV/RT$ , can easily be calculated, because all the other factors are known. The vapour pressure of mercury is therefore 2.78E-5 kPa at 273K. The number of moles ( $n$ ) can be used in  $m = M_r n$  to calculate the mass of mercury where  $M_r$  is the molar mass.

Table 3.13: The results obtained from experimental method A, using gold trap to trap mercury in a gas stream for analysis with the SIR GALAHAD mercury analyzer are presented:

Sample	Temperature	Carrier Gas flow rate	Volume	Expected Hg	Obtained Hg
	K	cm <sup>3</sup> /min	dm <sup>3</sup>	ng	
1	327	40	2.4	4914	22.63
2	340	40	2.4	4727	22.63
3	353	40	1.48	2807	22.63
4	321	40	0.4	834	5.43
5	338	40	0.2	396	0.84

Table 3.14: Mercury results obtained in experimental method B (injecting a fixed volume of gas with known amount of mercury) are presented. Temperature and flow rate of **carrier gas** were constant at 273K and 20 cm<sup>3</sup>/min respectively. The results are from both the gold trap and the activated carbon trap.

Sample number	Volume injected	Expected Hg	Obtained Hg	*Penetration
	cm <sup>3</sup>	ng		
<b>Activated carbon trap</b>				
1	20	49.05	33.62	4
2	40	98.11	93.47	1
3	20	49.05	27.71	1
4	20	49.05	26.19	0
5	40	98.11	197.81	1
6	40	98.11	241.79	1
7	20	49.05	63.93	0
<b>Gold trap</b>				
8	15	36.17	22.07	
9	7	16.88	0.04	
10	5	12.06	15.58	
11	Blank	0	0.38	
12	15	36.17	0.12	
13	7	16.88	0	
14	5	12.06	0	
15	5	12.06	0.66	
16	Blank	0	0	
17	15	36.17	0.63	
18	7	16.88	0	
19	5	12.06	0	
20	5	12.06	0.16	

\* The penetration is only valid for the activated carbon tube as it has 2 compartments separated by a filter. The mercury content is measured in each compartment and compared. Values of around 1 show that there was no breakthrough of mercury in the trap during sampling.

### 3.7.2 Results Discussion

Results (Table 3.13) obtained when using method A were all above the operating range of 22ng of the mercury analyzer, thus mercury content could only be quantified as 22ng

which was the maximum. There was also some difficulty in manually controlling the volume of the gas to flow through to the gold tubes.

Considering the difficulties experienced in experiment A, experiment B followed. Using the vapour pressure of mercury (Figure 3.1), the concentration of mercury in a known volume of gas was calculated. The results presented in Table 3.14 show a significant difference between the obtained results and the expected results. The large variation can be attributed to the poor operation of the SIR GALAHAD mercury analyser, as the experimental side was double checked to eliminate possible errors.

The activated carbon tubes were analyzed using a DMA 80 mercury analyzer instrument. Sample 1 reported 67% recovery and sample 2 reports even an improved recovery of 94%. Although samples 3 and 4 reported a lower mercury recovery of 55%, it is still acceptable because of the good repeatability of the results. Samples 5 to 7 reported over-recoveries of mercury, which may be contributed to some contamination of the original carbon tube, or contamination within the instrument. On average the results obtained for the activated carbon tube using the DMA 80 instrument, are reasonably acceptable.

### ***3.8 Pyrolysis Experimental Results***

The pyrolysis experiment as well as the experimental set-up was explained in details in Chapter 2. In this section, the results obtained for coal A and coal B in two pyrolysis experiments, will be presented. Mercury content was determined in the feed coal, in the char (remaining solid in the pyrolyser after pyrolysis has taken place) and in the liquid samples used in the impinger train. The results of the mercury concentration in the different liquid samples collected during the pyrolysis experiments 1 and 2 are presented in Table 3.16 (a) and (b). Solid samples were prepared and analysed according to standard procedure while liquid samples were analysed using proprietary methods of Sasol laboratories. As ICP-AES was used for the analysis of other trace elements (such as As, Se, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V and Zn) in the liquid samples, it was found that most of the elements were below the instrument detection limits. These were thus omitted from the results presentation. Cold Vapour Atomic Absorption Spectrometry was used to determine the mercury content in the impinger

solutions. Results of proximate, ultimate and trace elements in the feed coal and char are presented in Table 3.15

Table 3.15: The results of the total amount, proximate, ultimate and trace element analysis results of the two feed coals with their corresponding char are presented.

		Coal B		Coal A	
		coal	char	coal	char
Mass	g	1220	971	1194	997
Moisture	g/100g	4.96	1.08	4.76	1.72
Volatiles	g/100g	22.83	7.80	22.34	13.44
Fixed Carbon	g/100g	47.49	62.72	49.30	62.44
Ash	g/100g	24.72	28.40	23.60	22.40
C	g/100g	53.68	63.80	55.38	65.39
H	g/100g	2.85	1.63	2.84	2.08
N	g/100g	1.35	1.42	1.37	1.70
S	g/100g	1	0.92	0.84	0.94
Hg	mg/kg	0.2	0.15	0.17	0.16
As	mg/kg	4.41	7.36	2.84	2.02
Se	mg/kg	0.9	2.29	1.32	1.07
Co	mg/kg	8.5	8.7	6.17	25
Ni	mg/kg	17.2	103	14.27	66.6
Mn	mg/kg	101.5	141	89.47	119.9
Cr	mg/kg	33.3	189	38.07	105
V	mg/kg	30.77	41	28.4	31.6
Zn	mg/kg	9.5	42	11.53	31.6
Cu	mg/kg	13.99	23	11.17	228
Pb	mg/kg	6.45	20	6.77	170.2
Cd	mg/kg	1.06	0	0.71	2.5
Mo	mg/kg	0	21	0.6	0.48
Ba	mg/kg	461.5	655	448.33	623

Table 3.16 (a): The mercury content obtained from the different impinger solutions is presented together with the final volume recovered during the pyrolysis experiment of coal A. All solutions were 100 cm<sup>3</sup> at the beginning of the experiment.

Solutions	Sequence in the Train	Recovered Volume	Average Hg content	Mass Hg recovered
		cm <sup>3</sup>	mg/ dm <sup>3</sup>	mg
KCl	1	102	0.073	0.007
KCl	2	99	0.078	0.008
KMnO <sub>4</sub>	3	96	1.30	0.125
KMnO <sub>4</sub>	4	96	0.36	0.035
KMnO <sub>4</sub>	5	95	0.12	0.011
KMnO <sub>4</sub>	6	94	0.14	0.013
KMnO <sub>4</sub>	7	97	0.065	0.006
KMnO <sub>4</sub>	8	96	0.013	0.001
Sum				0.207

Table 3.16 (b): The mercury content obtained from the different impinger solutions is presented together with the final volume recovered during the pyrolysis experiment of coal B. All solutions were 100 cm<sup>3</sup> at the beginning of the experiment.

Solutions	Sequence in the Train	Recovered Volume	Average Hg content	Mass Hg recovered
		cm <sup>3</sup>	mg/dm <sup>3</sup>	mg
KCl	1	103	0.00093	9.56E-5
KCl	2	100	<dl	0
KMnO <sub>4</sub>	3	97	0.00068	6.6E-5
KMnO <sub>4</sub>	4	96	0.00058	5.57E-5
KMnO <sub>4</sub>	5	97	0.00087	8.44E-5
KMnO <sub>4</sub>	6	96	<dl	0
KMnO <sub>4</sub>	7	97	<dl	0
KMnO <sub>4</sub>	8	96	<dl	0
Sum				3E-4

It should be mentioned that the condensate collected as a result of cooling the gas from the pyrolyser, called gas liquor, was also analysed for mercury. It is believed from other work that mercury can condense at lower temperatures, thus the need to analyze the condensate. The condensate consists of oily material, as well as a high proportion of

water and tar. There was no standard method that could be used to analyse such a material, therefore in-house proprietary methods were developed for this analysis. The actual Hg analysis was conducted by CVAAS.

- The condensate mass recovered during pyrolysis of coal A was 145 g and mercury content obtained was 0.39 mg/kg, which calculates to 0.06 mg of Hg in the gas liquor.
- The condensate mass recovered during pyrolysis of coal B was 142 g and mercury content obtained was 0.13 mg/kg, which calculates to 0.018 mg of Hg in the gas liquor.

The volume of gas measured during the pyrolysis experiment of coal A and coal B was 1248 dm<sup>3</sup> and 1668 dm<sup>3</sup> respectively.

### Mercury Mass Balance

Table 3.17(a): The mercury mass balance calculated for the coal pyrolysis experiment is presented.

Coal	Total solutions	Char	Gas Liqour	Sum = (*T.sol+Char+**gasL.)	difference (coal - sum)	Hg balance
Hg amount in mg						
0.2	0.207	0.16	0.06	0.427	-0.227	-113.5%

\* T.sol = total solution

\*\*gasL = Gas liqour

The mercury balance in the pyrolysis experiment of the coal A is very poor, with an over-balance of 113%. This could indicate an error in the analysis, as difficulty with analysis at such a scale has been explained.

Table 3.17(b): The mercury mass balance calculated for the coal A pyrolysis experiment is presented.

Coal	Total solutions	Char	Gas Liqour	Sum = (T.sol+Char+gasL.)	difference (coal - sum)	Hg balance
Hg mg						
0.24	0.0003	0.15	0.018	0.17	0.07	29%

The mercury mass balance obtained for the coal B pyrolysis experiment is also very poor, indicating a 71% under-balance.

Mercury is known to be volatile; therefore a large proportion of the mercury originally present in coal during pyrolysis was expected to be in the gas phase and to condense in the solutions. However, analysis indicates that the char still contained a large amount of mercury. This analysis indicates an error in the analysis technique. There is a challenge in analyzing different phases of materials at trace level. In major plant operation 70 -130% balances of trace metals are considered acceptable, because of the challenges of analytical techniques at trace levels. Again, to obtain results from these techniques is very expensive, yet at the end the results are unreliable. Therefore, from these results it can be concluded that the method of impinger train sampling cannot be used for routine analysis in the plant, but can only be used by specialists in the field of sampling and analysis.

### **3.9 Results Discussion**

The trace elements observed in Table 3.15 appear to be more concentrated in the char. This indicates that these trace elements were not volatilized at this pyrolysis temperature. The non-volatility of some of these elements like Hg, As and Se during pyrolysis is contrary to what was observed by other researchers, including Guo et al. (2002), as these elements are known for their high volatility behavior during coal utilization, especially at pyrolysis temperature. It is noted that rock fragment particles present in South African coals may act as adsorbents for the volatile species during coal pyrolysis.

Wang and Tomita (2003) and Zajusz-Zubek and Konieczynski (2003) independently found arsenic to be the least volatile element in both pyrolysis experiments that were conducted at temperatures below 1150°C. Furthermore, Zajusz-Zubek and Konieczynski (2003) found the experimental atmosphere to not have an effect on the volatilization behaviour of trace elements. Contradicting results on the volatilization of As were reported by Guo et al. (2002), in which As was found to volatilize at temperatures below 500°C. In a separate study Guo et al. (2003) found atmosphere to have an influence on the release behaviour of elements during pyrolysis. Studies by Wang and Tomita (2003) and Zajusz-Zubek and Konieczynski (2003) indicate that the effect of pressure on the release behavior of trace elements during pyrolysis appears to be small. The important steps that may affect the release of the elements are the breaking of chemical bonds and the transfer of volatiles from coal pore to the gas phase.

In this study there was a significant decrease of volatiles in the coal during the pyrolysis experiment. However, it appears that the volatiles did not carry the trace elements as they are observed in the char material. It is still challenging to draw meaningful conclusions on results obtained at trace levels, with some unreliability associated with them. Thermodynamic modeling packages become useful as a test method to compare modeled results versus experimental results.

The impinger solutions appear to not be useful in repeatably trapping the amount of mercury volatilized during pyrolysis. In Table 3.16 (a) most of the mercury is captured

in the potassium permanganate impingers with a high concentration in the first  $\text{KMNO}_4$  impingers. However, this is not observed when the experiment is repeated with a different coal, the coal B as observed in Table 3.16(b).

According to the hypothesis, elemental mercury (gaseous  $\text{Hg}^0$ ) is collected in chilled acidified hydrogen peroxide ( $\text{HNO}_3\text{-H}_2\text{O}_2$ ) and the potassium permanganate ( $\text{H}_2\text{SO}_4\text{-KMNO}_4$ ) impinger solution. The oxidized mercury (gaseous  $\text{Hg}^{2+}$ ) is collected in the potassium chloride (KCl) impinger solution (Otero-Rey et al., 2003). In this work the  $\text{HNO}_3\text{-H}_2\text{O}_2$  solution was not used, after it showed less success at first attempt; instead more  $\text{H}_2\text{SO}_4\text{-KMNO}_4$  solutions were added in the train. In this experiment very little mercury was recovered in the KCl impinger. With reference to the hypothesis, the lack of mercury in the KCl impinger means that during pyrolysis mercury is not emitted in the oxidized form ( $\text{Hg}^{2+}$ ), but rather released as elemental mercury, since it is recovered in the acidified  $\text{KMNO}_4$  solution.

The reduced repeatability of results between experiments confirms the challenges encountered when analyzing at trace levels as has been explained earlier. It appears that the method of impinger train sampling cannot be applied successfully as a routine sampling method in the plant. The sampling of stacks in the plant should rather be contracted to specialists who have all the required instruments designed to work at such trace levels. Despite all the challenges, it can also be mentioned that Jose et al. (2003) obtained an acceptable Hg mass balance of 70% when sampling flue gases in the stacks using this procedure. The coal quality of the South African coal could also add to the problems experienced during analysis.

There was no significant amount of Hg recovered in the gas liquor. These could indicate that:

- The pyrolysis gas may not have had enough time to cool down in this condensate trap; therefore mercury could not condense because the gas temperature was not favorable.
- As mentioned, condensate is a complex material, therefore analysis of such a material using unsuitable methods (especially with volatile elements) remains challenging. The analytical method involves heating the sample in an open

vessel during sample preparation; there could be some mercury escaping from the sample during this heating phase.

### ***3.10 General Observations on the Pyrolysis Experimental Results***

- Pyrolysis experiments were time consuming, as one experiment could take up the entire day.
- The pyrolyser instrument was normally used for routine testing of physical properties of coal, including the amount of condensate that a particular coal could produce. It was constantly used for evaluating samples that could be used at the coal conversion process, making it difficult to conduct several pyrolysis experiments for this project.
- It has been observed from the presented results, that at trace concentrations the results are unreliable and have large errors.
- This pyrolysis experimental evaluation seems to not be a suitable exercise in evaluating the possible environmental risks posed by the different coals used in the plant, in terms of trace elements.
- Obtaining analysis results of all samples was a challenging and expensive task. A modeling approach might be as reliable as a laboratory method, but much less time-consuming and more cost effective. This would enable coal consumers to evaluate the environmental risk continuously with confidence.

### ***3.11 Thermodynamic Modeling of the Behavior of Trace Elements during Coal Pyrolysis - Modeled Results Compared to Experimental Results***

The final output data at each temperature was ultimately displayed in a table in the form of an interactive spreadsheet, which was then used to plot graphs of interest. The input analysis of the coal that was used in the model is presented in Table 3.18. As an example, the actual model data generated during pyrolysis at 650°C is also presented in Table 3.19, as the solid phase and the gas phase. The solid phase is all material present in the char that remains in the reactor. The gas phase species were further processed in the model, through the condenser up to the impinger solutions.

Table 3.18: The input coal analysis and the carrier gas used in the computation model are given:

Components	kg
Carbon	0.65
Hydrogen	0.035
Nitrogen	0.016
Oxygen	0.14
Sulphur	0.012
Moisture	0.061
SiO <sub>2</sub>	0.082
Al <sub>2</sub> O <sub>3</sub>	0.028
Fe <sub>2</sub> O <sub>3</sub>	0.037
CaO	0.12
MgO	0.0021
N	0.02
Se	2.7 x 10 <sup>-5</sup>
Mo	0
As	0.00013
HgO	6.03 x 10 <sup>-6</sup>
Cu	0.00042
Cr	0.0010
V	0.0009
Pb	0.0002
Zn	0.00029
Mn	0.003
Ba	0.014
Ni	0.005
K <sub>2</sub> O	0.007
TiO <sub>2</sub>	0.021
Sum	3.32
N <sub>2</sub> (carrier gas)	2.065

Table 3.19: The output composition of material, after pyrolysis has been conducted at 650°C at 24 bar using the model, is given. The total mass of all input components, including the carrier gas was 3.32kg.

Components	kg	%
<b>Solids</b>		
(CaO) <sub>3</sub> (V <sub>2</sub> O <sub>5</sub> )	3.2 x 10 <sup>-3</sup>	0.1
BaCO <sub>3</sub>	2.0 x 10 <sup>-2</sup>	0.6
C_graphite	5.6 x 10 <sup>-1</sup>	16.8
Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub> _gehlenite	4.2 x 10 <sup>-2</sup>	1.3
Ca <sub>3</sub> MgSi <sub>2</sub> O <sub>8</sub> _merwinite	1.7 x 10 <sup>-2</sup>	0.5
Ca <sub>3</sub> Si <sub>2</sub> O <sub>7</sub> _rankinite	1.4 x 10 <sup>-1</sup>	4.2
CaTiO <sub>3</sub> _perovskite-a	3.6 x 10 <sup>-2</sup>	1.1
Cu <sub>2</sub> S	1.0 x 10 <sup>-4</sup>	0
Cu <sub>3</sub> As_domeykite	4.7 x 10 <sup>-4</sup>	0
FeCr <sub>2</sub> O <sub>4</sub>	2.2 x 10 <sup>-3</sup>	0.1
FeO_wustite	5.7 x 10 <sup>-3</sup>	0.2
FeS	3.3 x 10 <sup>-2</sup>	1.0
K <sub>2</sub> Ca(CO <sub>3</sub> ) <sub>2</sub> _fairchildi	3.2 x 10 <sup>-3</sup>	0.1
KAlSiO <sub>4</sub> _kaliophyllit	2.0 x 10 <sup>-2</sup>	0.6
MnAl <sub>2</sub> O <sub>4</sub> _galaxite	9.6 x 10 <sup>-3</sup>	0.3
Ni	5.2 x 10 <sup>-4</sup>	0
Pb	1.3 x 10 <sup>-4</sup>	0
PbSe_claustite	5.7 x 10 <sup>-5</sup>	0
ZnS_sphal.ite	4.3 x 10 <sup>-4</sup>	0
<b>Ideal gas composition</b>		
H <sub>2</sub>	1.6 x 10 <sup>-2</sup>	0.5
CH <sub>4</sub>	5.8 x 10 <sup>-2</sup>	1.8
C <sub>2</sub> H <sub>4</sub>	1.7 x 10 <sup>-7</sup>	0
C <sub>2</sub> H <sub>6</sub>	4.9 x 10 <sup>-6</sup>	0
N <sub>2</sub>	2.1	63.2
NH <sub>3</sub>	8.2 x 10 <sup>-4</sup>	0
HCN	8.8 x 10 <sup>-7</sup>	0
H <sub>2</sub> O	9.7 x 10 <sup>-2</sup>	2.9
CO	4.9 x 10 <sup>-2</sup>	1.5
CO <sub>2</sub>	1.1 x 10 <sup>-2</sup>	3.3
H <sub>2</sub> CO	1.6 x 10 <sup>-7</sup>	0.0
CH <sub>3</sub> OH	1.3 x 10 <sup>-8</sup>	0.0
HNCO	5.2 x 10 <sup>-8</sup>	0.0
H <sub>2</sub> S	1.9 x 10 <sup>-4</sup>	0.0
COS	2.4 x 10 <sup>-6</sup>	0.0

KOH	$5.5 \times 10^{-8}$	0.0
Zn	$3.8 \times 10^{-7}$	0.0
H <sub>2</sub> Se	$5.8 \times 10^{-6}$	0.0
Hg	$5.6 \times 10^{-6}$	0.0
Pb	$3.0 \times 10^{-6}$	0.0
PbS	$1.1 \times 10^{-6}$	0.0
PbSe	$2.0 \times 10^{-5}$	0.0
Pb <sub>2</sub> Se <sub>2</sub>	$1.0 \times 10^{-7}$	0.0
Sum	3.32	100

### ***Explanatory notes based on Table 3.19***

- The percentage observed is the percentage contribution of that species in the entire output stream. For example, CO<sub>2</sub> in the gas phase is given as 0.11067kg. This means CO<sub>2</sub> is contributing 3.3% to the entire output material. If the contribution of carbon was to be calculated, then other species consisting of carbon in the output stream would need their percent fraction included in the calculation.

### ***Mass Balance of Elements***

The mass balance of elements is good in the model, e.g. Hg in the input material was  $6.03 \times 10^{-6}$ kg in the form of HgO. It is observed in the output stream in the gas phase as  $5.6 \times 10^{-6}$ kg, which calculates to 100% Hg balance. The high volatility behavior of mercury is also observed perfectly in this model. Although working with trace amounts of elements, results obtained tend to be more reliable. Actual experimental analysis proved futile. It appears that the model can be used to predict the behaviour of trace elements during coal utilization, especially in combustion and gasification processes.

### ***Model through the Condenser***

It was indicated earlier that the gas phase stream presented in Table 3.19 was then further modeled, passing through the condenser down to the solutions since this is the observed path of the gas phase stream in the actual pyrolysis experiment. The output result obtained after the condensing of the model is presented in Table 3.20.

Table 3.20: The output result obtained after the condenser at 5°C and 1 bar is presented:

components	kg	%
H <sub>2</sub> O *(l)	2.1 x 10 <sup>-1</sup>	8.5
Solid components		
C_graphite	4.5 x 10 <sup>-2</sup>	1.8
HgSe_tiemannite	7.78 x 10 <sup>-6</sup>	0.0003
K <sub>2</sub> SO <sub>4</sub>	8.85 x 10 <sup>-8</sup>	0
PbSe_claust.ite	2.60 x 10 <sup>-5</sup>	0
Se_trigonal	1.92 x 10 <sup>-6</sup>	0
ZnS_sphalite	5.65 x 10 <sup>-7</sup>	0
Ideal gas composition		
H <sub>2</sub>	4.48 x 10 <sup>-7</sup>	0
CH <sub>4</sub>	6.7 x 10 <sup>-2</sup>	2.8
N <sub>2</sub>	2.1	86.4
NH <sub>3</sub>	1.69 x 10 <sup>-5</sup>	0
H <sub>2</sub> O	1.3 x 10 <sup>-2</sup>	0.5
CO <sub>2</sub>	2.60 x 10 <sup>-5</sup>	0
H <sub>2</sub> S	1.9 x 10 <sup>-4</sup>	0
H <sub>2</sub> Se	1.22 x 10 <sup>-8</sup>	0

\*(l) = aqueous phase

#### ***Explanatory notes based on Table 3.20***

- Some of the components of the ideal gas condensed to aqueous and solid phases. The aqueous phase that was observed in the model corresponds to the gas liquor observed experimentally, while the solid phase corresponds to the tar that was generated in the actual experiment. So far there is good comparison of phases observed in the model and observed experimentally.
- Mercury condensed in the condenser at 5°C, during gas cooling into a solid material. Such condensation takes place at equilibrium, but the actual experiment does not reach equilibrium. The observed mercury in the impinger solutions could therefore be as a result of gas breakthrough, since the system was not at equilibrium.
- Mass balance of all material worked out to be 100%
- The ideal gas observed in Table 3.20 does not contain any of the trace elements of interest. It appears that all the trace elements remained in the different solid

phases. Modeling of this ideal gas through the solution could yield no interesting results. Therefore, Hg was added to this ideal gas so that it could be modeled further through the solution, to understand its behavior.

Table 3.21: The modeled output result obtained after the ideal gas (in Table 3.20 with  $5.6 \times 10^{-6}$ kg added gaseous Hg) has reacted with the KCl solution in the impinger train

Components	Kg
Liquids components	
H <sub>2</sub> O	$8.7 \times 10^{-2}$
H <sub>2</sub> SO <sub>4</sub> (H <sub>2</sub> O) <sub>6</sub>	$2.9 \times 10^{-4}$
Ideal gas composition	
N <sub>2</sub>	$9.6 \times 10^{-2}$
CH <sub>4</sub>	$3.1 \times 10^{-3}$
H <sub>2</sub> O	$5.8 \times 10^{-4}$
H <sub>2</sub> S	$6.4 \times 10^{-6}$
NH <sub>3</sub>	$2.4 \times 10^{-6}$
H <sub>2</sub>	$4.4 \times 10^{-8}$
CO <sub>2</sub>	$5.8 \times 10^{-8}$
Solid components	
KCl	$1 \times 10^{-3}$
HgS_cinnabar	$6.4 \times 10^{-6}$
HgSe_tiemannite	$4.21 \times 10^{-8}$

Note: In this model the amount of water was increased to 100g to enable dissolution of the KCl salt.

Table 3.22: The modeled output result obtained after the ideal gas (in Table 3.21 with  $5.6 \times 10^{-6}$  kg added gaseous Hg) has reacted with the  $\text{KMnO}_4$  solution in the impinger train

Components	kg
Liquid components	
H <sub>2</sub> O	$1.5 \times 10^{-1}$
H <sub>2</sub> SO <sub>4</sub> (H <sub>2</sub> O) <sub>6</sub>	$1.1 \times 10^{-3}$
Ideal gas composition	
N <sub>2</sub>	$9.9 \times 10^{-2}$
H <sub>2</sub> O	$8.8 \times 10^{-4}$
Hg	$3.7 \times 10^{-8}$
Solid components	
Mn <sub>3</sub> O <sub>4</sub>	1.41
MnCO <sub>3</sub>	$4.83 \times 10^{-1}$
MnO	$2.1 \times 10^{-2}$
HgSe_tiemannite	$4.21 \times 10^{-8}$

Note: The  $\text{KMnO}_4$  solution was replaced with 2 kg of  $\text{MnO}_2$  (strong oxidizing agent) in the model, because the modeling package did not have a data base of  $\text{KMnO}_4$ . This large amount of oxidising agent was needed to oxidise the hydrocarbons in the gas. Any reductant in the gas would prevent the oxidation of mercury at equilibrium in the model.

It appears the model does not easily handle solution chemistry and the potassium chloride and permanganate solutions were added in an indirect way. Based on results in Table 3.21, the mercury condenses as a sulphide solid in the KCl solution. The Hg analysis method requires that the mercury be reduced to elemental mercury. In this case the formed HgS is almost insoluble, with a solubility constant of  $3 \times 10^{-53}$  which makes it challenging to reduce the Hg to its elemental state in this compound. This could be one way of explaining the poor analysis results observed for the solutions: most of the mercury could have been in the HgS state, thus could not be reduced, therefore the analyzer could not detect it, leading to the poor results observed.

In a complex matrix like pyrolysis gas, very stable mercury compounds like HgS and HgSe are predicted. Under these conditions  $\text{Hg}^0$  is easily oxidized by other species, including hydrogen ions that are largely available from the water. To find a reducing

agent to keep mercury in elemental form in these conditions would be challenging. In the permanganate solution, the sulphur reacts with the permanganate species, thus allowing other mercury species to form, due to the lack of sulphur. The formed species could easily have been reduced to elemental Hg, as compared to HgS, thus leading to the improved results observed for the analysis of the KMNO<sub>4</sub> solution. It has been observed from this calculation that the knowledge of the matrix i.e. all species present, is important in order to obtain reliable results. Side reactions taking place within the matrix are also important. As observed in this case, Hg tends to have more affinity to the sulphur, thus leading to the mercury not being available for analysis, since it might not be reduced.

The model appears to suggest reasons associated with the poor results observed in the actual experiment. It is worthwhile to conduct a theoretical study like modeling before any experimental work is conducted. Such studies give an indication of the thermodynamic limits of the composition of the system. The outcome results can be predicted at an effective cost and be less time-consuming compared to obtaining unreliable results from actual costly experiments.

In general, the modeling work did not quantitatively compare well with experimental findings. This was to be expected, as the residence time of the carrier gas in the pyrolyser is quite short and thermodynamic equilibrium cannot be expected. During the cooling down period the discrepancy would become even larger as the real reaction rates slowed down. Even with these limitations, the observed behavior of many trace elements in coal was explained. If solutions are to be modeled, a modeling package that can handle solutions more effectively should be incorporated.

# CHAPTER 4

## Conclusions

### Chapter summary

In this chapter the major conclusions from the project are presented together with general observations of the project, citing successes and failures of the project.

### **4.1 Conclusions**

Analytical techniques for determining trace elements of environmental concern were investigated extensively in this work. After the thorough investigation of methods, some standard methods (ASTM methods) were then selected for the purpose of this project, based on their reliability. The microwave digestion method proved to be unreliable, as complete digestion of the coal was not always obtained. Some of the elements could still be encapsulated in the silicate matrix that did not digest. It was found that standard analysis methods could not simply be adapted for this study, but a thorough knowledge of matrix was needed to develop an analysis method. Analysis at trace levels was a challenging and expensive task and in most cases results were not reliable. It has been observed in this work that the problems associated with analysis at trace levels can be explained and partially solved by thermodynamic modeling. For the model, the initial coal sample of interest need only be analysed once to obtain the input into a thermodynamic model. The thermodynamic limited behavior of elements in different streams can then be predicted with reliability at a well reduced cost.

The methods of trapping mercury in the gas phase proved to be unsuccessful when applied in a major plant environment. The trapping tubes could quickly saturate, while there was still mercury present in the gas stream, thus giving false results. The impinger sampling train method was also not used with success in this work; it appears that it is a method to be used by specialists dedicated to analysis at trace levels. Again the thermodynamic modeling package appeared useful in predicting the species and amount of elements present in the different system streams, at a reduced cost. For example:

- In the model used, the Hg species was tracked from the input coal during pyrolysis up to its condensation to a solid phase at 5°C. It was not possible to detect the mercury content in all the different streams in the actual experiment,

hence an inaccurate mercury mass balance was obtained, however, the model provided an insight into the possible fate of the mercury.

- Mercury recovered in the solutions of the actual experiment could be resulting from the slow reactions taking place in the condenser unit, thus not reaching equilibrium. The model predicted all mercury present in the gas stream to condense in the condenser, because in the model the system assumes equilibrium.
- The model cannot predict chemical reactions of artifacts that occurred during crystallization, precipitation or encapsulation and adsorption of organic elements during pyrolysis of coal under reducing conditions.

The mode of occurrence of the trace elements of concern has been investigated in the two coals. The density separation method proved to be a better method of investigating the mode of occurrence of an element in this exercise, when compared to the sequential leaching method. Elements were assigned their occurrence based on the calculated concentration of the element in that density fraction. It was noted that for reliable results a good density separation of coal has to take place. Contamination by intermixing of density separated fraction could cause significant deviations in the final results.

The mode of occurrence of trace elements could be applicable in the modeling exercise applied in this work, as the assigned minerals of association of the trace elements could be used at the input of the coal. The elements were present in small amounts in the coal matrix, while in the model used in this work trace elements were input as free elements, not being associated with any minerals; for example, Pb was input as free solid Pb not as galena (PbS) or pyrite as its predicted minerals of association. For a major coal utilization process, the mode of occurrence of the trace elements of concern should be taken into account when performing modeling, as this may contribute to the real behavior of the elements during the coal utilization.

The pyrolysis behavior of trace elements during pyrolysis was understood to an extent in this project. To understand the partitioning behavior of trace elements in an actual experiment, all the streams generated need to be analysed for those trace elements of interest. This proved to be a very costly exercise in this project, yet unreliable. The

modeling package used predicted the phases in which trace elements are expected to be. At the high temperature, the thermodynamic model should be quite realistic, because of the higher reaction rates at elevated temperature. The model should be especially reliable to discriminate between volatile and non-volatile trace elements. This is especially important for environmental risk assessment.

It can be concluded that research should start with theoretical studies like a model rather than with an actual experiment, since the model predicts direction of the reaction.

#### **4.2 General comments**

- It was noted that analysis of elements at trace levels was challenging.
- A drawback in the developed analytical methods was the unreliability of the results. This is attributed to the analysis laboratory being a routine laboratory for analyzing plant samples, not being designed for trace level analysis. Plans are underway to overcome such-draw backs by setting up designated laboratories; for example the South African Mercury Assessment committee is planning to set up a mercury centre laboratory.

#### **4.3.1 Project successes**

- The partitioning behavior of trace elements in a plant scale was successfully determined and the results were presented at an international conference level.
- The modes of occurrence of some elements of environmental concern were successfully determined. It was not easy to compare these results to literature findings in this area, as the coal used in this work was different from that used by other researchers.
- The coal pyrolysis process was well understood and knowledge of operating the pyrolyser instrument was gained.
- Thermodynamic modeling experience was gained when using the FACTSAGE package. Such knowledge has been applied to other projects.

#### **4.3.2 Project failures**

- The application of the gold and carbon sampling tubes in sampling mercury in gas streams was not a success.
- Application of impinger solutions to determine content as well as speciation of Hg and other elements was also unsuccessful.
- Useful Hg-spiking experiments were developed during the course of this project and they can be applicable in calibrating some instruments.

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## **APPENDIX A**

### **Safety & Health Hazards of Mercury Compounds (salts) & Elemental mercury**

#### **Introduction**

Mercury traps (activated carbon and Gold tubes) are utilized at Sasol as a technique for measuring concentrations of mercury in the raw gas streams. In order to validate these methods it was suggested to spike the gas stream with a known amount of mercury in the lab. In a laboratory experiment (horizontal tube reactor) mercury salts (mercury chloride, mercury nitrate) with a known amount of mercury and which produce different species of mercury when decomposed will be used as the source of mercury. Before such experiment can be conducted it is necessary to address the safety and health hazards associated with mercury and its compounds.

#### **Objectives**

The objective of this exercise was to outline the safety measures required when handling these mercury compounds (mercury chloride, mercury nitrate) up to the disposal of the end products and waste materials during the experiment.

#### **Methodology**

The proposed experiment was set up in a fume hood with the mercury salts placed in a small boat, then into a horizontal tube reactor. Mild pyrolysis of the salt was conducted at a temperature of 400°C and nitrogen used as a carrier gas to transport the decomposition products to the mercury traps. The mercury salt was decomposed as the temperature gradually increases releasing mercury vapour in the process.

The aim of the experiment was to capture and quantify this vapour using the activated carbon and gold tubes. If the capturing process is successful, no vapour should be emitted to the environment. The possibility of emitting very small amounts of mercury vapour and mercury salts to environment air (through the fume hood) could not be excluded, but the effects were minimal because of the small amounts (5mg) of the salts used and the low number (4) of the proposed experiments. The occupational exposure limits for Hg is 0.1 mg/m<sup>3</sup>.

## **Disposal**

Substance and remains should be kept in appropriate sealed containers and separated from other substances. Only approved waste management can dispose mercury and its compounds. In this case WASTE-TECH (industrial waste management) will be contracted to dispose the waste generated from this experiment.

## **Safety of experiment**

All apparatus used during the experiment were blown with plant air and cleaned with a large amount of soapy water while in the fume hood. To ensure safety; two people were required to conducting the experiment. All protective clothing of the workers were washed at work several times immediately after the experiment. To avoid skin exposure, no skin was exposed near the experimental environment. The mercury compounds were opened, weighed and closed in the high risk fume hood.

## **Effects of exposure**

### Short term exposure

The substance irritates the skin and respiratory tract and is corrosive to the eye. The substance may cause effects on kidneys. Exposure far above Occupational Exposure Limits may results in death. If on the skin, wash with plenty of soapy water and seek medical attention. In all cases a doctor must be contacted to ensure no continuation of the damage occurs.

### Long –term exposure/repeated exposure

The substance may have effects on the kidneys resulting in nephritic syndrome. It may cause skin sensation.

## **Mercury Salts**

Mercury Chloride ( $\text{HgCl}_2$ )

Physical Properties

Appearance: white odourless crystalline powder

Boiling point  $277^\circ\text{C}$

Solubility: moderate in water (6.9g/100mL @  $20^\circ\text{C}$ )

## Dangers

The substance decomposes on heating producing toxic vapours of mercury and chloride. It reacts with light metals. Incompatible with strong acids, ammonia, carbonates, metallic salts, alkalies, phosphites, phosphates, sulfites, sulfates, arsenic, antimony, iron, copper and bromides.

## Toxicology

The substance is poisonous. It may be fatal if absorbed into the body by inhalation of its aerosol or through the skin or by ingestion.

The substance is corrosive to the eyes, the skin and respiratory tract. It is also corrosive on ingestion. It may cause effects on the kidneys. Special treatment is necessary in case of poisoning with this substance.

The substance may be a hazardous to the environment. In the food chain important to humans bioaccumulation takes place, specifically in aquatic organisms. Experts strongly advise not to let the chemical enter the environment.

## Protective Clothing

Laboratory protective clothing has to be worn at all times including a face protection when working with mercury nitrate. Clothes should be washed separately several times and not taken home after work.

## Mercury Nitrate [Hg(NO<sub>3</sub>)<sub>2</sub>]

### Physical properties

Appearance: white to yellow crystalline powder with HNO<sub>3</sub> acid odour

Melting point: 79°C

Solubility: good in water

## Dangers

The substance is stable but incompatible with strong reducing agents, combustible material and most metals. It decomposes on heating producing toxic fumes (mercury, nitrogen oxide) or on exposure to light. It can react with phosphine and sulphur to form shock-sensitive compounds. Vigorous reaction with petroleum hydrocarbons.

### Toxicology

The substance is highly toxic on absorption to the body through inhalation, ingestion and skin. It is also a neurological hazard. In the eye it causes pain, blurred vision and severe deep burns. Special treatment is necessary in case of poisoning with this substance.

The substance may be a hazardous to the environment. In the food chain important to humans bioaccumulation takes place, specifically in aquatic organisms. Experts strongly advise not to let the chemical enter the environment.

### Protective Clothing

Laboratory protective clothing has to be worn at all times including a face protection when working with mercury nitrate. Clothes should be washed separately several times and not taken home after work.

### Conclusion

The effects of exposure to any hazardous substance depend on the dose, duration, mode of exposure, personal traits and habits and whether other chemicals are present. It should be noted that the nervous system is very sensitive to all forms of mercury. The experiment was conducted in the fume hood, so exposure through inhalation was minimal as the amount of the substance used during the experiment was very small (5mg).

## **Addendum 1**

Elemental mercury ( $\text{Hg}^0$ )

Physical Properties

Appearance: liquid at room temperature

Boiling point  $357^\circ\text{C}$

Dangers

The substance toxicity is much lower than its salts or its vapour. When mixed with air or heated up, it vaporises to form mercury vapour. Mercury vapour is used in street lights, fluorescents lamps and advertising signs. Inhalation of elemental mercury is the most common route of exposure. Exposure can also occur through ingestion or dermal contacts, but these routes have a much smaller degree of absorption and are rarely the cause of elemental mercury toxicity.

Symptoms and health effects of elemental mercury exposure

Acute exposure to mercury vapour leads to pulmonary and central nervous system effects. Inhalation of high levels can cause the onset of symptoms such as cough, dyspnea, chest pain, nausea, vomiting, fever and a metallic taste in the mouth.

Protective Clothing

Laboratory clothing has to be worn at all times.

**Experiment**

A glass vessel of a volume about  $50\text{cm}^3$  was placed in a water bath at different temperatures up to  $100^\circ\text{C}$ . Copper filings were cleaned and coated with 2mL elemental mercury, to keep the mercury suspended and put into the glass vessel. Nitrogen gas was passed through the set up at a controlled flow rate and the mercury evaporated at that temperature was collected using gold tubes and measured. Excess vapour was dissolved in dilute HCl solution. A simplified sketch of the setup in Figure 1 below.

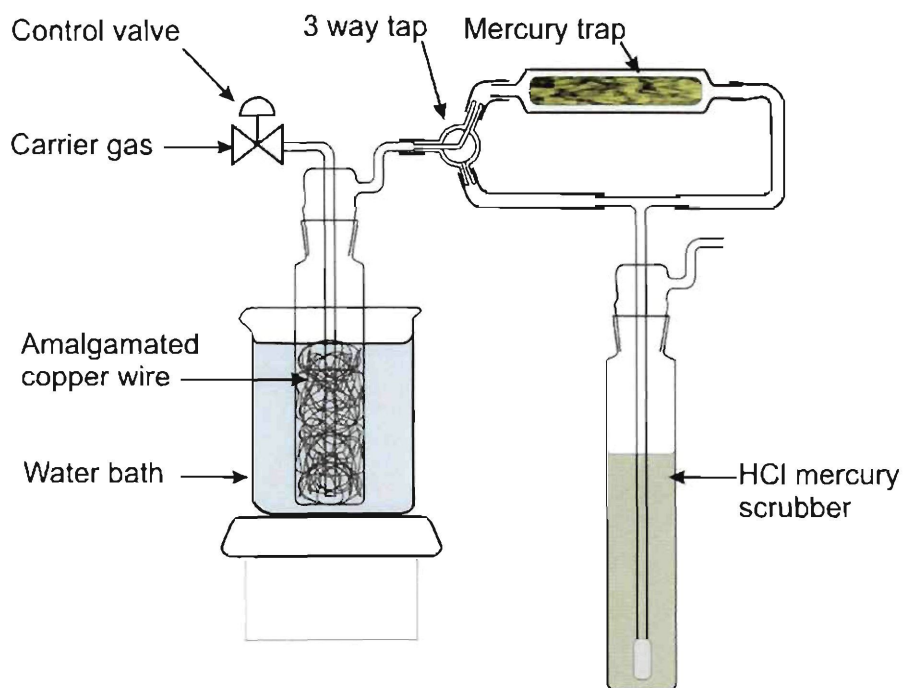


Figure 1: experimental setup for the Hg spiking instrument.

## APPENDIX B

### *Certificate of Analysis*

# COAL (SASOLBURG) SARM 20

## CERTIFIED REFERENCE MATERIAL

Distributed by  
SA BUREAU OF STANDARDS  
P/Bag X191, Pretoria 0001  
Republic of South Africa

Prepared by  
Council for Mineral Technology (MINTEK)  
P/Bag X3015, Randburg 2125  
Republic of South Africa

1. STATUS OF CERTIFICATE

This is the first issue of the certificate.

2. DATE OF ORIGINAL CERTIFICATION

June 1984.

3. AVAILABILITY OF OTHER SIZES OF THE MATERIAL

Only units of approximately 120 g of the powdered material are available.

4. SOURCE OF THE MATERIAL

The material is from the coal fields in the Sasolburg area of the Orange Free State, Republic of South Africa.

5. DESCRIPTION OF THE MATERIAL

The material is of low rank and is sub-bituminous to bituminous in range, falling within the vitrinite category  $V_3 - V_6$  averaging  $V_6$ .

6. INTENDED USE

As a reference material for the development of analytical techniques.  
As a control sample in the analysis of samples of a similar type.  
As a reference material for the calibration of instruments.

7. STABILITY, TRANSPORTATION AND STORAGE INSTRUCTIONS

The material should be stored in a desiccator and care should be taken to avoid undue vibration since this could cause segregation within the bottle.

The long term stability (> 1 year) for this SARM has not been established.

8. INSTRUCTIONS FOR THE CORRECT USE OF THE REFERENCE MATERIAL

A moisture determination (heating of the sample at 50 °C until a constant mass is obtained) should be done at the time of the weighing of the sub-sample for analysis. The results of the analysis should be adjusted on the basis of dry mass.

9. METHOD OF PREPARATION OF THE REFERENCE MATERIAL

Approximately 150 kg of the material was reduced in particle size until the majority of the sample (greater than 99 %) passed through a sieve with a nominal aperture size of 106  $\mu\text{m}$ . For full details of the comminution procedure see 17.

10. STATE OF HOMOGENEITY

The material was shown to be of sufficient homogeneity for its purpose (see 6). See 17 for a full description of the tests carried out as a check on the homogeneity of the sample.

## 11. CERTIFIED PROPERTY VALUES AND CONFIDENCE LIMITS

Constituent	Certified value (See 17) %	95 % Confidence Limits	
		Low	High
SiO <sub>2</sub> .....	17,66	17,48 .....	18,06
Al <sub>2</sub> O <sub>3</sub> .....	11,27	11,16 .....	11,73
Fe <sub>2</sub> O <sub>3</sub> .....	1,17	1,15 .....	1,19
TiO <sub>2</sub> .....	0,63	0,61 .....	0,65
CaO .....	1,87	1,85 .....	1,89
MgO .....	0,43	0,41 .....	0,45
Na <sub>2</sub> O .....	0,27	0,26 .....	0,28
K <sub>2</sub> O .....	0,14	0,14 .....	0,15
P <sub>2</sub> O <sub>5</sub> .....	0,14	0,13 .....	0,14
S .....	0,51	0,48 .....	0,53
L.O.I. ....	64,86	64,04 .....	65,06
μg/g			
As .....	4,7	4,6 .....	6,0
Ba .....	372	363 .....	384
Be .....	2,5	2,1 .....	3,0
Ce .....	87	73 .....	88
Co .....	8,3	7,6 .....	9,0
Cu .....	18	15 .....	19
Ga .....	16	15 .....	18
Hf .....	4,8	4,1 .....	5,1
Hg .....	0,25	0,18 .....	0,27
La .....	43	40 .....	57
Mn .....	80	77 .....	82
Ni .....	25	23 .....	26
Pb .....	26	20 .....	29
Rb .....	10	9 .....	14
Sc .....	10	10 .....	12
Se .....	0,8	0,7 .....	1,0
Sm .....	6,3	5,9 .....	6,6
Sr .....	330	318 .....	338
Ta .....	1,2	1,1 .....	1,6
Th .....	18	16 .....	20
U .....	4	3 .....	5
V .....	47	45 .....	50
Y .....	29	23 .....	30
Zn .....	17	14 .....	18

NOTE: The certified value is an estimate of the "true" value based upon the best available data at the time of the certification.

## 12. UNCERTIFIED/APPROXIMATE PROPERTY VALUES

Constituent	Uncertified value μg/g	Constituent	Uncertified value μg/g	Constituent	Uncertified value μg/g
B .....	90	Li .....	90	W .....	3
Br .....	2	Nb .....	16	Yb .....	2
Cr .....	67	Sb .....	0,4	Zr .....	180
Cs .....	2	Sn .....	4		
Eu .....	1	Tb .....	0,9		

## 13. VALUES OBTAINED BY INDIVIDUAL LABORATORIES

28 laboratories in 10 countries submitted analytical results on these materials. See 17 for all of the results.

## 14. MEASUREMENT TECHNIQUES USED FOR THE CERTIFICATION

Atomic absorption spectrophotometry  
 Colorimetric analysis  
 Emission spectroscopy  
 Emission spectroscopy with inductively coupled plasma source  
 Gravimetric analysis  
 Ion selective electrode  
 Mass spectrometry  
 Neutron activation analysis  
 Thermal conductivity  
 Volumetric analysis  
 X-ray spectrometry — fluorescence, energy and wavelength dispersive.

## 15. TREATMENT OF THE NUMERICAL VALUES

Statistical tests were used to determine outlying results which were then removed from the main population of results. Various estimators of central tendency were then calculated, and that most appropriate for the distribution of the data was assigned as the certified value. For full details of the statistical treatment of the analytical data, see 17.

## 16. CO-OPERATING LABORATORIES

See attached list.

## 17. REFERENCE

Ring, E J and Hansen, R G.: The preparation of three reference materials of South African coal. Randburg, Council for Mineral Technology. Report M169/1984.

This report is available from the Council for Mineral Technology, Private Bag X3015, Randburg, 2125, Republic of South Africa.

## 18. NAME OF CERTIFYING OFFICER

Mr R C Mallett  
Director  
Analytical Science Division  
Council for Mineral Technology.

## APPENDIX 1

## LIST OF CO-OPERATING LABORATORIES

**AUSTRALIA**

Australian Coal Industry .....	North Ryde
BHP Central Research Laboratory .....	Wallsend
Commonwealth Scientific and Industrial Research Organization .....	North Ryde
Department of Mineral Resources .....	Lidcombe
Electricity Commission of N.S.W. ....	Pyrmont
Herman Research Laboratory .....	Richmond
The Australian Mineral Development Laboratory .....	Eastwood

**BELGIUM**

University of Antwerp .....	Wilryk
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**FRANCE**

Aluminium Pechiney .....	Voreppe
IRSID .....	Mazieres-les-Metz

**FEDERAL REPUBLIC OF GERMANY**

Bergbau Forschung GMBH .....	Essen
Hoesh — Huttenwerke A.G. ....	Dortmund
Max Plank Institute .....	Mainz

**ITALY**

ISPRA .....	Varese
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**LUXEMBOURG**

Laborlux S.A. ....	Esch-sur-Alzette
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**NETHERLANDS**

ECN Netherlands Energy Research Foundation .....	Petten
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**NEW ZEALAND**

Department of Scientific and Industrial Research .....	Lower Hutt
--	------------

**REPUBLIC OF SOUTH AFRICA**

Council for Mineral Technology .....	Randburg
Council for Scientific and Industrial Research:	
National Institute for Coal Research .....	Pretoria
National Institute for Materials Research .....	Pretoria
Nuclear Development Corp. of SA (Pty) Ltd .....	Pretoria
Sasol 1 .....	Sasolburg
South African Iron and Steel Corporation Ltd .....	Pretoria
Transvaal Coal Owners Asscn. (Pty) Ltd .....	Richmond
University of Cape Town .....	Cape Town
University of Port Elizabeth .....	Port Elizabeth
University of the Witwatersrand	
— Nuclear Physics Research Unit .....	Johannesburg

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