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Purifying coal for the production of nuclear graphite

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DECLARATION

I, Phupheli Milingoni Robert declare that the thesis hereby submitted in partial fulfilment for the requirement of the degree Master of Science (Chemistry) at the University of Pretoria is my own work and has not been submitted by me for any other degree at any institution.

Signature:………………………………………………………………………………
Date:…………………………………………………………………………………

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I would like to dedicate this work to my deceased mother with great respect.

ABSTRACT

Carbon materials play a fundamental role in the development of fusion reactors, for both the generation of electric power and the production of nuclear materials. It is possible to synthesise graphite and carbon materials from coal. Coal is available in large quantities and could be used for the production of high-purity carbon graphite. However, it contains large quantities of impurities that need to be removed prior to graphitisation/carbonisation.

The impurity levels of certain elements in this graphite must be kept at very low levels. Boron, which absorbs neutrons strongly, should be below 500 ppb. Europium and gadolinium, which absorb neutrons and are activated to highly radioactive products, as is cobalt, should be as low as 50 ppb. Lithium transforms to tritium, which leads to the circulating helium becoming radioactive. Other elements, such as calcium, sodium, silicon, thorium and uranium, should not be ignored.

The purpose of this study was to lower or remove completely the impurities and trace elements in coal that affect the quality of nuclear-grade graphite. The organic part of Tshikondeni coal was dissolved in a solvent, dimethylformamide (DMF), on addition of sodium hydroxide. The first stage of purification is centrifugation and filtration, which removes most of the impurities. The recovered organic material, known as ‘Refcoal’, may be converted to graphitisable coke. Some elements, significantly boron and cobalt, associate with the organic material in solution and are not sufficiently separated by centrifugation and filtration. Further purification was employed during each process step in the conversion of coal solution into graphite.

Different methods of purification were employed in this study. They included chlorination, acid treatment and the ion-exchange or complexation method. Chlorine gas and hexachlorocyclohexane (benzene hexachloride) were used in the chlorination method. Acids such as hydrochloric, hydrofluoric and ascorbic were used in acid treatment. In the ion-exchange method, reagents such as methane, starch, potassium cyanide, ethylene-diaminetetraacetic acid, sodium fluoride, sodium sulphate, ice, glycerol and sodium nitrate were used. All the treated Refcoal was coked at 1 000 ºC. Pyrolysis was applied in other methods with the aim of volatilising elements that form volatile halides at higher temperatures.

Analysis was done for elements such as calcium, cobalt, europium, gadolinium, lithium, sodium, silicon, thorium and uranium, and other elements in the periodic table. Inductively coupled plasma mass spectroscopy and inductively coupled plasma optical emission spectroscopy were used to analyse the concentrations of the trace elements in the coal (treated and untreated) and the coked Refcoal. In inductively coupled plasma mass spectroscopy, microwave digestion and fusion were applied as methods of preparation. However, the instrumentation gave different results for the same sample. The results showed that specific methods work for specific elements. The chlorination method and the acid-treatment method (especially using hydrofluoric acid and hydrochloric acid) gave better purification for most of the trace elements and other elements.

Better purification was achieved with elements such as, boron, calcium, europium, gadolinium, lithium, sodium and silicon. All the treatments failed to lower uranium and thorium to the level required for nuclear-grade graphite. However, uranium has a low boron equivalent and does not pose serious problems with respect to nuclear usage. All the methods failed to remove cobalt and this remains a problem.

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ABBREVIATIONS

AES/AAS	atomic emission spectroscopy /atomic absorption spectroscopy
b.p.	boiling point
CPM	capacitatively coupled microwave plasma
DMF	dimethylformamide
EDTA	ethylenediaminetetraacetic acid
HCH	hexachlorocyclohexane
HCl	hydrogen chloride
HF	hydrogen fluoride
HTGR	high-temperature gas reactor
ICP	inductively coupled plasma
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectroscopy
INAA	instrumental neutron activation analysis
KCN	potassium cyanide
m.p.	melting point
$NaNO_2$	sodium nitrite
Na_2SO_3	sodium sulphite
NMP	N-methyl-2-pyrrolidinone
PBMR	Pebble bed modular reactor
ppb	parts per billion
ppm	parts per million
SIMS	secondary ion mass spectrometry
subl.p.	sublimation point
TMS	thermal ionisation mass spectrometry
XRD	X-ray diffraction
XRF	X-ray fluorescence

CHAPTER 1 INTRODUCTION

Eskom experiences short, sharp electricity demand peaks in winter that are difficult to accommodate with the existing large thermal power stations. Electricity demand is also expected to exceed capacity between 2005 and 2010 in South Africa. Eskom has come up with a project to use a Pebble Bed Modular Reactor (PBMR) to generate electricity. The PBMR is a helium-cooled, graphite-moderated High-Temperature Gas Reactor (HTGR). The technology was developed in Germany. The PBMR is advantageous because it is cheap to build, economical to operate, has a short construction period of about 24 months, do not emit any greenhouse gases and, lastly, is radiologically safe. The PBMR could offer South Africa and neighbouring countries sufficient, inexpensive electricity in most areas [1, 2, 3].

The PBMR consists of a vertical steel pressure vessel, 6 m in diameter and 20 m high. The pressure vessel is lined with a layer of graphite bricks. This graphite layer serves as an outer reflector for the neutrons generated by the nuclear reaction and as a passive heat-transfer medium. Vertical holes are drilled into the graphite brick lining to house the control elements. This graphite reflector encloses the core. The core is the region of the reactor in which the nuclear reaction takes place. The PBMR core is 3.7 m in diameter and 9.0 m in height. When fully loaded, the core would contain 456 000 fuel spheres. The geometry of the fuel region is annular and located around a central graphite column. The latter serves as an additional nuclear reflector. The nuclear reaction takes place in the fuel annulus. Helium is used as a coolant because it does not change during the operating range of the PBMR and the neutron absorption cross-section of helium is very small, which implies that the reactivity of the core will not increase due to a change in the state of the coolant [2, 3].

The PBMR fuel consists of moulded graphite spheres containing coated fuel particles. The fuel particles (kernels) consist of uranium dioxide (Figure 1-1). These kernels are coated with a layer of porous carbon and two high-density layers of pyrolytic carbon (a very dense form of heat-treated carbon), with a layer of silicon carbide in between (Figure 1-1). The porous carbon accommodates any mechanical distortion that the kernel may go through during the lifetime of the fuel and any fission products released from the kernel. The pyrolytic carbon and silicon carbide layers provide an impenetrable barrier containing the fuel and the radioactive products that result from the nuclear reactions [1, 2, 3, 4].

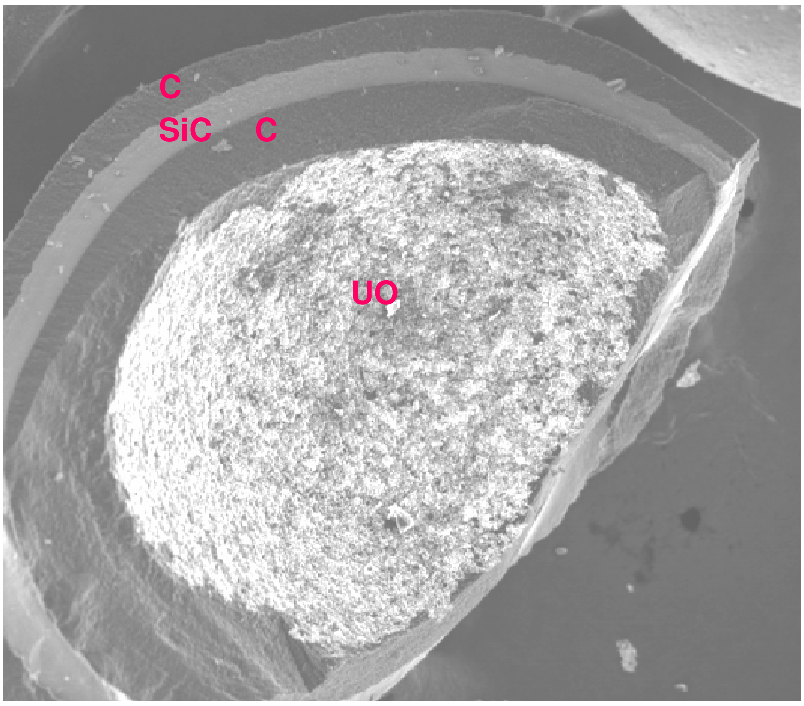

Figure 1-1. Fuel granule

The PBMR pebbles contain uranium enriched to about 8% in U-235, which is the isotope of uranium that undergoes the fission reaction in the core (Figure 1-2). The reactor is continuously refilled with fresh or reusable fuel from the top of the reactor, while used fuel is removed from the bottom after each cycle through the reactor. A fuel sphere will last about three years [1, 2, 3].

Graphite is used in nuclear technology, owing to its moderator and reflector qualities, combined with its structural strength and high-temperature stability. Graphite has a low neutron-capture section, low cost and it allows the efficient use of neutrons. A moderator slows fast neutrons to thermal velocities at which fission in U-235 and U-233 are most efficient. The reflector reflects neutrons back to the active core [5]. The graphite should be of high purity for use as a moderator in nuclear fission.

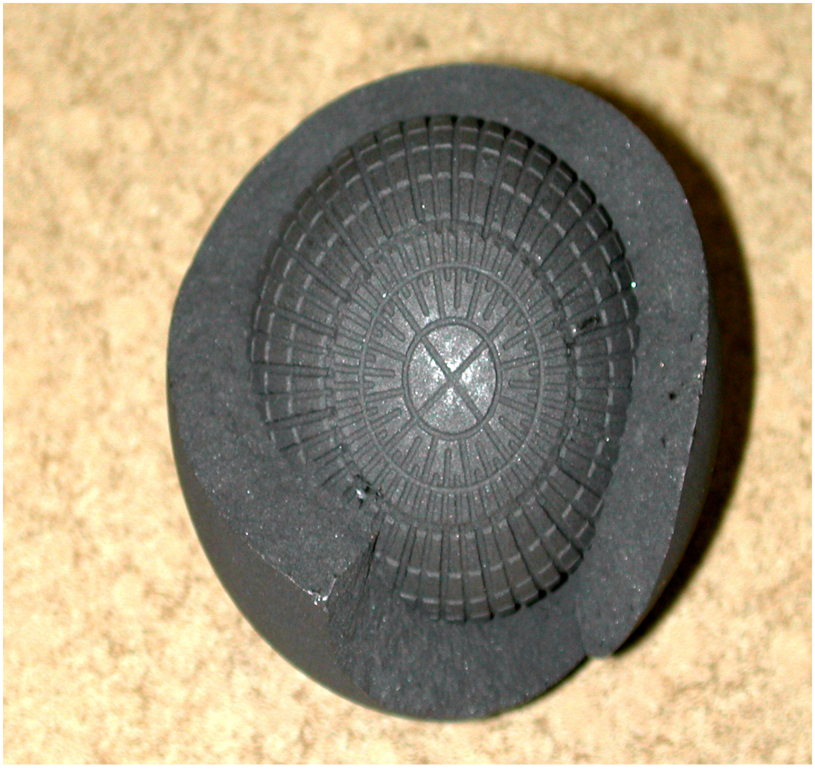

Figure 1-2. Pebble structure

The thermal neutron-capture cross-section is expressed in terms of an equivalent boron concentration by summing the concentrations of the individual impurities (elements), weighted by their thermal neutron-capture cross-section. A high thermal neutron-capture cross-section is associated with boron, cadmium, dysprosium erbium, europium, gadolinium, lithium mercury and samarium. Elements with medium thermal neutron-capture cross-sections are caesium, cobalt, hafnium, manganese, neodymium, praseodymium, scandium, selenium, silver and terbium. Elements with low thermal neutron-capture cross-sections are antimony, arsenic, copper, chromium, germanium, gallium, iron, lanthanum, nickel, potassium, sodium, thorium, titanium, tungsten and vanadium [1, 4].

Cobalt and rare-earth minerals are unwanted because they become activated by neutron capture to give medium-life radioactive isotopes. Without rapid isotope decay, the reactor would become highly active and this would have an adverse effect on the dismantling process at the end of the reactor's life. Lithium should not be present as an impurity. Lithium reacts with neutrons to produce tritium, making the circulating helium radioactive and thus spreading the radioactivity to the turbine part of the nuclear reactor plant [1, 4].

‘Refcoal’ is purified by chemical means prior to coking. It is treated with resins, complexing agents, acids and alkalis, and by adding compounds that contain chlorine and fluorine, with flushing of the chlorine prior to coking to lower the levels of impurities. Inorganic bound impurities are removed at this stage. Further purification is done during coking in the range of 900 to 1 000 ℃. Some of the volatile impurities are reduced at this stage. The metallic, metalloid and non-metallic impurities that remain after coking are purified at the graphitisation stage [4, 6, 7].

The purity of graphite is improved by graphitising at high temperature and through purification using drastic chemical means. Graphitisation is carried out in the range of 2 800–3 000 ℃ in an Acheson furnace. Fluorine and chlorine gases are flushed into the graphitising furnace during graphitisation, with the aid of converting boron and vanadium to volatile halides [5, 8]. The carbide-forming elements then form volatile halogen compounds. Conversion of the impurities to volatile halides allows the impurities to be swept out of the graphite and furnace [4, 5, 8]. Purification improves the neutron characteristics. Various purification methods can be used to reduce the level of impurities in the coal, although chemical purification increases the cost of production of the graphite.

In the past graphitisable carbon was manufactured from petroleum and pitch coke. Petroleum produces highly isotropic graphite blocks. Isotropic graphite gives the best dimensional stability under irradiation and achieves uniform thermal expansion in all directions. In this project Tshikondeni mine coal was employed as an alternative for manufacturing nuclear-grade graphite. Petroleum products have limited availability, whereas coal is still available in large quantities [1, 8].

1.1 Aim of the Study

Some coals would be excellent precursors for graphitising cokes, but have impurity levels far too high to find application in nuclear reactors. The organic part of suitable coals may be very efficiently dissolved in solvents, such as dimethylformamide, on addition of sodium hydroxide. Centrifugation and filtration of the insoluble part removes the great bulk of the impurities. The recovered organic material, known as ‘Refcoal’, can be converted into graphitisable coke. Volatile impurities are removed during the coking and graphitisation stage, by halogenations. However, for coal to be used as a synthetic material for nuclear-grade graphite, it must be purified and be free from certain impurities.

1.2 Content of the Research

The dissertation consists of six chapters. Chapter One gives an overview of the purpose of this study. The second chapter is a detailed literature review on coal and its purification, carbonisation and analytical methods. Chapter Three presents the experimental methods used. Chapter Four gives the results. Chapter Five discusses selected elements and the methods used. The general conclusions from the study are presented in Chapter Six.

CHAPTER 2 LITERATURE SURVEY

2.1 Coal

Coal is the most abundant of the three major fossil fuels – oil, coal and gas. Coal can be burned to provide heat and light, and to generate electricity. It contains a number of chemicals, which are used for various purposes. It is also the basis for various manufacturing processes (plastics, pharmaceutical products, iron and steel, aluminium and many other materials in daily use). From coal we get dyes, floorings, antiseptics and fertilisers. Currently, coal is needed to make graphite for coating fuel pebbles in order to generate electricity in a high-temperature nuclear reactor. Coal is therefore a very important natural resource and much effort is still being expended on making the most of it [9, 10, 11]. It can either be used as a heating and steam-raising fuel, or carbonised to form cokes and chars, or converted into synthetic gaseous and liquid hydrocarbons. It is a major source of carbon materials.

2.2 The Formation of Coal

2.2.1 Origin of coal

Coal is a major source of carbon materials. Graphite and diamond are the polymers of carbon. Coal consists of organic chemical substances containing carbon, hydrogen and oxygen in chemical combination, with a small quantity of nitrogen and sulphur. Coal is basically composed of the fossilised remains of plant debris, which have undergone progressive physical and chemical change through geological time [9, 10, 11].

Coals are organic sedimentary rocks originating from a variety of plant materials (higher plants, ferns, fungi and algae) and different tissues (leaves, stalks, woody trunks, bark, pollen, pores, resins, etc.). Coal became a heterogeneous mixture and a complex rock form, reflecting the original constituents, the conditions of deposition and the condition of the strata. The climate, vegetation types and the area in which the plant matter developed are therefore the factors that give particular characteristics to a coal. Coals that are composed of decomposed algae (‘boghead coal') or of spores ('cannel coal') are called *sapropelic*. *Humic* coal is composed of woody or cellulosic materials (residues of stalks and roots) and also cutinised or suberised materials (leaves, bark, cortial materials) [9, 10, 11].

The characteristics of coal also depend on the conditions of deposition (paleoclimate, paleogeography, whether or not dead plant matter has moved, the presence of salt and fresh water and its pH, the possibility of aerobic and anaerobic bacterial action, the presence of fungi) and on geological conditions (the presence of catchment basins for the constituents, slow or rapid subsidence, the protection of the deposits and tectonic movement). The evolution of coal from plant matter begins by degradation in an aquatic environment of the cellular structures and of the organic matter by the action of fungi and bacteria. Bacterial activity plays a role in the formation of pyrite deposits. Continual deposition of plant remains and mineral matter covers the earlier layers, which subside, and stops bacterial action. This burial drives out air and water, compresses the more or less jellified constituents and orientates them. This first stage is called *diagenesis*. The sinking of the bottom sedimentary basin, called *subsidence*, causes burial at great depth of the plant debris and forms the deposit. It causes, through increases in temperature and pressure, metamorphism, which modifies the organic material. This is the stage called *catagenesis*. This evolution progresses from peat to anthracite and is accompanied by physical and chemical changes, such as a reduction of the hydrogen and oxygen contents and of the volatile matter, and an increase in the reflectance [9, 10, 11].

Coal is composed of different organic and inorganic materials. The organic materials are derived mainly from plants which have undergone decomposition in the peat swamps, and physical and chemical alterations after burial. Evolution in the plant kingdom played an important role in the make-up of the plant source material in the swamps, ultimately affecting the petrographic composition of coal. Optically homogeneous discrete organic materials in coal are called *macerals*. There are three major groups of macerals: the vitrinite, liptinite (exinite) and inertite groups. The inorganic materials in coal consist primarily of mineral matter, clay minerals, quartz, carbonates, sulphides and sulphates [4, 9, 10, 11].

2.2.2 Coalification

Coalification is the name given to the development of the series of substances – peat, lignite or brown coal, bituminous coal and anthracite. The degree of rank of the coal increases progressively from lignite through low-rank coal to high-rank coal to anthracite. The carbon content increases and the oxygen and the hydrogen contents decrease all the way through the progression, while the reactivity decreases [11]. Coal rank is defined by the reflectance of the vitrinite (and by volatile matter). The rank of coal increases with geological age [9, 10, 11].

2.3 Coal Macerals

Differences in the plant materials and the degree of their decomposition during the first stage mostly determined the different petrographic types known as *macerals*. The action of pressure and heat during the geological phase caused the differences in coalification or the maturity of coal, known as *rank*. Macerals are the analog of minerals in organic rocks. The three maceral groups – vitrinite, exinite and inertinite – form the basis of coal petrography [12]. Macerals groups can be distinguished by the use of microscopy. They have different properties which become smaller as the rank increases [11].

2.3.1 Exinite

Exinite is derived from organisms that are relatively poor in oxygen: algae, spores, pollens, cuticles, suberin, and secretions such as resins. It is fluorescent under ultraviolet light. It is the lightest maceral (density between 1.1 and 1.25). It is not very brittle and increases the shock resistance of the lithotypes that contain it. Chemically, it is distinguished by the presence of 10 or 20% of aliphatic carbon in non-cyclic long chains. It is the most fluid maceral during the coking process. It has an aliphatic skeleton with aliphatic side chains. Exinite yields much more volatile matter on heating than any other maceral group. It increases in reflectance as the rank increases [9, 10, 11, 12].

2.3.2 Inertinite (in particular fusinite)

Inertinite is the residue of the most woody and resistant components. Cellular structures can be recognised which correspond to plant vessels. Inertinite often originates from plant matter that is partly burnt or has undergone lengthy aerobic oxidation before burial. It is the most dense maceral ($d = 1.4 – 2.0$), hard but friable, rich in carbon, and poor in hydrogen and volatile matter. It remains inert during the coking process. It is much more aromatic than vitrinite or exinite in low-rank coals. It shows very little change in its physical and chemical properties with increasing rank. The oxygen content is high and the hydrogen content is low. The carbon:hydrogen ratio increases with rank. The reflectance and the volatile matter are affected by these changes [10, 11, 12].

2.3.3 Vitrinite

Vitrinite originates from lignocellulosic tissues, which are gellified by bacterial action. Gellification is accompanied by the total disappearance (telinite) of cellular plant structures. It appears to be cement that surrounds the other macerals and mineral matter. Its density increases with rank from 1.2 – 1.7. It swells and agglomerates during the coking of medium-rank coals. Vitrinite in low-rank coal is composed of various humins, which consist of an aromatic nucleus surrounded by peripheral aliphatics. The peripheral groups (such as OH, COOH and CH_3) are lost when rank increases and the aromatic nuclei become larger. The oxygen content decreases as the rank increases. The aromaticity and carbon content increase with an increase in rank. The higher the carbon contents, the higher the reflectance [9, 11, 12, 13, 14].

Microscopic examination shows that the reflectances of these three groups of macerals increase with rank, converging towards the same value, reached at 4 or 5% at the anthracite level [9, 11].

2.4 Mineral Matter in Coal

Mineral matter is the term used to describe all forms of inorganic material associated with coal and mineral phases, as well as complexed metals and anions. The mineral matter content of coal is the actual weight percentage of the minerals present. There is no standard test for mineral matter, although low-temperature ashing (<150 ºC) with an oxygen plasma device is widely used [13]. The mineral matter in coal results from several separate processes. Some of mineral matter enters coal as the constituents of parent vegetation. Mineral matter was formed during the diagenetic stage of coal development, when inorganic matter was carried into the exposed decaying debris by wind and water, during the transport of debris from its original site to another, by deposition from percolating mineral waters during the metamorphic stage and by various ion-exchange processes during either or both stages of development [9, 10, 11, 12].

A number of instruments may be used to determine mineral content. Techniques such as X-ray diffraction, infrared spectroscopy, differential thermal analysis, electron microscopy and petrographic analysis may be used in determining the mineral content of coal.

The mineral matter is composed of major and minor constituents. The major constituents are:

1. Clay minerals (aluminosilicates), which occur mostly as illite, kaolinite, montmorillonite and mixed illite-montmorillonite, and usually make up to 50% of the total mineral contents.
2. Carbonate minerals, principally calcite ($CaCO_3$), siderite ($FeCO_3$), dolomite ($FeCO_3$) and ankerite ($CaCO_3 . MgCO_3 . FeCO_3$).
3. Sulphides, which are present as pyrite and mascarsite (i.e. dimorphs of FeSx).
4. Silica, which is present mainly as quartz and accounts for up to 20% of all mineral matter [9, 11, 15].

Minor inorganic constituents are present in concentrations of parts per million (ppm) and they are termed *trace constituents*. The most common detrital minerals are the various clay minerals. Other common ones are apatite, augite, quartz, epidote, feldspar, garnet, muscovite, kyanite, zircon, rutile, staurolite, topaz and tourmaline. The secondary minerals are normally kaolinite, calcite and pyrite. An analysis of the elements in mineral matter shows the presence of almost all elements in trace quantities. Some elements are found primarily in association with the organic matter in coal, e.g. germanium, beryllium, boron and antimony. Some elements, such as zinc, cadmium, manganese, arsenic, molybdenum and iron, are found in association with the inorganic material. Elements such as aluminium, silicon, iron, calcium, magnesium, sodium and sulphur are the primary elemental constituents of mineral matter in coal. The concentration of these elements depends primarily on the geographical location of the seam, and varies in different coalfields. In other countries, e.g. the eastern United States, the most abundant mineral elements are silicon, aluminium and iron, and there are much lower amounts of alkali and alkaline earth elements [15]. It has been reported that the most abundant minerals in South African coals are clays, together with carbonates, sulphides, quartz and glauconite. Phosphate minerals such as apatite are present as submicroscopic grains and also as discrete microscopic grains in some coal. They sometimes occur together with rutile and zircon [12]. To the west of the Mississippi River in the USA the relative amounts of silicon, aluminium and iron are much less and the alkaline earth and alkali elements are much greater [11, 15].

2.5 Action of Solvents on Coal

Some solvents are active at moderate temperatures, below 200 ºC. Polar aromatic amines such as pyridine, aliphatic amines such as ethylenediamine, and oxygenated compounds such as dimethylformamide form about 20% of the substance of low- and medium-rank coals [9, 11].

Dissolution is assisted by an increase in temperature and also by the presence in the solvent of the amine and phenol groups. High-temperature solvents become more effective as their chemical constitution approaches that of coal. The presence of an aromatic ring also increases the effectiveness of solvents: this is caused by the transfer of hydrogen from the solvent to the coal, thus increasing its solubility. Vitrinite is the easiest maceral to dissolve, whereas inertite is almost insoluble [9, 10, 11].

2.6 Chemical Properties of Coal

The chemical properties of coal are those that determine its response to oxidation and reduction, its behaviour during pyrolysis and its solubility in organic solvents. All coals (anthracites) and coal components (inertinites) are so sensitive to oxidation that even a minute addition of oxygen will alter their properties. Exposure of freshly mined coal to air at ambient temperature for few days adversely affects its caking propensities, its solubility, tar yield, heating value and other properties. The chemical changes responsible for such deterioration are for the most part still uncertain. However, there is agreement that they are connected with the progressive destruction by oxygen of the non-aromatic configuration in the coal molecule. Oxidation is characterised by the chemisorption of oxygen at readily accessible (aromatic and non-aromatic) surface sites and by the formation of acidic functional groups, in particular, -COOH, =CO, and phenols –OH. Moisture generated from chemically combined hydrogen in the coal reacts with chemisorbed oxygen to form peroxide or hydroperoxide complexes, which can oxidise ferrous thiocyanate, titanous chloride and hydroquinine [5, 9, 10, 11, 16].

All coals contain oxygen and the quantity decreases as the rank increases. Organic sulphur is present mostly in the form of thioethers (-S-) and inheterocyclic nuclei of the thiophen type, which are remarkably stable. Nitrogen would also combine in heterocycles [9, 11, 16].

Coalification is expressed by a series of consecutive reactions, primarily:

1. Decarboxylation: elimination of CO_2 from carboxyl groups (-COOH)
2. Dehydroxylation: elimination of water from hydroxyl groups
3. Dealkylation: elimination of methyl ($-CH_3$) groups, in the form of methane (CH_4)
4. Dehydrogenation or aromatisation: elimination of hydrogen from naphthalenic groups ($-CH_2-$) with transformation of hydroaromatic or naphthalenic rings into aromatic rings
5. Condensation of cyclic systems with elimination of hydrogen and formation of direct C-C bonds and new rings attached to those already existing.

As the rank increases, the chemical structure of the exinite approaches that of vitrinite by a further process of aromatisation [9, 10, 11].

2.6.1 Oxidation of coal

Coals exposed to air at ambient temperature are oxidised slowly by an exothermic reaction. The oxidation of fine coking coals causes deterioration in their caking properties. The rate of oxidation depends on the chemical composition and porosity of the coal [5, 9, 13, 16].

The chemical reactions of greatest interest are hydrogenation and oxidation at low temperature. Combustion and gasification occur at above 500 ºC, forming the products of carbonisation, i.e. coke and volatile matter, which then react [9, 13, 16].

2.6.2 Oxidising agents

Various oxidants act in an aqueous phase, such as nitric acid, hydrogen peroxide and potassium permanganate. The reaction of nitric acid with coal has been envisaged as one method of producing polycarboxylic acids [9, 11, 13].

2.6.3 Other chemical reactions of coal

Chlorine has an action analogous to that of oxygen: hydrochloric acid is formed, together with an infusible carbonaceous substance. Chlorine trifluoride transforms the coal entirely into gaseous or liquid hydrocarbons. Treatment with an alkaline solution under pressure at about 350 ºC converts most of the coal of a very low rank into soluble products such as phenols and hydrocarbons. Sulphonation of coal with sulphuric acid results in a product that has ion-exchange properties of some interest. Coal has a very resistant aromatic structure [9, 16, 17, 18].

2.6.4 Practical determination of mineral matter

The mineral content is determined via the ash yield. The changes that occur during combustion are loss of the water of constitution from aluminosilicates, loss due to the conversion of pyrite to iron oxide with the evolution of sulphur dioxide, and loss of CO_2 through the decomposition of carbonates [10, 11].

2.6.5 Ash yield

The ash yield is measured from the weight of the solid residue left after combustion of the organic matter under given conditions (combustion at a maximum temperature of 815 ºC until the residue attains constant weight). During the ashing process, the mineral matter present in the coal undergoes changes, of which the following are worthy of mention:

- Removal of carbon dioxide from carbonates
- Loss of water of constitution from silicates
- Transformation of pyrite into ferric oxide
- Volatilisation of chlorides of alkali metals [4, 10, 11].

2.7 Characterisation of Coals

Coals are characterised by various chemical and physical methods that have been established as national and international standards. These include proximate analysis, carbonisation assay, heating value (caloric value) determination, ultimate analysis, sulphur distribution, caking and coking behaviour, fusibility and ash composition. These tests are done on representative prepared coals, pre-treated coal samples and treated coal samples [10, 11, 19].

2.8 Carbonisation and Coking

Coal can be carbonised and coked at low and high temperatures. Low-temperature carbonisation involves heating of the coal in the presence of nitrogen. This removes the condensable hydrocarbons (pitch, tar and oil), gas and gas liquor, leaving a solid residue of coke. The process is done at temperatures up to 1 000 °C, at a controlled rate. Low-temperature carbonisation produces fine coke and fairly large quantities of liquid and gaseous products [5, 8, 13, 20, 21].

High-temperature coking is used primarily for the production of high-temperature lump coke. High-temperature coking takes place at temperatures above 1 000 ºC and is carried out in batch-operated coke ovens. The coking properties depend primarily on the softening and resolidification temperatures and on the swelling behaviour. The coking time depends on the operating conditions and the type of oven used. The main product is metallurgical coke. Coking technology may be assisted with additives and auxiliary technology. Additives such as petroleum, coke, bitumen and oil are used. Coke may be used for steel production. Numerous process developments, such as briquette coking or hot briquetting of a mixture of char and caking coal, have been demonstrated on an industrial scale [5, 13, 22, 23].

2.8.1 Coking properties

During the initial stage of pyrolysis, the volatiles consist of tar vapours, which must effect a passage through the porosity of the particle in order to escape. Porosity facilitates the retention of tar and causes plastic swelling of the particle (brought about by the internal gas pressure), all of which contribute to the improvement of the caking properties [9, 11]. According to coal coking theory, primary coal carbonisation occurs at 400 ºC, semi-coke formation at 600 ºC, secondary coal carbonisation at 850 ºC and coke formation at 1 000 ºC [11, 23].

2.8.2 Carbon as a source of graphite

Carbon must be of high purity, containing minimum quantities of desorbing and evolving gases, minimum quantities of particulate materials released by erosion and corrosion, and must have minimum reactivity with silicon and plasma for application in nuclear-grade graphite and in the manufacture of semi-conductors. Minimum amounts of metalloid, metallic and non-metallic impurities are specified for the carbon. For use in semi-conductors, the carbon's impurity levels must be 10^{-9} ppm or less. Carbon is considered to be the best material because of its electric conductivity, anti-spoiling properties and resistance to corrosion [21, 22]. The physical properties of nuclear-grade graphite are tabulated in Appendix 2, Table A2.2.

2.8.3 Purification of carbon

For purification, Refcoal solution and gel are treated with complexing agents and halogens prior to carbonisation. Carbon is treated with halogen gas above 200 °C during carbonisation or coking to convert metallic impurities into volatile halides. Fluorine and chlorine gas are used for this type of purification. Phosgene is also used as a chlorinating agent in coal purification. The minerals can be converted completely already at a temperature 200 °C by phosgene. The reactivity of minerals and phosgene depend on the reaction temperature; the reactivity is high during the first 10 minutes. About 80% of the minerals can be extracted from fly ash at 1 050 °C [8, 21, 22, 24].

Chlorination is effective in removing phosphorus from fly ash at 1 000 °C. The phosphorus content can be reduced from 2 100 to 24 ppm in 10 minutes during the chlorination process. Some elements may react with the chlorinating agent to form chlorides of those elements which are volatile and can be removed. However, chlorides with high boiling and melting points cannot be removed from a system as volatile matter under typically reasonable temperatures (T<1 200 °C) because they are in condensed phases (such as CaCl, m.p. = 782 °C, b.p. = >1 600 ° C; MgCl, m.p = 708 °C, b.p. = 1 412 ^{o}C; KCl, m.p. = 776 °C, b.p. or subl.p.= 1 500 °C) [24]. Graphitised carbon block contains metallic and non-metallic impurities, which contaminate silicon and compound semi-conductor crystals to create defects or to trap carriers (electrons and holes), so causing their properties to deteriorate. Carbon for semi-conductor manufacture must be exceptionally pure [8, 21, 24, 25, 26].

Further purification is done in a graphitisation stage. The metallic, metalloid and non-metallic impurities that remain after coking are purified during graphitisation by halogen gases such as fluorine and chlorinated gas, at temperatures above 2 000 °C. The halogens diffuse into the carbon block through the pores to react with the metallic impurities and form halides of low boiling point that vaporise from the block [8, 21, 22, 27]. Some metallic impurities that cannot come into contact with the halogen gas because of their location in the wall of closed pores in the carbon block are not removed by this type of purification. The extent of purification depends on the temperature and the time of purification. Carbon blocks must be placed correctly in the furnace to allow uniform contact with the gas. The size and shape of the blocks determine the time required for purification. Non-metallic impurities vaporise out of graphite during the graphitisation stage. Sometimes sulphur remains within the graphite lattice, hence its removal is never achieved by halogen gas treatment. Some elements, such as phosphorus, chlorine, fluorine and hydrocarbons, may remain adsorbed in the pores of the graphite. Thus the carbon part must be baked carefully so as not to retain any non-metal impurities. Na, K and Ca are carefully kept out of the processes because secondary contamination takes place easily [20, 26].

2.9 Trace Elements in Coal

2.9.1 Introduction: General considerations

Almost all elements of the periodic table are present in coal [6, 20, 28, 29], but their contents differ. These elements can be divided into three groups: (1) major elements (C, H, O, N, S), whose amounts are above 1 000 ppm; (2) minor elements, which include coal mineral matters (Si, Al, Ca, Mg, K, Na, Fe, Mn, Ti), and halogens (F, CL, Br, I), present in concentrations between 100 and 1 000 ppm; and (3) trace elements, which are constituents with concentrations below 100 ppm [20]. Trace elements, which occur in minute amounts in rocks or coal, water and soil, have major influences on health. Trace elements are found in coal in combination with minerals. Some of the elements are associated with the organic part of the coal, others with the inorganic part and some with both parts.

Coal contains both minor (e.g. Cu, Zn, B, Co, Mn, etc.) and major trace elements. Coals of different ranks have different trace element concentrations. Different techniques are used for trace element analysis. Some techniques are effective only for analysing certain elements. Instrumental neutron activation analysis is the technique recommended for most trace elements [30, 29].

2.9.2 Occurrence of trace elements in coal

Trace elements may occur in coal principally in either organic or inorganic forms; most trace elements are found in both combinations. Trace element combinations and contents differ from one coal to another due to the different coalification processes. Elements are present in various compounds in the coals and their distribution is different. Some trace elements are found predominantly in mineral species. Elements combined with mineral matter may remain in the ash. It has been reported that Be, Sr and Ge have an organic affinity, whereas Ba, B, Ce, Co, La, Mn, Ni, Rb and Zr have an inorganic affinity [20, 29, 31]. Tables A2.4, A2.5 and A2.6 in Appendix 2 show the elements that occur in coal with their inorganic and organic affinities.

Trace element concentrations and their chemical affinity vary strongly with the coals considered [20, 29, 32, 33]. The concentrations of trace elements usually decrease with increasing coal rank [33].

In the organic fraction, the trace elements may be associated with amide, carboxylic, phenolic and sulphhydroxy functional groups in the organic fraction of coal. In the inorganic fraction, the trace elements are often associated with clays, carbonates, silicates, sulphides, sulphates and other minerals. The elements with high organic affinity are present as chelates. The concentration of elements as both mineral matter and organically combined species varies in the locations in which coal is extracted or mined [6, 29, 30, 34, 35, 36, 37].

2.9.3 Emission of trace elements during combustion, coking and graphitisation

The release of trace elements from coal during combustion is affected by their modes of occurrence in coals, i.e. their chemical affinities. The volatility of the elements varies with coal type [32]. Mercury and selenium are more volatile trace elements.

The elements associated with the coal's organic and sulphides fractions tend to vaporise first [32]. Devolatilisation and sulphur removal through heat treatment of coal prior to combustion also solves the sulphur-emission problem. The chemical forms and the state of the trace elements may also change during such treatment. The thermal stability and distribution of trace elements are important factors to be considered during the heat treatment of coal [32]. Trace element reduction tends to increase with total ash reduction [32]. Trace elements are washed out during the cleaning process, but they are not removed to the same extent as the bulk ash [32]. Trace elements are emitted from coal furnaces in both the gaseous and solid phases [6, 7, 33, 34].

The release of volatiles is observed in the temperature range from 400 °C and 800 °C and the ultimate volatile yield is 35 – 45% [38]. Fluorine volatility increases with increasing pyrolysis temperature [38]. Coal pyrolysis leads to significant changes in the coal structure and chemical constitution and to the formation of solid, gaseous and liquid products [31, 33, 39].

2.10 Analytical Methods

2.10.1 Introduction

Various analytical methods are used for coal and ash analysis. Some analytical techniques cannot be used for multi-element analysis on an individual sample. Analytical methods such as atomic absorption spectroscopy, potentiometry, voltametry and absorption spectrometry are used for coal analysis. All these methods require coal sample preparation and fly ash matrices. Sample preparation includes wet or dry ashing of the coal or dissolution of the fly ash through acid treatment or fusion. The detection limits can be good when appropriate standard methods or the method of standard additions is used. Analytical methods such as X-rays, mass spectroscopy and activation analysis (neutron and charged particles) can be used for multi-element analysis on an individual sample [12, 40, 41].

A number of techniques have evolved for determining trace elements in coal, coke and coal ash. Chemical, calorimetric or wet technique procedures are faster, less tedious and yield acceptable results. Particular analytical techniques are suited for specific elements. Combinations of instruments may be applied to achieve better results. Most elements in coal are detectable with varying degrees of acceptable accuracy and precision. The methods most frequently used for analysing trace elements in coal are activation analysis, atomic absorption, optical emission, inductive coupled plasma spectroscopy, mass spectroscopy and X-ray fluorescence or a combination of these methods. Atomic absorption and neutron activation methods offer lower detection limits, usually 1 ppm or better for applicable elements. X-ray fluorescence and optical emission methods are useful for many elements in the range of 1 to 10 ppm and above.

Different laboratories also have different procedures for coal analysis. Ideally, a method of analysing trace elements in coal combustion products should determine a large number of elements of interest simultaneously, require relatively simple sample preparation, be capable of automation, produce an output compatible with computerised data and be rapid [12, 17, 40, 42].

2.10.2 Atomic absorption spectroscopy

In this method, the sample in a solution is atomised by a flame or electrical energy source, where it produces atomic vapour of the element being analysed. Monochromatic light which has the same wavelength as that of the required element is then passed through the same vapour. The atoms present in the ground state of the vapour absorb radiation from the monochromatic light source in proportion to their concentration present in the sample.

Atomic absorption spectroscopy is a highly sensitive method which always gives an accurate analysis for specific elements because it does not provide information on more than two elements concurrently [43, 44]. It is used mostly for the analysis of metals because the sensitivity of the method declines with increasing non-metallic character of the element. The method is also less sensitive to elements that form refractory oxides and hence atomise with greater difficulty. This method requires sample dissolution. Coal requires a dissolution technique capable of decomposing large quantities of organic materials. Coal slag and fly ash require techniques capable of dissolving acid-resistant minerals and glasses [40].

When atomic absorption spectroscopy is used for coal or ash samples, it encounters interferences such as chemical interferences or inter-element matrix effects (from large concentrations of acids and solids in solution), and molecular absorption (from molecules such as SrO and $Ca(OH)_2$ and errors in the absorption measurement) [40]. Using standard addition calibrations, a precision of ±10% for all analyses can be obtained. Low-temperature or high-temperature ashing methods can be used for sample preparation. Wet chemistry has to be used for sample preparation for conventional atomic absorption spectroscopy [40, 43, 44].

2.10.3 Atomic emission spectroscopy

This method is capable of measuring with suitable sensitivity all elements except fluorine and phosphorus. Emission spectroscopy is also a multi-element technique, and the analysis of more than one element is less expensive and more rapid. There are three types of plasma: the electrodeless, inductively coupled plasma (ICP), the single-electrode capacitatively coupled microwave (CPM) plasma and the double-electrode D-C arc plasma jet. Inductively coupled plasma optical emission spectroscopy (ICP-OES) has relatively lower detection limits and is free of inter-element effects and capable of rapid multi-element analysis of trace elements. In these methods a low-temperature ashing procedure is applied to minimise the loss of volatile elements. The analytical procedure provides an estimation of 68 elements, including minor, major and trace constituents. Samples can be analysed by the direct reading method or by photographic techniques [40, 45, 46].

2.10.4 Inductively coupled plasma (ICP) mass spectroscopy

Inductively coupled plasma mass spectroscopy is a recently developed technique. Mass spectrometries offer several advantages over ordinary ICP methods. These spectra are used for quantitative measurements based upon calibration curves, often with an internal standard. ICP is based on the extraction of the ions, formed by plasma, for elemental analysis by mass spectrometry. Several elements in the periodic table have been determined with little spectral interference. The method is capable of determining elements with detection limits as low as the range between

0.1 and 10 ppb. It is suitable for the semi-quantitative analysis of samples that are difficult to decompose or dissolve, such as geological materials, alloys, glasses, agricultural products, urban particulates and soils. Together with laser ablation it can provides quantitative surface information and requires minimal sample preparation [4, 42, 43, 45, 47].

More energetic sources permit the determination of elements in low concentrations that tend to form refractory compounds (i.e. compounds that are highly resistant to decomposition by heat or other rigorous treatment). This applies to elements such as boron, phosphorus, tungsten, uranium, zirconium and niobium. Plasma sources allow the determination of non-metals such as chlorine, bromine, iodine and sulphur. Plasma procedures usually require the decomposition of a sample to yield solutions for injection into the source. Spectra of several elements can be recorded or obtained simultaneously [42, 43, 45, 47, 48].

2.10.5 Instrumental neutron activation analysis (INAA)

Neutron activation analysis methods are based on measuring the radioactivity that has been induced in samples by irradiation with neutrons or charged particles, such as hydrogen, deuterium or helium-3 ions [43]. Neutron activation methods have high sensitivity. They require minimal sample preparation and calibration is simple. The methods are applicable to the analysis of art objects and coins, and forensic and archaeological specimens. This method has been applied to the analysis of metals, alloys, archaeological objects, semi-conductors, biological specimens, rocks, minerals and water owing to its high sensitivity and non-destructive aspect. The disadvantages of neutron activation methods are their need for large and expensive equipment and special facilities for handling and disposing of radioactive materials. These methods have been used for the analysis of various elements in coal. They are sufficiently sensitive to allow the determination of some elements in concentrations down to 1 ppb [4]. Cobalt, gadolinium and the rare-earth elements can be satisfactorily determined by INAA [4].

2.10.6 X-ray fluorescence spectroscopy

X-ray fluorescence spectroscopy is capable of measuring most of the elements specified simultaneously. It is capable of measuring elements with atomic numbers greater than 15 and indeed is more sensitive to elements with higher atomic numbers. It has the merit of an internal standard which neutralises matrix effects and makes for high accuracy. Energy-dispersive X-ray spectroscopy is suited for coupling to a computer because analysis of the fluorescent X-ray spectrum from the sample is done by a solid-state detector and a pulse-height analyser which provides digital data for computer processing [40, 43, 49].

2.11 Refined Coal

2.11.1 Introduction

Solvent extraction has been developed as a technique for investigating coal composition and producing waxes, resins or other coal derivatives of potential commercial value. Coal extraction or dissolution is another way of purifying coal – the inorganic mineral components are separated from the organic components. Mineral matter is extracted from coal with different solvents, alkalis and acids. Mineral matter in coal consists largely of aluminosilicate compounds such as kaolinite and clays, in conjunction with quartz [1, 4, 25, 27].

2.11.2 Extraction of mineral matter

Mineral matter can be extracted from coal by using sodium hydroxide or hydrofluoric acid. The use of an alkaline solution consisting of sodium, potassium or ammonium hydroxide, and hydrosulphide or carbonate, followed by acid washing using formic, acetic, sulphuric or hydrochloric acid, has been reported [50, 51]. In these methods, coal is treated with aqueous sodium hydroxide at temperatures ranging from 100 ºC to 350 ºC [4, 27, 52]. Mineral matter such as aluminosilicate compounds reacts in this condition to form insoluble sodalite ($Na_8Si_6Al_6O_{24}$), which is soluble in acid. This provides a basis for coal cleaning, using dilute alkali followed by washing with mineral acid [52, 53]. A two-step acid-washing process has been reported [54]. In this process the coal is treated with sodium hydroxide and then washed with H_2SO_4 or HCl, followed by washing with HNO_3. An ash content of <0.1 to 1% can be obtained with this method. Washing with calcium hydroxide, followed by hydrochloric acid leaching, is effective as calcium hydroxide reacts with kaolinite and quartz to form calcium-bearing hydrated silicates, such as tobermorite and hibschites, which can be dissolved in acid [55].

Hydrofluoric acid (HF) is considered the main demineralising reagent. HF produces ultra-clean coal when used for coal cleaning or purification. It penetrates the coal matrix and dissolves aluminosilicates more completely than NaOH. It forms insoluble fluorides such as calcium fluoride (CaF_2) and magnesium fluoride (MgF_2), and fluoroaluminate compounds such as $NaAlF_4$, $MgAlF_5$ and K_2NaAlF_6, which are of the major concern in the process when HF is used [4, 27, 56, 57, 58, 59, 60].

2.11.3 Solvent extraction

2.11.3.1 Coal extraction with DMF/NaOH at various temperatures

Coal is extracted with dimethylformamide (DMF) plus sodium hydroxide. The ratio of solvent: coal: sodium hydroxide is 1 000:100:10; extraction is done for 5 – 6 hours at 90 ºC. The process is conducted in oil or water-bath jacketed reactor under nitrogen. Nitrogen is used to prevent oxidation of the solution. The rate of extraction is monitored by taking samples of the solution at different time intervals, centrifuging the sample, diluting it with DMF in a volumetric flask and then measuring the absorbency at 600 nm. The insoluble materials are separated from the solution by centrifugation [1, 25].

Extraction can also be done for 24 hours at room temperature, using the same ratio of solvent: coal: sodium hydroxide (1 000:100:10). In this case the process is conducted in a centrifuge bottle under nitrogen. Nitrogen is used to prevent oxidation of the solution. The rate of extraction is monitored in the same way as described above and again the insoluble materials are separated from the solution by centrifugation [1, 4].

2.11.3.2 Coal extraction with NMP (N-methyl-2-pyrrolidinone)

NMP has been found to be a good solvent for the extraction of bituminous coals. The pyrrolidinone ring interacts strongly with aromatic rings, especially polycondensed aromatic compounds. Coal extraction with NMP on its own is low because of its high viscosity and low penetration. However, NMP gives a better extraction when mixed with CS_2 (carbon disulphide) in a ratio of 1:1. CS_2/NMP mixed solvent has low viscosity; it is capable of entering the internal network of coal, giving complete extraction and increasing the extraction yield. Nevertheless, DMF gives a better extraction yield as compared with CS_2/NMP solvent [61].

2.12 Graphite

2.12.1 Introduction

Graphite is one of the allotropic forms of carbon; the other ones are black amorphous carbon and diamond. Black lead is another name for graphite. Graphite occurs in nature as a mineral, which contains constant impurities. It is distributed worldwide, being found in Africa, Canada, the United States, Mexico, etc. It is made artificially by baking a mixture of petroleum coke and coal tar pitch at about 950 °C for 11 to 13 weeks. The baked products are graphitised in a graphitising furnace at about 2 800 °C to 3 000 °C for about four to five weeks. The process of graphitisation is also a purifying step in that the metal impurities in the raw carbon are reduced to metal and vaporised [8, 40, 62].

Graphite is black, opaque and metallic in lustre. It has a density of 2.09 to 2.2 and its hardness is 1 to 2. It is consists of weakly bonded plane layers of atoms that are arranged in a hexagon. It is a good conductor of heat. Graphite has many applications: it is used in pencils, as an electrode in electrochemical industries, for electric furnaces and crucibles that reach high temperatures, as a lubricant either by itself or combined with grease, oil, or water, and in industrial paints. Graphite is a good moderator for nuclear reactors. It slows down the neutrons and makes a chain reaction possible [5, 8, 21, 62].

2.12.2 Structure and properties of graphite

The operation and durability of graphite as a moderator are also determined by its structure. Graphite is composed of stacked parallel layer planes, with the trigonal sp2 bonding. Carbon is bonded within each layer plane, forming a continuous hexagon. The molecules are arranged in infinite two-dimensional molecules. The spacing between the molecules is more than twice that between the atoms within the basal plane and approximately twice the Van der Waal's radius of carbon [5, 8, 21, 22]. The stacking of the layer planes occurs in two forms: hexagonal and rhombohedral. Hexagonal is the thermodynamically stable form of graphite and this is the form found in all synthetic graphite. Hexagonal is also the most common stacking sequence of the graphite structure, with a –ABABAB– stacking order. The carbon atoms are superimposed upon each other in every layer. In the hexagonal form of graphite, the atoms are of the alpha type. Rhombohedral graphite is thermodynamically unstable and can be considered as an extended stacking fault of hexagonal graphite. It has a stacking order –ABCABCABC–. It is found in combination with hexagonal graphite (up to 40%) in some natural and synthetic materials. Rhombohedral graphite has never been found in pure form. It reverts to the hexagonal form during heat treatment above 1 300 ºC [4, 22, 25].

Graphite undergoes structural damage during neutron irradiation. This damage can be reduced by careful selection of the raw material and purification during the manufacture of graphite. Impurities have additive effects on graphite [4, 8, 21]. The physical properties of graphite are given in Appendix 2, Table A2.2.

2.12.3 Manufacture of graphite from Refcoal

Coal is under investigation for use in the manufacture of nuclear-grade graphite because it is the cheapest source of graphite. Bituminous coal, which is a coking coal, could be used as a replacement for petroleum coke in the manufacture of graphite. Coal can be extracted to yield a solvent-refined coal, called *Refcoal* which is almost free of all mineral matter. The preparation of Refcoal serves as a purification step. Refcoal itself can be easily purified prior to coking and graphitisation. Purified Refcoal is coked and then graphitised at high temperatures.

Refcoal recovered by precipitation forms a better coke than Refcoal recovered by solvent evaporation [4]. Refcoal obtained by the extraction of coal with addition of sodium sulphide at room temperature produces better graphite than the one obtained by means of high-temperature extraction [4, 8, 15, 22, 25, 27].

2.12.4 Manufacture of graphite from petroleum and pitch cokes

Petroleum and pitch cokes are also used for the manufacture of graphite. The cokes that are used to manufacture conventional nuclear-grade graphite are classified as needle cokes from petroleum, pitch cokes, Gilsonite pitch cokes and Santa Maria cokes. Cokes and pitch cokes yield either anisotropic or isotropic graphite. Nuclear-grade graphite should have isotropic properties to give the best possible dimensional stability under irradiation [4, 8]. Anisotropic graphite can be converted to isotropic graphite by grinding it to an appropriate particle size, mixing it with pitch binder, and moulding or extruding and impregnating it as in the normal manufacturing process. This process takes several days [4].

2.13 Specific Elements

Specific elements are those elements considered to affect and reduce the life-time of a reactor when they react with the neutrons that are generated in the nuclear graphite. The total neutron-capture cross-section must be low to allow efficient use of the neutrons generated. This is usually expressed in terms of an equivalent boron concentration by summing the individual impurity element concentrations, weighted by the thermal neutron-capture cross-sections [1]. Specific elements include boron, cobalt, europium, gadolinium, sodium, lithium, thorium and uranium.

2.13.1 Boron

2.13.1.1 Effect of boron in nuclear graphite

Boron (B) is one of the trace elements that have a negative impact on nuclear graphite as it is an important absorber of neutrons. Carbon, on being heated at graphitising temperatures, loses much of its impurity load, except, in general, for carbide-forming elements, boron in particular, which tends to come off too slowly at higher temperatures. Various methods of purification have been employed in this study to purify the boron in Refcoal.

2.13.1.2 Boron in coal

Boron may be present in high concentrations in some coal. It has three possible modes of occurrence in coal, namely organically bound, fixed into the clay minerals (illite) and bound to the crystal lattice of tourmaline. The organically bound mode of occurrence is the one most commonly cited. The inorganic mode may dominate with an increase in coal rank. Clay minerals such as illite adsorb boron and fix it into their lattices [11, 27, 63].

Tourmaline is a complex borosilicate mineral with up to 3% wt boron. The boron present in tourmaline is less volatile during coal combustion. The concentration of boron in coal ranges from 0.5 to 2 455 ppm, with most coals having between 5 and 400 ppm. In combustion, boron is considered a Group II element. Group II elements are volatilised and later condense on, and become adsorbed into, fly ash. Between 20% and 80% of the boron will volatilise during combustion. Boron actually lies in the overlap between the Group III elements (lost to flue gas) and the Group II elements (condensed on fly ash particles) [64, 65, 66].

Boron partitioning depends on the temperature of the combustion system, as well as on the combustion method, the mode of occurrence of the element in the coal and the chemistry of the ash. Boron is generally retained at temperatures up to 815 ºC, but in some cases significant loss of boron at 370 ºC and, in one case, at 150 ºC during low-temperature radiofrequency ashing has been noted. Organoboron volatility is favoured at low temperatures, and oxidative retention of boron is favoured at higher temperatures. Doolan *et al.* [31] concluded that the chemical forms of the element present in the individual coals and the degree of oxidation control the variable volatility of boron during ashing. Gaseous boron exists as boric acid $B(OH)_3$, or boron may react with oxides at elevated temperatures to form B_2O_3 [6]. The oxidised form of boron has a lower boiling point (1 800 ºC). Boron present in the oxidised form on fly-ash particles is readily dissolved when mixed with water and is thought to be one of the mobile trace elements in ash-disposal impoundments [7]. Mobilisation of trace elements into solution by leaching of fly ash is primarily a function of pH [7]. The oxyanions (arsenic, boron, molybdenum and selenium) are most mobile at a pH of about 11, and the cations (cadmium, copper, lead, nickel and zinc) are mobile at pH 4 – 7, other controls not withstanding [63, 64, 65, 66].

2.13.1.3 Boron determination – A review of analytical methods

The methods most commonly used for the determination of boron are spectrophotometric and usually those that make use of plasma sources. Most spectrophotometer methods are based on the colorimetric reactions of boron with carmine, azomethane-H or curcumin; other colorimetric and fluorometric methods have poor sensitivity, suffer from serious memory defects and interferences, so their application remains limited with respect to the determination of boron. Nuclear reaction and atomic emission/absorption spectrometric (AES/AAS) methods have poor sensitivity and suffer from serious memory defects and interferences, so their application remains limited in boron determination [40, 67]. Some of these methods are also time-consuming and are not suitable for the detection of low-level boron. An inductively coupled plasma optical emission spectroscope (ICP-OES) is a suitable instrument for boron determination because of its simplicity, sensitivity and multi-element capability. For the measurement of boron's isotopic composition a mass spectrometer is required. Thermal ionisation mass spectrometry (TMS) and secondary ion mass spectrometry (SIMS) have been used to measure the isotopic composition of boron, but these methods are time-consuming and require extensive sample preparation and purification. Inductively coupled plasma mass spectrometry (ICP-MS) is capable of measuring boron isotopes. Plasma source MS is the method of choice in present day technology [40, 67].

Boron concentrations have been found to increase with ashing temperatures from 300 ºC to 600 °C, and then drop slightly between 600 ^{o}C and 700 ^{o}C. The amount of boron also increases when coal is ashed in uncovered platinum crucibles, but this increase in boron concentration is unexplainable [40, 63].

2.13.2 Cobalt

Cobalt (Co) is one of the undesirable elements in nuclear graphite. It becomes activated by neutron capture to give medium-life radioactive isotopes. The reactor structure becomes highly radioactive, without rapid decay, adversely affecting dismantling at the end of the reactor life. Methods of cobalt purification have been developed in this study with the aim of removing cobalt from the Refcoal prior to graphitisation [15, 62].

The major oxidation states of cobalt are +2 and +3 [1]. Cobalt (III) is the main oxidation state in complex ions, the few known complexes of Co (II) being fairly unstable. Other oxidation states that have been characterised are Co (IV), Co (I) and Co (0). State III is relatively unstable in simple compounds, but the low-spin complexes are exceedingly numerous and stable. Of several known cobalt isotopes, radioactive cobalt-60 is the most important. It has a half-life of 5.7 years and produces intense gamma radiation. Cobalt-60 is used extensively in industry and in radioisotope therapy [15, 62].

Dilute acids such as hydrochloric and sulphuric slowly react with the metal, with liberation of hydrogen and the formation of cobalt (II), Co^{2+} (aq) ions. Concentrated nitric acid renders the metal passive, but it reacts with dilute nitric acid, forming cobalt (II) ions and oxides of nitrogen [15]. The action of fluorine or other fluorinating agents on cobalt halides at 300 ºC to 400 ºC gives dark brown CoF_3, commonly used as a fluorinating agent. It is reduced by water.

Cobalt (II) forms numerous complexes, mostly either octahedral or tetrahedral, but five co-ordinate and square species are also known. Tetrahedral complexes, $[CoX_4]^{2}$, are generally formed with monodentate anionic ligands such as Cl^-, Br^-, I^-, SCN^-, N_3^- and OH^-. With a combination of two such ligands and two neutral ones, tetrahedral complexes of the type CoL_2X_2 are formed [15].

Coal contains organometallic compounds, which are known as *porphyrins*. Porphyrin complexes of nickel and vanadium are derived from the porphyrin structures in chlorophyll and haemoglobin present in the original plant and microbiological sources [4]. Cobalt could have originated from vitamin B_{12}, where it is presented complexed in the related corrin ring system. Battersby's method for complexing cobalt has been employed using 1,3 propanedithiol as complexing agent. It appears that this method did not work well [4].

2.13.3 Europium

Europium (Eu) is a most important neutron absorber. It occurs in coal in small quantities. It is a soft, silvery metallic rare-earth element and its atomic number is 63. It is in the lanthanide series of the periodic table. It occurs in bastnaesite, monazite, and other rare-earth minerals. Europium also occurs in fission products of uranium, thorium and plutonium. It boils at 822 °C and melts at 1 527 °C. Its relative density is 5.2 [15, 62, 63]. It is used to control nuclear fission in reactors and also as a phosphor activator [1, 4].

2.13.4 Gadolinium

Gadolinium (Gd) has the largest known cross-section or stopping power. It stops neutrons from any elements in nuclear reactors. Gadolinium boils at about 3 273 °C and melts at about 1 313 °C. It is used in electrical apparatus such as capacitors and masers, in metal alloys, in high-temperature cooling furnaces and in apparatus for magnetic cooling. It is also used as a component of control rods in nuclear reactors [5, 8, 22, 62, 68].

Gadolinium occurs in minerals such as gadolinite, monazite and samarskite. It normally occurs with other rare-earth elements in these minerals [15, 62, 70].

2.13.5 Sodium

Sodium (Na) and other alkali metal impurities in graphite are not of significance to the operation of nuclear reactors because if the hot graphite is exposed to air, this will catalyse its oxidation. Sodium is a highly reactive, soft metallic alkali element. It is in group 1A of the periodic table and its atomic number is 11. Sodium oxidises when exposed to air and reacts violently with water, forming sodium hydroxide and hydrogen. Sodium boils at about 883 ℃, melts at about 98 ℃ and has a relative density of 0.97. The atomic mass of sodium is 22.989 g/mol [15, 62, 63].

2.13.6 Lithium

Lithium (Li) is very undesirable as an impurity as its reaction with neutrons gives rise to tritium, making the circulating helium radioactive and thus spreading radioactivity to the turbine part of the nuclear reactor [1].

Lithium is a silvery-white, chemically reactive metallic element. It is an alkali metal in group 1A of the periodic table. Its atomic number is 3, and it has an atomic weight of 6.941. The density of lithium is 0.534. Lithium does not occur in nature in a free state – it normally occurs in compounds. Lithium boils at about 1 342 ℃ and melts at about 180.5 ℃. It tarnishes instantaneously and corrodes rapidly when exposed to air. When stored it must be immersed in a liquid such as naphtha. Lithium metal is used as a deoxidiser and removes unwanted gases during the manufacture of non-ferrous castings. Lithium vapour is used to prevent oxygen and carbon dioxide from forming scale in furnaces during the heat treating of steel. Lithium forms important compounds such as hydroxide, hydride and its heavy hydrogen [15, 62, 63].

2.13.7 Thorium

Thorium-232 is a naturally occurring isotope and has a large neutron-capture cross-section, like uranium-238. The process may be represented as [20]:

$$ {}_{90}\mathrm{Th}^{232} + {}_{0}\mathrm{n}^{1} \rightarrow {}_{90}\mathrm{Th}^{233} + \gamma $$

Thorium (Th) is one of the radioactive elements; it also forms radioactive elements such as protactinium-233 [8, 69]. Thorium reacts with neutrons to form radioactive fusion products in the reactor.

2.13.8 Uranium

Uranium (U) is the densest of all the naturally occurring elements. It occurs in different forms of isotopes. Natural uranium as found in the Earth's crust consists of three isotopes: uranium-238 (U-238), U-235 and U-234. The isotope U-235 is important because under certain conditions it can readily be split, yielding a great amount of energy. It is said to be *fissile,* hence the expression 'nuclear fission' [8, 70]. The fission reaction can be written as:

$$_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{92}U^{236*} \rightarrow F1 + F2 + n + \text{energy}$$

$$235_{92}U + 10n \rightarrow 14456Ba + 9036Kr + 2\ 10n + 200\ \text{MeV (or } 3.2 \text{ x } 10^{-11} \text{ J)}$$

Uranium decays like any other isotope. U-238 decays very slowly, its half-life being the same as the age of the earth (4 500 million years). This means that it is barely radioactive. The U-235 atom is fissile, whereas the U-238 atom is said to be fertile – this means that it can capture one of the neutrons that are flying in the core of the reactor and become indirectly plutonium-239 (Pu-239), thus yielding a great amount of energy. Sometimes the Pu-239 atom simply captures a neutron without splitting and becomes Pu-240 [20, 68, 69]. Uranium-238 is a neutron capturer and the process may be represented as:

$$_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239} + \gamma\ .$$

Uranium-238 and thorium-232 both undergo spontaneous fission and are neutron absorbers [8, 69].

2.13.9 Methods of purification

Purification methods were developed with the aim of lowering impurities and reducing the level of trace elements in coal. The requirement of PBMR reflector graphite is 4 ppm boron equivalent. The effect of specific elements and other elements cannot be ignored. The lower the original load of impurities, the purer the final product. Direct chemical de-ashing, using strong acids and alkalis, has been used in this study, as well as different chemical complexing agents. Effective purification may be achieved by reaction of the carbon with chlorine- or fluorine-containing compounds at temperatures around 2 300 ºC [1].

2.14 Carbon Materials for Nuclear Energy Application

2.14.1 Introduction

Carbon materials play a major role in the development of fission reactors, for both the generation of electric power and the production of weapons-grade material. Graphite-moderated power plants are used world-wide. Graphite and carbon materials (carbon-carbon composites and pyrolytic graphite) play vital roles in nuclear fusion reactors [5, 8, 21]

Nuclear fission involves splitting of the nucleus of an atom to produce two more or less equal fragments, together with a large amount of energy. The nuclear fission energy is derived when a heavy element such as ${}_{92}U^{235}$ splits apart. The fission reaction can be written as:

$${}_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{92}U^{236*} \rightarrow F1 + F2 + n + \text{energy}$$

$$235_{92}U + 10n \rightarrow 14456Ba + 9036Kr + 2\ 10n + 200\ \text{MeV (or } 3.2 \times 10^{-11}\ \text{J)}$$

The fission reaction produces an average of 2.5 neutrons per fission. The fission fragments (F1 and F2) and the neutron produce kinetic energy. The kinetic energy produced can be degraded to heat and harnessed to raise steam and hence drive turbine generators. The amount of energy produced per fission is very large. The role of carbon in the fission reactor is to facilitate the nuclear chain-reaction by moderating the high-energy fission neutrons [8, 21].

Carbon materials can be used for ablation and thermal insulation, and to absorb thermal shock and impact energy. The carbon materials used for nuclear applications are different. For example, graphite is used in fission reactors, graphite and carbon-carbon composites in fusion reactors and both porous and dense carbon-carbon composites are used in space nuclear applications [8, 15, 21].

2.14.2 Application of fission reactors

Nuclear fission reactors generate thermal energy from the fission of heavy isotopes such as ${}_{92}U^{235}$. The fission fragments produce kinetic energy, and are degraded to heat by collisions within the uranium fuel. The fission neutrons give up energy within the moderator via the process of elastic collision. The γ-energy given up is absorbed in the bulk of the reactor outside the fuel, i.e. in the moderator, pressure vessels and shielding. A moderator is a material responsible for slowing down the fast fission neutrons in a thermal reactor [8, 15].

A moderator material selected for the fission process should not react with the neutrons (if they are captured in the moderator, they cannot sustain the fission process). The moderator material must be cheap and compatible with the other materials used in the reactor. It should be stable and should not undergo any damaging physical or chemical changes when bombarded with neutrons. A good moderator should efficiently thermalise fast neutrons through the process of elastic collision. The choice of moderating materials is limited to a few elements with atomic numbers of less than 16. Gases are not often used as moderators because of their lower density, but can be used in chemical compounds such as H_2O and D_2O. Heavy water is a good moderator because ${}_1H^2$ and ${}_8O^{16}$ do not absorb neutrons, but the cost of separating heavy hydrogen isotopes is high. Beryllium or beryllium oxide are good moderators but are expensive, not easy to machine and suffer from toxicity problems. Graphite is a good and acceptable moderator. It offers a compromise between nuclear properties, utility as a core structural material and cost [8, 15, 21].

The fuel used in a graphite-moderated reactor may be natural uranium (a mixture of U^{238}, U^{235} and U^{234}) or enriched (U^{235}) uranium, typically contained in a metal sheath. Another core layout utilises integral fuel or moderator elements in which the uranium fuel is placed directly into cavities in the moderator blocks. In this design of fuel elements, the fuel is typically a ceramic (UO_2 or UC_2), and is coated with a layer of SiC and pyrolytic graphite. The coated fuel particles are formed into fuel rods, but may be consolidated into fuel balls or pebbles. The SiC and carbon act as the fission product barrier and cancel out the use of metallic fuel cladding, allowing the reactor to operate at a very high temperature (>1 000 ℃). Neutron-absorbing materials can be introduced into the core to reduce the number of neutrons available to sustain the fission process [8, 15, 21].

Heat is generated by the moderation of the fission fragments in the fuel, and by the moderation of fast neutrons from graphite. The heat is removed from the core by a coolant, typically a gas. Helium is commonly used as a coolant. The secondary coolant is raised to steam temperature and is passed to the turbine where it gives up its energy to drive an electric generator. A concrete biological shield encloses the reactor core and primary to protect the staff and the public from gamma radiation and fission neutrons, and also to prevent the escape of radioactive contamination and fission gases originating from fuel pins or blocks. A reactor is built in such a way that fuel elements can be loaded easily [8, 15].

2.14.3 Application of fusion reactors

In fusion reactors the hot plasma (ionised gas) is magnetically confined within a toroidal-shaped vacuum vessel [20]. The plasma temperature required to maintain the fusion reaction is greater than 50 x 10^6K (>10 keV). The inner wall of the vessel is protected by a material with a low atomic number or a highly refractory material. The interactions that occur between the plasma-facing material and the plasma are particularly severe and can result in failure due to high thermal stress, melting, sublimation, excessive surface erosion and neutron damage [8, 15].

Graphite, pyrolytic graphite and carbon-carbon composites, and beryllium have many of the desirable attributes for plasma-facing material. However, the use of beryllium is complicated because of its low melting temperature. Most of the current plasmas use carbon materials as their plasma-facing component. Carbon is used to facilitate the nuclear chain-reaction by moderating the high-energy fission neutrons [5, 8, 15, 21, 22].

2.15 Overview of Previous Studies on Coal Purification

Similar studies have been done on coal purification with the aim of lowering the impurities and the trace elements which adversely affect nuclear-grade graphite.

Mthembi [4] used the same type of bituminous coal with different ash contents. He undertook purifying extractions with and without the addition of sodium sulphide. In both cases the Refcoal was treated with chelating resins, hydrofluoric acid, hydrochloric acid, sulphonic acid resins, ammonia hydroxide solution and anionic resins [4].

Mthembi managed to purify elements such as Cs, Eu, Fe, La, Sc, SM and Tb when the coal gel was treated with acid. Treatment with chelating resins gave better purification for the elements Ba, Cs, Eu, Fe, Hf, La, Sc, Sm, Tb, Th and U. The same results were observed after treatment with sulphonic acid. Treating the gel with concentrated acid followed by the sulphonic acid resins was found to be best method for reducing the concentration of alkali metals (represented by caesium) and rare-earth elements (europium and samarium). Treating the gel with acid followed by chelating resins was the second best method. Solvent extraction and ion-exchange methods did not yield satisfactory results. Cobalt purification was not achieved [4].

CHAPTER 3 EXPERIMENTAL PROCEDURE

3.1 Materials Used

The instruments used were:

- Bechman GPR centrifuge operated at a speed of 5 000 r/min
- LKB Bromma 2160 Midispin centrifuge operated at a speed of 4 000 r/min
- Hettich EBA 3S centrifuge
- Clements GS 150 centrifuge
- Spectronic Genesis 5 spectrophotometer

All chemicals used were analytical grade.

3.2 Coal Used for the Study

A flotation coal from Tshikondeni Mine in Limpopo Province was used for this study.

3.3 Coal Extraction

Coal was dissolved in a mixture of dimethylformamide and sodium hydroxide, using procedure reported by Morgan [1, 4]. To a 3-litre reactor with a hot oil jacket and operated at temperature of 90 ºC to 95 °C, 240 g of coal was added together with 2 400 g of dimethylformamide. At this stage 24 g of sodium hydroxide (CP) in pearl form was added. A slow stream of nitrogen was flushed into a reaction mixture in a reactor to avoid oxidation. The progress of extraction was monitored as follows; samples of the slurry were taken at suitable time interval. The samples were centrifuged for a six minutes at 4 000 r/min using the Clements centrifuge. About 1 g of supernatant solution was weighed accurately into a 50 ml volumetric flask and made up to the mark with dimethylformamide solvent. The measured absorbance was then corrected to a 0.1 g sample. The extraction period was five to six hours with the 3-litre reactor. The mixture of Refcoal solution and the inorganic components, together with undissolved organic components of the coal was transferred into a centrifuge bottle. The mixture was centrifuged at a room temperature at 4 500 r/min for 1 hour, using the Beckman GPR centrifuge. The Refcoal solution (supernatant) was separated from residue by decantation.

3.4 Extraction of Water-Soluble Organic/Mineral Matter from Refcoal

The mixture of Refcoal solution (1 g) and ice (approximately 6.13 g) was placed in a centrifuge bottle for seven days. The supernatant was decanted. The remaining mixture was separated by centrifugation.

3.5 Recovery of Refcoal

Refcoal solution (200ml) (from Section 3.3) was precipitated with distilled water (400ml) in a centrifuge bottle. The mixture was then centrifuged for 30 minutes at room temperature at 4 500 r/min. The supernatant solution was then replaced by distilled water and the Refcoal gel was resuspended in the water by shaking the mixture for 5 minutes. The resulting Refcoal gel was washed five times with fresh distilled water by resuspending it to in water, followed by centrifugation at 4 500 r/min. The washed Refcoal gel was either used for different experiment, somewhere dried in an oven at about 60 °C for 24 hours. Refcoal (dried Refcoal gel) was analysed.

3.6 Acid Washing Methods

3.6.1 Purification of Refcoal gel with hydrochloric acid

Refcoal gel (200 g, from Section 3.5) was mixed with 32% hydrochloric acid (50 ml). The mixture was boiled for 15 minutes at high temperature on a hot plate. The Refcoal gel was then separated from acid by centrifugation. The Refcoal gel was then washed 6 times with distilled water. Refcoal gel was dried in an oven at 60 °C for 24 hours. Some of Refcoal was coked. Both Refcoal and coke were and analysed.

3.6.2 Purification of Refcoal gel with hydrofluoric acid

Refcoal gel (200g, from Section 3.5) was mixed with 40 % hydrofluoric acid (50 ml). The mixture was boiled for 15 minutes at high temperature on a hot plate. The Refcoal gel was then separated from acid by centrifugation. The Refcoal was then washed six times with distilled water. Refcoal gel was dried in an oven at 60 °C for 24 hours. Some of dried Refcoal was coked. Both Refcoal and coke were and analysed.

3.6.3 Purification of Refcoal gel with hydrochloric acid and hydrofluoric acid

Refcoal gel (200 g, from Section 3.5) was mixed with 40 % hydrofluoric acid (10 ml) and hydrochloric acid (10 ml). The mixture was boiled for 15 minutes at high temperature on a hot plate. The Refcoal gel was then separated from the acid by centrifugation. It was washed six times with distilled water and then dried in an oven at 60 °C for 24 hours. Some of the dried Refcoal was coked. Both Refcoal and coke were analysed.

3.6.4 Purification of Refcoal gel with ascorbic acid

Refcoal gel (100 g, freshly prepared) was mixed with ascorbic acid (20 g) and stirred for 24 hours in a centrifuge bottle at room temperature under nitrogen. The Refcoal gel was recovered and then washed six times with distilled water under nitrogen. The gel was filtered through a Buchner funnel, dried overnight at 60 °C under nitrogen and coked at 1 000 °C. Both Refcoal and coke were analysed.

3.6.5 Complexing of cobalt with ethylenediaminetetraacetic acid (EDTA)

Refcoal gel (100 g, from Section 3.5) was mixed with ethylenediaminetetracetic acid EDTA (20 g) and water (55 ml). The mixture was refluxed for 4 hours, after which the Refcoal gel was recovered by centrifugation. The Refcoal gel was washed six times with distilled water, followed by centrifugation at 4 500 r/min. The gel was filtered and dried in an oven at 60 °C for 24 hours. The dried Refcoal was then coked. Both Refcoal and coke were analysed.

3.6.6 Complexing of cobalt with sodium sulphite (Na_2SO_3)

Refcoal gel (100 g, from Section 3.5) was mixed with Na_2SO_3 (20 g) and water (40 ml). The mixture was refluxed for 4 hours. The Refcoal gel was recovered by centrifugation. Refcoal gel was washed six times with distilled water, followed by centrifugation at 4 500 r/min. The gel was filtered and dried in an oven at 60 °C for 24 hours. Dried Refcoal was coked. Both Refcoal and coke were and analysed.

3.6.7 Complexing of cobalt with ammonia solution

Refcoal gel (100 g, from Section 3.5) was mixed with ammonia solution (40 ml). Mixture was reflux for 4 hours. Refcoal gel was recovered by centrifugation. Refcoal gel was washed six times with distilled water, followed by centrifugation at 4 500 r/min. The gel was filtered and dried in an oven at 60 °C for 24 hours. Dried Refcoal was coked. Both Refcoal and coke were and analysed.

3.6.8 Complexing of cobalt with potassium cyanide (KCN)

Refcoal gel (100 g, from Section 3.5) was mixed with potassium cyanide (20 g) and 50 ml water. The mixture was refluxed for 4 hours. The Refcoal gel was recovered by centrifugation. The gel was then washed six times with distilled water, followed by centrifugation at 4 500 r/min. The gel was filtered and dried in an oven at 60 °C for 24 hours. The dried Refcoal was coked. Both Refcoal and coke were analysed.

3.6.9 Complexing of cobalt with sodium nitrite ($NaNO_2$)

Refcoal gel (100 g, from Section 3.5) was mixed with $NaNO_2$ (20 g) and 50 ml water. The mixture was refluxed for 4 hours. The Refcoal gel was recovered by centrifugation. The gel was then washed three times with distilled water, followed by centrifugation at 4 500 r/min. The gel was filtered and dried in an oven at 60 °C for 24 hours. The dried Refcoal was coked. Both Refcoal and coke were analysed.

3.6.10 Complexing of cobalt with sodium sulphite (Na_2SO_3) and sodium nitrite ($NaNO_2$)

Refcoal gel (100 g, from Section 3.5) was mixed with $NaNO_2$ (10g) + Na_2SO_3 (10 ml) and 50 ml water. The mixture was refluxed for 4 hours. The Refcoal gel was recovered by centrifugation. The gel was washed three times with distilled water, followed by centrifugation at 4 500 r/min. The gel was then filtered and dried in an oven at 60 °C for 24 hours. The dried Refcoal was coked. Both Refcoal and coke were analysed.

3.6.11 Coking

Refcoal (about 2 g) was ground into fine particles and weighed in a ‘boat’ (boat-shaped container). The boat (with a sample) was placed in the middle of some silicon tubing. The tubing was placed in the coking furnace, making sure that the boat was in the middle of the furnace. The coking was done at 500 ºC for 1 hour at first, then the temperature was increased to 1 000 ºC for 2 hours under nitrogen. Coke was analysed.

3.6.12 Coke chlorination

Chlorine was generated by adding hydrochloric acid, drop-wise, to calcium hypochlorite, bubbled through sulphuric acid (to dry the chlorine) and then passed through a tube into the furnace.

The reaction is as follows:

$$Ca(OCl)_2 + 2HCl \rightarrow CaCl_2 + 2Cl_2 + 2H_2O$$

The coke (about 2 g) was ground into fine particles and then weighed in a coking boat. The boat was placed in the middle of the coking tube and the tube was then placed in a furnace. The set-up was first flushed with nitrogen to avoid oxidation and then chlorination took place at 1 000 ºC for 1 hour.

3.7 Purification of Boron

3.7.1 Standard wash

Refcoal gel (200 ml) was recovered and then washed six times with distilled water (400 ml). The gel was filtered and then dried in an oven at 60 °C overnight, after which it was coked at 1 000 °C. Both Refcoal and coke were analysed.

3.7.2 Complexing of boron with potato starch

Refcoal solution (750 g, freshly prepared) was mixed with potato starch (75 g) and stirred for 24 hours in a centrifuge bottle at room temperature under nitrogen. The solution was filtered at high pressure under nitrogen. The Refcoal gel was recovered and then washed six times with distilled water under nitrogen. The gel was filtered through a Buchner funnel and dried overnight at 60 °C under nitrogen and coked at 1 000 °C. Both Refcoal and coke were analysed.

3.7.3 Complexing of boron with sugar

Refcoal gel (500 g, freshly prepared) was mixed with sugar (50 g) and stirred for 24 hours in a centrifuge bottle at room temperature under nitrogen. The Refcoal gel was recovered and then washed six times with distilled water under nitrogen. The gel was filtered through a Buchner funnel and dried overnight at 60 °C under nitrogen, after which it was coked at 1 000°C. Both Refcoal and coke were analysed.

3.7.4 Complexing of boron with glycerol

Refcoal gel (200 g) was washed with 5 % glycerol (400 g) eight times. The gel was filtered through a filter paper and dried overnight at 60°C under nitrogen. The dried gel was coked at 1 000 °C. Both Refcoal and coke were analysed.

3.7.5 Standard wash in acidic medium

Concentrated hydrochloric acid and ammonia were used to adjust the pH of the mixture to below 7, with the purpose to make the solution to remain in acid medium. The Refcoal gel was washed with distilled water eight times, with pH adjustment, under nitrogen. The gel was dried at 60 °C overnight under nitrogen and then coked at 1 000 °C. Both Refcoal and coke were analysed.

3.7.6 Methanol wash

Refcoal gel (200 g) was washed three times with methanol under nitrogen, then filtered. The gel was dried at 60 °C under nitrogen and then coked at 1 000 °C. Both Refcoal and coke were analysed.

3.7.7 Treatment of Refcoal with waste isomer (hexachlorocyclohexane)

Waste isomer (8 g) was mixed with 500 g of Refcoal solution (i.e. 40 g of Refcoal) so as to make up 20% of the final solution. The mixture was stirred overnight in a centrifuge bottle and then washed five times with distilled water. The gel was filtered and dried at 60 °C and then coked. Both Refcoal and coke were analysed.

3.7.8 Refcoal chlorination

Washed Refcoal gel was refluxed for 1 hour under chlorine. The chlorinated Refcoal gel was then washed with distilled water and dried at 60 ℃ overnight, after which it was coked at 1 000 ºC and then analysed.

3.7.9 Treatment of Refcoal with sodium fluoride

NaF (1 g) was dissolved in 100 ml of distilled water and then mixed with 500 g of washed Refcoal gel. The Refcoal gel was dried at 60 °C overnight and then coked or pyrolysed. Both Refcoal and coke were analysed.

CHAPTER 4 RESULTS

Two different coals were used for this study, labelled coal A and coal B. They were both from Tshikondeni mine, the difference between the two being the time of extraction from the mine. Coal B was used after coal A had been used up. The proximate analysis, ultimate analysis, ash analysis and major petrographic analysis of coal A were analysed by SABS and are the same as reported by Mthembi [4]. The proximate, ultimate, ash and major petrographic analyses of both coals are given in Tables 4.1 to 4.7. The trace elements in coal A were analysed by ICP-OES at the Tshwane University of Technology. Coal B was analysed by ICP-MS using two different preparation methods, i.e. the fusion method and the microwave digestion method. Both analyses of coal B were done at the Council for Geoscience.

Table 4-1. Proximate analysis of coal A

Moisture	0.90%
Ash	9.40%
Volatile matter	23.30%
Fixed carbon	66.40%
Total sulphur	0.81%

Table 4-2. Ultimate analysis of coal A

Carbon	90.86%
Hydrogen	4.88%
Nitrogen	2.07%
Oxygen (by difference)	2.19%

Table 4-3. Ash analysis of coal A

SiO_2	51.40%
Al_2O_3	25.50%
Fe_2O_3	6.00%
P_2O_5	0.81%
TiO_2	2.24%
CaO	5.05%
MgO	2.52%
K_2O	1.46%
Na_2O	0.36%
SO_3	4.45%
TOTAL	99.79%

Table 4-4. Major petrographic characteristics of coal A

Rank (ECE-UN in-seam classification)	Meta-bituminous (Medium Rank B)
Mean random reflectance	1.33
Vitrinite class distribution	V 10 to V 16
Standard deviations	0.177
Abnormalities	Extended vitrinite class distribution
Petrographic composition Maceral analysis	
Vitrinite content %	93
Liptinite content %	<1
Total reactive maceral %	94
Total inertinite %	6
More highly reflecting material %	1
Cracks and fissures	Occasionally observed
Signs of advanced weathering/thermal effects	Very occasionally seen

Table 4-5. Proximate analysis of coal B

Sample	**Tshikondeni (flotation concentrate – 355 µm)**
% Moisture content (air-dry)	0.6
% Ash content (dry basis)	9
% Volatile matter content (dry basis)	23.3
% fixed carbon (calculation) (air-dry)	67.4
% Total sulphur (dry basis)	0.858
Calorific value (MJ/kg)	33.5
Free swelling index	9
Roga index	86

Table 4-6. Ash composition of coal B analysis by XRF

Sample	**Tshikondeni (flotation concentrate – 355 µm)**
% Al_2O_3	24.85
% CaO	3.49
% Cr_2O_3	0.06
% Fe_2O_3	4.47
% K_2O	1.69
% MgO	1.82
% MnO	0.04
% Na_2O	0.84
% P_2O_5	0.52
% SiO_2	55.24
% TiO_2	2.16
% V_2O_3	0.1
% ZrO_2	0.16
% Ba	0.21
% Sr	0.18
% SO_3	2.31
% Total	**98.14**

Table 4-7. Ash fusion temperature (reducing atmosphere) of coal B

Sample	**Tshikondeni (flotation concentrate – 355 µm)**
Initial deformation temperature, ºC	1 424
Softening temperature, ºC	1 444
Hemispherical temperature, ºC	1 460
Fluid temperature, ºC	>1 550

Table 4-8. Ultimate analysis of coal B

Sample	**Tshikondeni (flotation concentrate – 355 µm)**
% Carbon (dry basis)	93.7
% Hydrogen (dry basis)	4.5
% Nitrogen (dry basis)	2.17
% Oxygen (dry basis)	0.5

Table 4-9. Forms of sulphur in coal B

Sample	**Tshikondeni (flotation concentrate –355 µm)**
% Pyritical sulphur	0.14
% Sulphate sulphur	0.01
% Organic sulphur	0.71

Table 4-10. Concentration of trace elements in coal A, Refcoal and chlorinated coal, as determined by ICP-OES (ppm)

Sample	**Al**	**B**	**Ca**	**Co**	**Cu**	**Cr**	**Fe**	**Li**	**Mg**	**Mn**	**Ni**	**Si**
Coal	026	9.5	1819.4	4.1	2	6.3	1286.4	3.0	712	20.23	3.75	7 692.8
Standard Refcoal	413	6.1	86.4	2.6	0.05	8.2	31.1	0.1	16.2	0.25	6.52	414.75
Coke @ 600 °C	4 598	7.4	121.6	5.2	0.2	23.4	113.0	0.6	122	1.29	18.345	1 205.88
Coke @ 1 000 °C	12 857	13.1	132	5.6	0.4	35	140.0	0.6	251	3.065	17.315	1 642.78
Cl_2 Refcoal	250	4.8	58.0	2.1	2.3	9.0	81.8	0.1	8.1	0.65	4.04	511.9
Cl_2 coke @ 600 °C	4 189	9.0	88.0	4.0	0.10	19.1	66	0.04	91	0.775	15.93	1 379.48
Cl_2 coke @ 1 000 °C	15 699	9.5	88.5	3.2	0.2	44.2	90.9	0.7	437	0.95	14.105	2616.7

Table 4-11. Concentration of trace elements in coal B, Refcoal, acid-treated Refcoal and chlorinated Refcoal, as determined by ICP-MS (ppm) (microwave digestion method)

Sample	**B**	**Ca**	**Co**	**Eu**	**Gd**	**Li**	**Na**	**Si**	**U**	**Th**
Coal	9	570	6.1	0.02	0.1	3.5	272	14450	1.1	0.01
Standard Refcoal	1.3	81.9	6.5	0.2	0.4	0.3	308	625	1.1	0.1
Standard coke	1.5	165	9	0.1	0.7	1	384	994	1.7	0.2
Acid-treated Refcoal										
HF Refcoal	0.8	35	4.5	0.04	0.3	<0.10	10	101	0.8	0.04
HF coke	1.2	21.1	6	0.01	0.02	0.5	18	195	1.1	0.02
Chlorinated Refcoal										
Cl_2 Refcoal	0.7	21.3	5	0.02	0.1	0.20	<10	368	1	0.01
Cl_2 coke	0.5	53.5	6	0.1	0.5	<0.1	<10	260	1	0.1
HCH Refcoal	0.7	45.1	6.1	0.14	0.8	0.3	27	830	1.1	0.12
HCH coke	1.1	82	8.2	0.12	0.9	0.4	77	1125	1.4	0.12

Table 4-12. Concentration of trace elements in coal B, Refcoal, acid-treated Refcoal, chlorinated Refcoal and complexed Refcoal as determined by ICP-MS (ppm) (fusion method)

Sample	Ca	Co	Eu	Gd	Li	Na	Si	U	Th
Coal	3 936.2	6.3	0.5	2.7	5.9	433.9	26 008	2.6	4.7
Standard Refcoal	110.99	7.7	0.2	1	0.5	363.3	906	1.2	2.2
Standard coke	150.4	10.1	0.2	1.1	1.1	532.8	1 282	2	3.8
Acid-treated Refcoal									
HCl Refcoal	35	5.9	<0.05	0.1	0.4	15	910	1	0.1
HCl coke	165.1	9.0	<0.05	0.2	0.6	33.3	2 063	1.4	0.2
HF Refcoal	51.1	0.2	<0.05	<0.05	-	2.2	10	<0.05	<0.05
HF coke	73.1	1.0	<0.05	0.2	-	7.2	83	<0.05	0.4
HF + HCl Refcoal	91	5.9	0.08	0.3	<0.10	5.6	511	0.3	1.2
HF + HCl coke	52.9	2.4	0.1	0.4	<0.10	9.2	602	0.3	1.4
Ascorbic acid Refcoal	50	7.0	0.1	0.7	-	30.0	1 112	2	3.1
Ascorbic acid coke	185	11.0	0.2	1	-	61.1	2 051	3.1	5.1
Chlorinated Refcoal									
Cl_2 Refcoal	41.3	5.8	<0.05	<0.05	0.7	33.2	819	<0.05	<0.05
Cl_2 coke	47.5	7	<0.05	0.2	0.2	38.9	932	0	0.8
Cl_2 + HF Refcoal	292.9	<1	<0.05	0.2	-	2.7	21	1.0	2
Cl_2 + HF coke	81	<1	<0.05	0.2	-	26.1	1 094	1.1	2.2
HCH Refcoal	20.3	5.8	0.1	0.7	0.4	46.1	817	1.6	2.1
HCH coke	122	13	0.3	1.7	-	105.5	2 217	3.8	5
Ion-exchange or complexed Refcoal									
Starch Refcoal	169.8	9.4	0.2	1.2	-	608	1 171	2	3.6
Starch coke	236.7	12.8	0.3	1.7	-	526	1 959	2.7	4.8
Methanol Refcoal	241.2	10	0.2	1.3	-	213	1 296	2	3.6
Methanol coke	291.3	19	0.3	1.8	-	349	2 069	3	5.2
KCN Refcoal	150.6	7.9	0.2	1.4	0.6	67	1 337	1.8	3.6
KCN coke	149.1	10.1	0.3	2	6.1	85	1 735	2.1	4
EDTA Refcoal	29	7	<0.05	0.2	1.2	78	1 117	1.3	0.8
EDTA coke	98	11.3	0.1	0.4	1.0	126	2 060	2.1	1.8
NaF Refcoal	5	1.3	<0.05	0.2	0.1	2 855	331	0.2	0.5
NaF coke	266.2	12.8	0.3	2	0.6	14 074	2 090	2.8	4.9
NH_3 Refcoal	90.1	9	0.2	1.2	0.6	29	1 898	2	3
NH_3 coke	58.1	8.3	0.2	1.1	1.4	27	1 163	1.9	3.2

Sample	**Ca**	**Co**	**Eu**	**Gd**	**Li**	**Na**	**Si**	**U**	**Th**
Na_2SO_3 Refcoal	86.8	10	0.2	1.3	1	3 285	1 766	2.3	4.1
Na_2SO_3 coke	81.3	11	0.3	2.0	10.3	3460	2275	2.6	4.7
$NaNO_2$ Refcoal	149.6	10.9	0.3	1.9	0.6	2829	6403	2.4	4.3
$NaNO_2$ coke	84.8	12.8	0.3	2.1	7	1960	1916	2.9	5.1
Na_2SO_3 +$NaNO_2$ Refcoal	63.2	9.9	0.3	1.4	0.5	5708	1409	2.3	4.1
Na_2SO_3+$NaNO_2$ coke	66.8	12.7	0.3	1.8	7.9	6172	1996	3	5
Ice Refcoal	359.2	9.2	0.2	1.1	-	128	1113	2.1	3.1
Ice coke	666.8	15	0.4	2.2	-	174	2117	3.0	5
5% Glycerol Refcoal	91.8	10	0.2	1.2	-	242	1207	1.8	3.1
5% Glycerol coke	131.5	11.9	0.3	1.5	-	209	1979	2.3	4
Sugar Refcoal	120	10	0.2	1.4	-	230	1340	2	3.2
Sugar coke	181.8	12.2	0.3	1.7	-	79	2178	2.5	4.5

Table 4-13. Progress of extraction with NaOH

Time	**Average corrected absorbance**
0	0.003
10	0.008
15	0.022
20	0.031
30	0.046
45	0.167
60	0.288
120	0.634
180	0.804
240	0.888
300	0.927
360	1.010

CHAPTER 5 DISCUSSION

5.1 Coal Used for the Study

Coal A is similar to the coal used by Mthembi [4]. The coal is classified as medium rank B (meta-bituminous). The proximate and ultimate analyses and the major ash analysis were done using various analytical methods as listed in Appendix 2, TableA2.1. The total sulphur in coal A is 0.81% – lower than in coal B, which is 0.86%. The percentage of carbon in coal B is 93.1% – higher than in coal A (the coal which was also used by Mthembi), which is 90.86%. The total ash analysis of coal A is 99.7%, which is higher than for coal B at 98.14%. The detailed analyses are given in Tables 4.1 to 4.10.

5.2 Coal Extraction

The extraction of Tshikondeni coal was done by using a solvent, dimethylformamide, and an alkali, sodium hydroxide, at a high temperature. About 90% extraction was achieved with this method. Figure 5.1 is a plot of the average corrected absorbance versus time, showing the progress of the extraction runs with sodium hydroxide and dimethylformamide. The extraction was repeated several times. The different runs are shown in Appendix 1, Table A1.5 and A1.6, and the plot is the average of the three runs. The extraction shows a trend similar to that reported by Mthembi and to the CSIR-developed Refcoal process [1, 4]. A maximum absorbance of 1 was reached during extraction. This shows that the concentration of the solution obtained was 8%. Water precipitation was used to recover the Refcoal. The precipitated Refcoal was purified using various methods to reduce the level of impurities in the coal. Water precipitation reduces the amount of ash in Refcoal and yields better cokes.

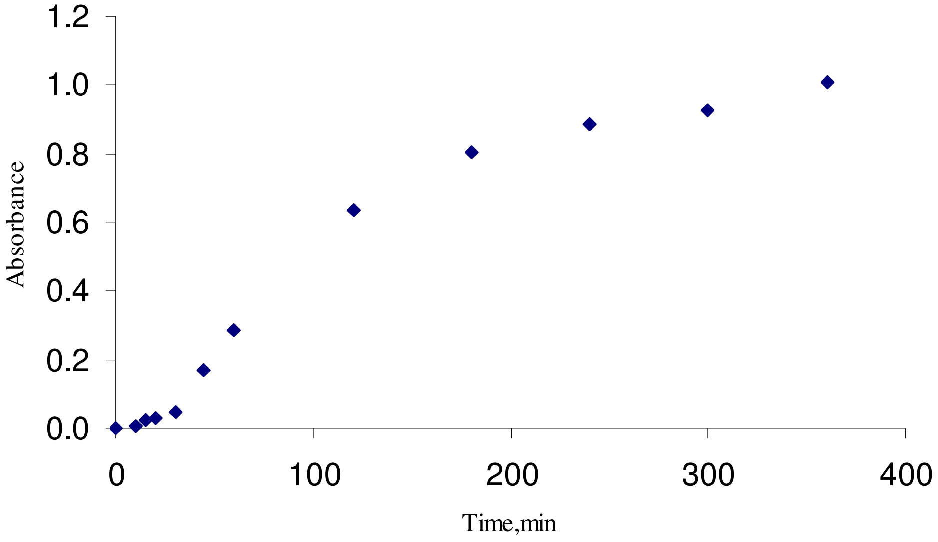

Figure 5-1. Progress of extraction with NaOH and DMF. Mass ratio used: 100:10:1, DMF:Coal:NaOH

5.3 Trace Element Analysis

Trace element analysis of the coal used for the study, i.e. Refcoal and purified Refcoal, was done by means of ICP-OES and ICP-MS. Two different coals were used and analysed, i.e. coal A and coal B. Coal A was analysed by ICP-OES and coal B was analysed by ICP-MS. With ICP-OES, the slurry method was used for analysis. Two preparation methods were used with ICP-MS, i.e. the fusion method and the microwave digestion method. A few samples were submitted to Prof. McChrindle for ICP-OES analysis at the Tshwane University of Technology. Most of the samples were also submitted to the Council for Geoscience for ICP-MS analysis. Almost all the elements in the periodic table were analysed by ICP-MS. ICP-MS gives consistent results as compared with ICP-OES. The results are given in Appendix 3. The concentrations are the average of the two determinations as shown in Appendix 1, Tables A1.1, A1.2 and A1.3. Different results were obtained with the different instruments and also with the different methods. Boron was not analysed with the fusion method because lithium borate was used as the flux during analysis.

Three methods of purification were used in this study, i.e. the acid treatment method, the chlorination method and the ion-exchange or complex formation method. With the acid treatment method, acids such as HCl, HF and ascorbic acid were used for trace element purification. Chlorine gas, a combination of chlorine gas and HF acid, and HCH (hexachlorocyclohexane) were used for the chlorination method. For the ion-exchange method, the Refcoal was treated with starch, methanol, KCN, EDTA, NaF, NH_3, Na_2SO_3, $NaNO_2$, $Na_2SO_3 + NaNO_2$, ice, 5% glycerol and sugar.

5.3.1 Trace element analysis with ICP-OES spectroscopy

The discussion below is based on the results shown in Table 4.10. The concentrations of the elements Al, B, Ca, Co, Cu, Cr, Fe, Li, Mg, Mn, Ni and Si are discussed as determined with ICP-OES in coal A. The concentrations given are an average of at least two determinations, as tabulated in Appendix 1, Table A1.1. The coal analysed by ICP-OES was coal A. Standard Refcoal is the untreated Refcoal precipitated with water, obtained only from extraction of coal A. The degree of purification was based on a comparison between the standard Refcoal and the treated Refcoal, treated with any method. The concentrations of the elements in the coal samples (Refcoal, chlorinated Refcoal and cokes at 600 ºC and 1 000 ºC) are discussed. The discussion below is based on coal A.

Aluminium: The aluminium concentration was lowered from 5 072 ppm in the coal to 418 ppm in the standard Refcoal. This shows that the leaching of aluminium is very high, which suggests that aluminium occurs predominantly in inorganic association in coal. Coked Refcoal at 600 ºC and 1 000 ºC, shows an increase in aluminium concentration. The concentration increases because some of the volatiles are removed when the Refcoal is converted to coke. After chlorination of the Refcoal, the aluminium concentration decreased to 251 ppm. The coke of chlorinated Refcoal at 600 ºC and 1 000 ºC shows an increase in the aluminium concentration, as indicated in the results.

Boron: The concentration of boron was reduced from 9.6 ppm in the coal to 6.25 ppm in the standard Refcoal. This shows that boron is not easily washed out of the solution. The low purification value of boron shows that boron occurs predominantly in the organic part of coal. (Organically bound boron is the form most often cited.)

Boron was found to occur less frequently in the inorganic part of coal. This is consistent with literature reports [11, 27, 49]. Boron is not easily removed from coal by simple precipitation because it occurs predominantly in the organic part of the coal. Coked Refcoal shows a slight increase in boron concentration at 600 ºC and 1 000 ºC as compared with the standard Refcoal. Purification by chlorination lowered the concentration to 5 ppm. The coke of chlorinated Refcoal at 600 ºC and 1 000 ºC, shows a slight increase in the concentration of boron. The concentration increases because some of the volatiles are removed during the conversion of Refcoal to coke; volatiles are also removed from glass, hence silicate glass was used.

Calcium: The concentration of calcium was lowered from 1 839 ppm in the coal to 87 ppm in the standard Refcoal. The leaching of calcium is high, which suggests that calcium is predominantly in inorganic association in coal and therefore it is easily separated from the organic component of coal. By using calcium as an indicator element for alkali earth metals, we can conclude that alkali earth metals are predominantly in inorganic association in coal. On the basis of this conclusion, alkali earth metals can be easily separated from the organic component of coal. This observation is consistent with those made in the literature [4, 47, 49]. The coked Refcoal at 600 ºC and 1 000 ºC shows a slight increase in the concentration of calcium as compared with the standard Refcoal concentration. The concentration in chlorinated Refcoal shows a slight decrease as compared with the concentration in the standard Refcoal. Coked chlorinated Refcoal at 600 ºC and 1 000 ºC, shows an increase in calcium concentration. It is suggested that the increase in calcium concentration is due to the loss of volatiles at high temperatures during coking.

Cobalt: The cobalt concentration was lowered from 4.2 ppm in the coal to 2.6 ppm in the standard Refcoal. This concentration is still higher than the maximum required concentration (0.05 ppm) for nuclear graphite. The low purification value shows that cobalt is organically bound in coal. Other methods for the purification of cobalt were applied and these are discussed under the purification of Refcoal in the next discussion on cobalt. The concentration of cobalt increases after coking at 600 ºC and 1 000 ºC. The cobalt concentration in chlorinated Refcoal was lowered to 2.2 ppm compared with the standard Refcoal. The cobalt concentration shows a slight increase in the chlorinated sample coked at 600 ºC and 1 000 ºC. This increase in concentration is suspected to be due to the concentration of cobalt during the coking of Refcoal.

Chromium: The concentration of chromium was not lowered at all, in fact it increased from 7 ppm in the coal to 8 ppm in the standard Refcoal. The chromium concentration shows an increase in coked Refcoal, chlorinated Refcoal and coked chlorinated Refcoal as compared with the standard Refcoal.

Iron: The concentration of iron was lowered from 1 303.9 in the coal to 32 ppm in the Refcoal. The sharp decrease in iron concentration confirms the fact that iron occurs predominantly in the inorganic component of the coal, as reported in the literature [4, 47, 49]. Iron has a low boron equivalent (7 x 10e-4), and the concentration obtained at the initial stage of purification is lower than 50 ppm, which is suitable for nuclear-grade graphite. Further purification is not very necessary with iron. The concentration of iron shows an increase in the coked Refcoal, chlorinated Refcoal and coked chlorinated Refcoal. This shows that the iron contamination was very high in relation to the overall purification.

Lithium: The concentration of lithium was lowered from 3 ppm in the coal to 0.2 ppm in the standard Refcoal. The high purification value shows that lithium occurs predominantly in the inorganic component of the coal. Using lithium as an indicator element, it appears that alkali metals occur in the inorganic component of the coal and are easily purified. The concentration of lithium shows a slight increase in the coked standard Refcoal at 600 ºC and 1 000 ºC and decreases to 0.1 ppm in the chlorinated Refcoal. In the coked chlorinated Refcoal the lithium concentration decreased to 0.04 at 600 ºC and increased slightly at 1 000 ºC. The chlorination method could therefore be used for lithium purification.

Nickel: The concentration of nickel increased from 4 ppm in the coal to 7 ppm in the standard Refcoal. Some of transition elements show this kind of behaviour. Using nickel and chromium as indicator elements, it appears that transition elements are not easily removed by precipitation and they appear to occur predominantly bound to the organic component of coal. The nickel concentration shows an increase in the coked samples at 600 ºC and 1 000 ºC. The concentration of nickel increases in chlorinated Refcoal and coke. This shows that nickel is not volatile at low temperatures.

Silicon: The silicon concentration was lowered from 7 752 ppm in the coal to 428 ppm in the standard Refcoal. The high purification shows that silicon occurs predominantly in the inorganic component of coal and is lowered by precipitation. The concentration of silicon shows an increase in the standard Refcoal coked at 600 ºC and 1 000 ºC, and also in the coked chlorinated Refcoal. The increase in concentration could be a result of contamination due to the many steps involved in purification and the silicate glass used during purification.

Conclusions:

Pyrolysis needs to be done at temperatures higher than 1 000 ºC since some elements form volatile halides at higher temperatures. The results from inductive coupled plasma optical emission spectroscopy (ICP-OES) are not consistent.

5.3.2 Trace element analysis with ICP-MS (microwave digestion method)

The discussion below is based on the results shown in Table 4.11. The concentrations of the elements B, Co, Eu, Gd, Li, Na, Ca, U, Th and Si are discussed as determined from coal B (see Table 4.11). The concentrations given are an average of at least two determinations as tabulated in Appendix 1, Table A1.2. The concentration of the elements in the coal, Refcoal, Refcoal treated with acid and chlorinated Refcoal are discussed. Coal B had different ash contents to coal A and it was used after coal A had been used up. Standard Refcoal is the untreated Refcoal precipitated with water, obtained only from extraction of coal B. The results obtained with all the methods are compared with those obtained from the standard Refcoal. The discussion below is based on coal B.

Boron: The concentration of boron was reduced from 9 ppm in the coal to 1.3 ppm in the standard Refcoal. This shows the different behaviour of boron compared with the analysis done on coal A with ICP-OES. Boron was easily washed out of the solution by precipitation. It is reported in the literature [11, 27, 49] that boron occurs predominantly in the organic part of coal and less frequently in the inorganic part.

With the high purification value achieved, it could be concluded that boron occurs just as frequently in the inorganic part of coal. The boron concentration was increased to 1.5 ppm in coked Refcoal as compared with the standard Refcoal. The slight increase might be due to the concentration of boron at high temperatures or because some of the volatiles were released during coking.

Boron in acid-treated Refcoal: The boron concentration was lowered to 0.8 ppm after the Refcoal had been treated with hydrofluoric (HF) acid. This acid decomposes the inorganic part of coal and therefore boron is predominantly associated with the organic part. The concentration of boron increases to 1.2 ppm in coked Refcoal treated with hydrochloric acid.

Boron in chlorinated Refcoal: The concentration of boron was lowered to 0.7 ppm after chlorination of Refcoal with chlorine gas. The concentration was lowered to 0.5 ppm in coked chlorinated Refcoal. The results show that boron forms volatile halide compounds and volatilises during coking or combustion. This supports what has been reported in the literature [8, 21]. The HCH Refcoal shows the same boron concentration, 0.7 ppm, as the chlorinated Refcoal. The concentration increased to 1.3 ppm in coked Refcoal chlorinated with HCH. The increase in concentration might be due to the volatiles released during coking. Chlorination with chlorine gas is considered to be the best method for boron purification, followed by HF and HCH.

Calcium: The concentration of calcium was lowered from 570 ppm in the coal to 82 ppm in the standard Refcoal. The leaching of calcium is high, which suggests that calcium is predominantly in inorganic association in coal and therefore it is easily separated from the organic component of coal. By using calcium as an indicator element for alkali earth metals, we can conclude that alkali earth metals are predominantly in inorganic association in coal. On the basis of this conclusion, alkali earth metals can be easily separated from the organic component of coal. This observation is consistent with those made in the literature [47, 49]. The calcium concentration increases to 165 ppm in a coke from the standard Refcoal.

Calcium in acid-treated Refcoal: The concentration of calcium was lowered to 35 ppm after treatment of Refcoal with HF. It was also lowered to 21 ppm in coke from the Refcoal treated with HF. The high purification achieved suggests that calcium is easily purified by use of HF. Hydrofluoric acid decomposes inorganics and therefore the decrease shows that calcium occurs predominantly in association with the inorganic part of coal.

Calcium in chlorinated Refcoal: After chlorination of Refcoal with chlorine gas, the concentration of calcium was lowered to 22 ppm. The calcium concentration increased to 54 ppm in a coke from Refcoal chlorinated with chlorine gas and increased to 45 ppm after treatment of Refcoal with HCH. It also increased in a coke from the Refcoal treated with HCH. This increase in concentration could be due to contamination from the furnace and the instruments used.

Cobalt: The cobalt concentration increased from 6 ppm in the coal to 6.5 ppm in the standard Refcoal. These results are directly opposed to those obtained with coal A. (The concentration of cobalt must be lower than 0.05 ppm in nuclear graphite.) The results further support the perception that cobalt is organically bound in coal and is not easily purified by precipitation only. The concentration of non-volatile elements increases when Refcoal is converted to coke. Contamination from the reagents and the steel reactor used for extraction might also be a factor causing the increase in concentration. The concentration increased to 9 ppm in the standard coke.

Cobalt in acid-treated Refcoal: The cobalt concentration was lowered to 5 ppm after treatment of Refcoal with HF, but increased to 6 ppm in a coke from HF acid-treated Refcoal. The increase might be due to concentration at high temperature.

Cobalt in chlorinated Refcoal: The concentration of cobalt decreased to 5 ppm after chlorination of Refcoal with chlorine gas, but increased to 6 ppm in coke from Refcoal chlorinated with chlorine gas. The concentration was found to be 6 ppm after treatment of Refcoal with HCH and increased to 8 ppm in coke from Refcoal treated with HCH. The hydrofluoric acid and chlorine gas methods seem to be the most suitable methods of the purification of cobalt. Further studies need to be done on cobalt purification.

Europium: The concentration of europium increased from 0.02 ppm in the coal to 0.2 ppm in the standard Refcoal and to 0.1 ppm in coked standard Refcoal. The low purification suggests that europium occurs predominantly in the organic part of the coal matrix, which is consistent with the literature reports [47, 49].

Europium in acid-treated Refcoal: The concentration of europium was lowered to 0.04 ppm after treatment of Refcoal with hydrofluoric acid. The europium concentration was lowered to 0.01 ppm in a coke from Refcoal treated with hydrofluoric acid.

Europium in chlorinated Refcoal: All the chlorination methods failed to lower the concentration of europium and no one method showed better purification of europium.

Gadolinium: The concentration of gadolinium increased from 0.1 ppm in the coal to 0.4 ppm in the standard Refcoal. Analytical error or instrument interference might be the cause of the increase in concentration. The concentration also increased in a the standard Refcoal coke to 0.7 ppm. The concentration increases in coke because some of the volatiles are removed.

Gadolinium in acid-treated Refcoal: The concentration of gadolinium increased to 0.3 ppm after treatment of Refcoal with hydrofluoric acid, but decreased to 0.02 ppm in a coke from Refcoal treated with hydrofluoric acid. Hydrofluoric acid treatment of Refcoal coke results in better purification than the other methods.

Gadolinium in chlorinated Refcoal: The gadolinium concentration was lowered to 0.1 ppm after chlorination with chlorine gas, but increased in a coke from chlorinated Refcoal. The concentration increased during chlorination with HCH methods, which shows that gadolinium did not react with chlorine. Only the hydrofluoric method shows a positive result on analysis.

Lithium: The concentration of lithium was lowered from 3.5 ppm in the coal to 0.3 ppm in the standard Refcoal. The high purification value shows that lithium occurs predominantly in the inorganic component of the coal. Using lithium as an indicator element, it appears that alkali metals occur in the inorganic component of the coal and are easily purified. The concentration of lithium increased to 1 ppm in coke from the standard Refcoal. The increase in lithium concentration might be due to the removal of volatiles during coking or because lithium becomes concentrated during coking.

Lithium in acid-treated Refcoal: The concentration of lithium was lowered to less than 0.1 ppm after treatment of Refcoal with hydrofluoric acid, but increased to 0.5 ppm in a coke from Refcoal treated with hydrofluoric acid. HF treatment is one of the best methods for the purification of lithium from coal. Hydrofluoric acid decomposes inorganics, which suggests that lithium is also associated with the inorganic part of coal.

Lithium in chlorinated Refcoal: The lithium concentration was lowered to 0.2 ppm in chlorinated Refcoal and also lowered to less than 0.1 ppm in a coke from chlorinated Refcoal. The purification was therefore better than with the chlorination method. The lithium concentration was lowered to 0.3 ppm after chlorination of Refcoal with HCH, but increased to 0.4 ppm in a coke from Refcoal chlorinated with HCH. The increase in concentration is probably the result of contamination as waste HCH was used.

Sodium: The sodium concentration increased from 272 ppm in the coal to 308 ppm in the standard Refcoal. The increase in sodium might be a result of sodium added during extraction. The concentration also increased to 384 ppm in a coke from the standard Refcoal.

Sodium in acid-treated Refcoal: The concentration of sodium was lowered to 10 ppm after treatment with hydrofluoric acid. The decrease in concentration suggests that sodium is associated with the inorganic part of the coal since hydrofluoric acid decomposes inorganics. The concentration of sodium increased to 18 ppm in a coke from Refcoal treated with hydrofluoric acid. This increase might be because sodium becomes concentrated at the coking temperature.

Sodium in chlorinated Refcoal: The concentration of sodium was lowered to less than 10 ppm after chlorination of Refcoal with chlorine gas and also in a coke from Refcoal chlorinated with chlorine gas. The concentration of sodium was lowered to 27 ppm after treatment with HCH, but increased to 77 ppm in a coke from Refcoal chlorinated with HCH. Chlorination with the chlorine gas method gives the best results for sodium purification.

Silicon: The silicon concentration was lowered from 14 450 ppm in the coal to 625 ppm in the standard Refcoal. The high purification shows that silicon is predominantly associated with the inorganic component of the coal and it could be lowered by precipitation. The concentration of silicon shows an increase in the standard Refcoal coke to 994 ppm compared with the standard coke. This increase in concentration could be a result of silicon becoming concentrated during coking or could have come from the tubes used for coking.

Silicon in acid-treated Refcoal: The silicon concentration was lowered to 101 ppm after treatment of Refcoal with hydrofluoric acid. Hydrofluoric acid decomposes inorganics, which supports the fact that silicon is predominantly associated with the inorganic fraction. The concentration increased to 195 ppm in a coke from Refcoal treated with hydrofluoric acid. Hydrofluoric acid is the best method for silicon purification.

Silicon in chlorinated Refcoal: The concentration of silicon was lowered to 368 ppm after chlorination of Refcoal with chlorine gas and further lowered to 260 ppm in a coke from a chlorinated Refcoal. The concentration of silicon increased to 830 ppm after treatment of Refcoal with HCH and to 1 125 ppm in a coke from Refcoal treated with HCH.

Thorium: The concentration of thorium increased from 0.01 ppm in the coal to 0.1 ppm in Refcoal. All the methods failed to give a better purification of thorium.

Uranium: Uranium occurs in small quantities in coal. The concentration of uranium remained the same at 1.1 ppm after precipitation. This suggests that uranium occurs predominantly in the organic part of the coal. All the methods failed to either purify or lower the concentration of uranium.

Conclusions:

Boron: Chlorination with chlorine gas is considered to be the best method for boron purification, followed by hydrofluoric acid and hexachlorocyclohehane.

Calcium: The lowest purification value was obtained by chlorination, followed by hydrofluoric acid treatment.

Cobalt: Neither acid treatment nor chlorination was able to purify cobalt to the expected level. Cobalt must be lower than 0.05 ppm in the coal used for nuclear-grade graphite. Therefore, further purification is necessary for cobalt.

Europium: All the methods failed to purify europium to the level expected for a nuclear-grade graphite. Europium has a high boron equivalent (4 x 10^{-1}), so further purification is required to bring its concentration down to less than 0.005 ppm.

Gadolinium: Chlorination may be a better method for the purification of gadolinium.

Lithium: Hydrofluoric acid and chlorine gas treatment are the best methods for lithium purification.

Sodium: Treatment with chlorine gas is the best method for the purification of sodium, followed by hydrofluoric acid.

Silicon: Hydrofluoric acid is the best acid to use for silicon purification.

Uranium and thorium: None of the methods works for uranium and thorium. However, these two elements occur in low quantities in coal. Since uranium has a low boron equivalent (2 x 10^{-4}), it does not pose a serious problem with respect to nuclear-grade graphite [4].

5.3.3 Trace element analysis with ICP-MS (fusion method)

The discussion below is based on the results shown in Table 4.12. The concentrations of the elements, Co, Eu, Gd, Li, Na and Si from coal B were analysed with ICP-MS instrumentation. The fusion method was used as the preparation method. Boron was not analysed by this method, because lithium borate was used as the flux during analysis. The concentrations of the elements in coal, Refcoal, acid-treated, chlorinated and ion-exchanged Refcoal and cokes are discussed. The concentrations given are an average of at least two determinations as tabulated in Appendix 1, Table A1.3. Coal B had different ash contents to coal A, it was used after coal A had been used up. Standard Refcoal is the untreated Refcoal, precipitated with water only, obtained from extraction of coal B. The results obtained with all the methods are compared with those obtained from the standard Refcoal. The discussion below is based on coal B:

Calcium: The concentration of calcium was lowered from 3 936 ppm in the coal to 111 ppm in the standard Refcoal. The leaching of calcium is high, which suggests that because calcium is predominantly in inorganic association in coal, it is easily separated from the organic component of coal. By using calcium as an indicator element for alkali earth metals, we can conclude that alkali earth metals are predominantly in inorganic association in coal. On the basis of this conclusion, alkali earth metals can be easily separated from the organic component of coal. This observation is consistent with those made in the literature [47, 49]. The calcium concentration increased to 150 ppm in a coke from the standard Refcoal.

Calcium in acid-treated Refcoal: The concentration of calcium was lowered to 35 ppm after treatment of Refcoal with hydrofluoric acid, but increased in the coke to more than that in the standard Refcoal. The concentration of calcium was lowered to 51 ppm after treatment of Refcoal with hydrofluoric acid, but increased to 73 ppm in coke from Refcoal treated with hydrofluoric acid. After the Refcoal had been treated with a mixture of hydrofluoric acid and hydrochloric acid, the concentration was lowered to 91 ppm. The concentration of calcium was again lowered to 53 ppm in a coke from Refcoal treated with the mixture of hydrofluoric acid and hydrochloric acid. It was also lowered to 50 ppm after treatment of Refcoal with ascorbic acid, but trebled in a coke from Refcoal treated with ascorbic acid. The increase in concentration could be due to contamination from the reagents and the furnace used. Hydrofluoric acid gives better purification than all the other acids.

Calcium in chlorinated Refcoal: After Refcoal had been chlorinated with chlorine gas, the concentration of calcium was lowered to 41 ppm. The calcium concentration increased to 48 ppm in a coke from Refcoal chlorinated with chlorine gas. It increased after treatment with chlorine gas and hydrofluoric acid and then lowered to 81 ppm. The calcium concentration was lowered to 20 ppm after treatment of Refcoal with HCH, but increased in a coke from the Refcoal treated with HCH. The increase in concentration could be due to loss of volatiles during coking.

Calcium in ion-exchange or complexed Refcoal: Some of the ion-exchange methods lower the concentration of calcium. After treatment of Refcoal with EDTA, the concentration of calcium was lowered to 29 ppm and increased to 98 ppm in a coke. The concentration of calcium was lowered to 5 ppm after treatment of Refcoal with sodium fluoride, but was very high in a coke from Refcoal treated with sodium fluoride. The concentration was lowered to 87 ppm after treatment of Refcoal with sodium sulphate, and was also lowered to 81 ppm in a coke from Refcoal treated with sodium sulphate. The concentration was lowered to 63 ppm after treatment with a mixture of sodium sulphate and sodium nitrate. The calcium concentration increases to 67 ppm in a coke from a treated Refcoal. All the other methods listed for ion-exchange in Table 4.12 were unable to lower or purify the calcium in the Refcoal. The increase in concentration after coking could be due to the loss of some volatiles.

Cobalt: The cobalt concentration increased from 6 ppm in the coal to 8 ppm in the standard Refcoal. The concentration of cobalt must be lower than 0.05 ppm in nuclear graphite. The results support the perception that cobalt is organically bound in coal [9, 11, 27] and is not easily purified by precipitation only. The steel reactor used for extraction might also have been a factor causing the increase in concentration. The concentration increased to 10 ppm in the standard coke. The microwave digestion method produced almost the same results as the fusion method, the difference between the two being a few insignificant figures.

Cobalt in acid-treated Refcoal: The cobalt concentration was lowered to 6 ppm after treatment of Refcoal with hydrochloric acid, but increased to 9 ppm in a coke from Refcoal treated with hydrofluoric acid. The increase might be due to concentration at high temperature and because the concentration increases in a non-volatile element from Refcoal to coke. The concentration of cobalt was lowered to 0.2 ppm after treatment of Refcoal with hydrofluoric acid, but increased to 1 ppm in coke from Refcoal treated with hydrofluoric acid. After treatment of Refcoal with a mixture of hydrofluoric acid and hydrochloric acid, the cobalt concentration was lowered to 6 ppm, and was lowered further to 2 ppm in a coke from Refcoal treated with a mixture of the two acids. Treatment of Refcoal with ascorbic acid was unable to lower the cobalt concentration in both Refcoal and coke. Hydrofluoric acid was found to be the best for the purification of cobalt with acid.

Cobalt in chlorinated Refcoal: The concentration of cobalt decreased to 6 ppm after chlorination of Refcoal with chlorine gas, but increased to 7 ppm in a coke from chlorinated Refcoal. The concentration of cobalt was lowered to less than 1 ppm after treatment of Refcoal with chlorine gas and hydrofluoric acid and was also less than 1 ppm in coke from treated Refcoal. The concentration of cobalt was lowered to 6 ppm after treatment of Refcoal with HCH, but increased to 13 ppm in a coke. Hydrochloric acid and a mixture of chlorine gas and hydrofluoric acid are the best methods for cobalt purification. These two methods produced the best results in this study for cobalt purification.

Cobalt in ion-exchange or complexed method: None of the methods was able to the lower cobalt concentration in both Refcoal and coke. The concentration of cobalt increases when ion-exchange methods are used.

Europium: The concentration of europium was lowered from 0.5 ppm in the coal to 0.2 ppm in the standard Refcoal and remained at 0.2 ppm in the standard coke. This low purification suggests that europium occurs predominantly in organic association in the coal matrix, which is consistent with the literature reports [47, 49].

Europium in acid-treated Refcoal: The concentration of europium was lowered to less than 0.05 ppm after treatment with hydrofluoric acid and hydrochloric acid. It also remained the same in coke. The europium concentration was lowered to 0.05 ppm after the treatment of Refcoal with a mixture of hydrofluoric acid and hydrochloric acid, but increased to 0.08 ppm in a coke from Refcoal treated with the mixture of acids. The concentration of europium was lowered to 0.1 ppm after the treatment of Refcoal with ascorbic acid, but increased to 0.2 ppm in coke from Refcoal treated with ascorbic acid.

Europium in chlorinated Refcoal: The concentration of europium was lowered to less than 0.05 ppm after chlorination of Refcoal with chlorine gas and after treatment of Refcoal with chlorine gas and hydrofluoric acid. The concentration remained the same in both the cokes from treated Refcoal. The europium concentration was lowered to 0.1 ppm after chlorination of Refcoal with HCH, but increased to 0.3 ppm in a coke from Refcoal treated with HCH.

Europium in ion-exchange or complexed Refcoal: Almost all the ion-exchange methods used were unable to lower the europium concentration, except in Refcoal treated with KCN and sodium fluoride, where the concentration was lowered to less than 0.05 ppm.

Gadolinium: The concentration of gadolinium was lowered from 3 ppm in the coal to 1 ppm in the standard Refcoal. The high purification value suggests that gadolinium occurs predominantly in inorganic association in the coal matrix. The concentration of gadolinium did not change after coking of the Refcoal. Factors such as loss of volatiles, concentration at high temperatures and instrument interference might have caused the increases in concentration.

Gadolinium in acid-treated Refcoal: The concentration of gadolinium was lowered to 0.1 ppm after treatment with hydrofluoric acid, and increased to 0.2 ppm in a coke from Refcoal treated with hydrofluoric acid. The concentration was lowered to less than 0.05 ppm after treatment with hydrofluoric acid, but increased to 0.2 ppm in a coke from Refcoal treated with hydrofluoric acid. After treatment of Refcoal with chlorine gas and hydrofluoric acid, the concentration was lowered to 0.3 ppm and to 0.4 ppm in a coke from treated Refcoal. The concentration of gadolinium was lowered to 0.7 ppm after treatment with ascorbic acid but increased to 1 ppm in coke from the Refcoal treated with ascorbic acid. Hydrochloric acid and hydrofluoric acid are the best acids for the purification of gadolinium. The high leaching after hydrofluoric acid treatment of Refcoal suggests that gadolinium occurs predominantly associated with the inorganic component in coal.

Gadolinium in chlorinated Refcoal: The concentration of gadolinium was lowered to less than 0.05 ppm after chlorination of Refcoal with chlorine gas, but increased to 0.2 ppm in a coke from Refcoal chlorinated with chlorine gas. This shows that the gadolinium reacted with the chlorine. After treatment with chlorine gas and hydrofluoric acid, the concentration of gadolinium was lowered to 0.2 ppm and also remained at 0.2 ppm in coke from the treated Refcoal. The concentration of gadolinium was lowered to 0.7 ppm after chlorination of Refcoal with HCH, but increased to 2 ppm in a coke from Refcoal chlorinated with HCH. The increase after coking might be a result of concentration at high temperatures.

Gadolinium in ion-exchange or complexed Refcoal: Almost all the ion-exchange methods were unable to lower the gadolinium concentration. Only EDTA showed a better purification in the ion-exchange methods. The concentration was lowered to 0.2 ppm after treatment of Refcoal with EDTA, but increased to 0.4 ppm in a coke from Refcoal treated with EDTA. The purification results for the other methods are shown in Table 4.12.

Treatment with hydrochloric acid, hydrofluoric acid, chlorine gas, a mixture of chlorine and hydrofluoric acid, and EDTA could be the best methods for gadolinium. These methods showed positive results and if they could be applied with the necessary precautions and modifications, it might be possible to lower the gadolinium concentration to less than 0.005 ppm.

Lithium: The concentration of lithium was lowered from 6 ppm in the coal to 0.5 ppm in the standard Refcoal. The high purification value shows that lithium occurs predominantly in association with the inorganic component of the coal [9, 11, 27]. By using lithium as an indicator element, we can conclude that alkali metals occur in association with the inorganic component of the coal and are easily purified. The concentration of lithium increased to 1 ppm in the standard coke compared with the concentration in the standard Refcoal. The increase in concentration might be caused by a loss of volatiles and by the concentration of lithium during coking.

Lithium in acid-treated Refcoal: The concentration of lithium was lowered to less than 0.4 ppm after treatment of Refcoal with hydrofluoric acid, but increased by 0.2 ppm in a coke from Refcoal treated with hydrofluoric acid. The concentration was lowered to less than 0.1 ppm after treatment of Refcoal with a mixture of hydrofluoric acid and hydrochloric acid and remained the same in coked treated Refcoal. A mixture of hydrofluoric acid and hydrochloric acid is the best method for the purification of lithium from coal.

Lithium in chlorinated Refcoal: The lithium concentration was increased to 0.7 ppm after chlorination of Refcoal with chlorine gas, but was lowered to 0.2 ppm in a coke from a Refcoal treated with chlorine gas. The lithium concentration was lowered to 0.4 ppm after Refcoal had been chlorinated with HCH.

Lithium in ion-exchange or complexed Refcoal: Almost all the ion-exchange methods were unable to lower the concentration of lithium in both Refcoal and coke, except for the sodium fluoride method. The lithium concentration was lowered to 0.06 ppm after treatment with sodium fluoride and increased to 1 ppm in coke from the Refcoal treated with sodium fluoride.

A mixture of hydrofluoric acid and hydrochloric acid method gave the best results for lithium purification in this study compared with the other purification methods tested.

Sodium: The sodium concentration was lowered from 434 ppm in the coal to 363 ppm in the standard Refcoal. The smaller decrease in sodium concentration might be a result of the addition of sodium during extraction. The concentration also increased to 533 ppm in the standard coke and this could be due to a loss of volatiles during coking.

Sodium in acid-treated Refcoal: The concentration of sodium was lowered to 15 ppm after treatment of Refcoal with hydrochloric acid and was found to be 33 ppm in a coke from Refcoal treated with hydrochloric acid. The concentration of sodium was lowered to 2 ppm after treatment of Refcoal with hydrofluoric acid and increased to 7 ppm in coke from Refcoal treated with hydrofluoric acid. The high leaching after purification of Refcoal with hydrofluoric acid suggests that sodium is predominantly associated with the organic fraction in coal. The increase in sodium concentration in coke compared with Refcoal could be due to coking at high temperature, which causes the elements to become concentrated. The sodium concentration was lowered to 6 ppm in a Refcoal treated with a mixture of hydrofluoric acid and hydrochloric acid, but increased to 9 ppm in a coke from Refcoal treated with the same mixture. Ascorbic acid lowered the sodium concentration to 30 ppm in Refcoal. The concentration of sodium was 61 ppm in a coke from Refcoal treated with ascorbic acid. Hydrofluoric acid was found to be the best method for the purification of sodium in Refcoal with acids.

Sodium in chlorinated Refcoal: The concentration of sodium was lowered to 33 ppm after chlorination of Refcoal with chlorine gas but increased to 39 ppm in a coke from Refcoal chlorinated with chlorine gas. The concentration was lowered to 3 ppm in Refcoal chlorinated with hydrofluoric acid, but rose to 26 ppm after the treated

Refcoal had been coked. The concentration of sodium was lowered to 46 ppm in a Refcoal treated with HCH but increased to 106 ppm in coke from HCH-treated Refcoal. The use of a combination of chlorine gas and hydrofluoric acid gives the best purification for sodium.

Sodium in ion-exchange or complexed Refcoal: Almost all the methods used for this stage of purification showed lower and no purification of sodium, except for the Refcoal treated with KCN, EDTA, ammonia and ice. After treatment of Refcoal with KCN, the concentration of sodium was lowered to 67 ppm. The concentration increased to 86 ppm in a coke from Refcoal treated with KCN. The concentration was lowered to 78 ppm after treatment of Refcoal with EDTA, but increased to 126 ppm in a coke from Refcoal treated with EDTA. The concentration of sodium was lowered to 29 ppm in Refcoal treated with ammonia solution and was also lowered to 27 ppm in a coke from Refcoal treated with ammonia solution. Ammonia solution shows better purification of sodium in the ion-exchange or complexed method. The results of treatment with other reagents are shown in Table 4.12.

Three methods show better results for sodium purification, i.e. the use of hydrofluoric acid, a mixture of hydrofluoric acid and hydrochloric acid, and ammonia solution.

Silicon: The silicon concentration was lowered from 26 008 ppm in coal to 906 ppm in the standard Refcoal. This high purification shows that silicon is predominantly associated with the inorganic component of coal and it could be lowered by precipitation. The concentration of silicon showed an increase in the standard Refcoal coke to 1 282 ppm. This increase could be a result of silicon becoming concentrated during coking and could be due to the silicate glass used.

Silicon in acid-treated Refcoal: The silicon concentration was increased to 930 ppm after treatment with hydrochloric acid and also increased to 2 063 ppm in a coke from Refcoal treated with hydrochloric acid. The concentration of silicon was lowered to 10 ppm after treatment with hydrofluoric acid. The high purification with hydrofluoric acid shows that silicon occurs predominantly in association with the inorganic fraction in coal. The concentration increased to 83 ppm in a coke from Refcoal treated with hydrofluoric acid. The concentration of silicon was lowered to 511 ppm after treatment with a mixture of hydrofluoric acid and hydrochloric acid and increased to

602 ppm in a coke from Refcoal treated with the mixture of acids. Ascorbic acid was unable to lower the concentration of silicon. Hydrofluoric acid was found to be the best for silicon purification.

Silicon in chlorinated Refcoal: The concentration of silicon was lowered to 819 ppm after Refcoal had been chlorinated with chlorine gas, but increased to 932 ppm in a coke from Refcoal chlorinated with chlorine gas. The concentration was lowered to 21 ppm after treatment with chlorine gas and hydrofluoric acid, but increased to 1 094 ppm in a coke from the Refcoal treated in this way. The concentration of silicon was lowered to 817 ppm in Refcoal treated with hydrochloric acid, but increased to 2 217 ppm in a coke from Refcoal treated with hydrochloric acid. The increase after coking might be due to contamination from the silicon tube used at high temperature.

Silicon in ion-exchange or complexed Refcoal: Almost all the treatments were unable to lower the concentration of silicon. The silicon concentration was only lowered after treatment with sodium fluoride (NaF). The detailed results are given in Table 4.12.

Hydrofluoric acid treatment is the only method that gives high purification.

Thorium: The concentration of thorium was lowered from 5 ppm in the coal to 2 ppm in Refcoal. The concentration increased to 4 ppm in a coke from the standard Refcoal. The lower purification shows that thorium is predominantly in organic association in coal.

Thorium in acid-treated Refcoal: The concentration of thorium was lowered to 0.1 ppm after treatment of Refcoal with hydrochloric acid, but increased to 0.2 ppm in a coke from Refcoal treated with hydrochloric acid. The concentration was lowered to less than 0.05 ppm after treatment of Refcoal with hydrofluoric acid and also increased to 0.4 ppm in a coke from Refcoal treated with hydrofluoric acid. The concentration was lowered to 1.2 ppm after treatment with a mixture of hydrofluoric acid and hydrochloric acid, but increased to 1.4 ppm in a coke from Refcoal treated with the mixture of acids. Ascorbic acid was unable to lower the thorium concentration. A mixture of hydrofluoric acid and hydrochloric acid is the best method for thorium purification.

Thorium in chlorinated Refcoal: The concentration of thorium was lowered to less than 0.05 ppm after chlorination of Refcoal with chlorine gas, but increased to 1 ppm in a coke from chlorinated Refcoal. Hydrochloric acid on its own and a mixture of chlorine gas and hydrofluoric acid were unable to purify thorium.

Thorium in ion-exchange or complexed Refcoal: Only EDTA was able to lower the concentration of thorium in Refcoal. After treatment of Refcoal with EDTA, the thorium concentration was lowered to 1 ppm, but it increased to 2 ppm in a coke from Refcoal treated with EDTA. All the other ion-exchange methods were unable to purify thorium in Refcoal.

Uranium: The concentration of uranium was lowered from 3 ppm in the coal to 1 ppm in Refcoal. The concentration increased to 2 ppm in a coke from the standard Refcoal. The low purification suggests that uranium occurs predominantly in organic association in the coal.

Uranium in acid-treated Refcoal: The concentration of uranium was lowered to 1 ppm after treatment of Refcoal with hydrofluoric acid and remained at 1 ppm in a coke from a Refcoal treated with hydrofluoric acid. The concentration was lowered to less than 0.05 ppm after treatment with hydrofluoric acid and stayed the same at 0.05 ppm in a coke from Refcoal treated with hydrofluoric acid. The concentration of uranium was lowered to 0.3 ppm after treatment of Refcoal with a mixture of hydrofluoric acid and hydrochloric acid. The uranium concentration remained unchanged at 0.3 ppm in a coke from Refcoal treated with the mixture of acids. Ascorbic acid was unable to lower the uranium concentration. Hydrofluoric acid is the best acid for uranium purification.

Uranium in chlorinated Refcoal: Chlorination of Refcoal with chlorine gas lowers the uranium concentration to less than 0.05 ppm. The concentration of uranium increased to 0.1 ppm in a coke from Refcoal chlorinated with chlorine gas. The concentration was lowered to 1 ppm in a Refcoal treated with both chlorine gas and hydrofluoric acid, but rose in a coke from a Refcoal treated in this way. Hydrochloric acid was unable to lower the uranium concentration.

Uranium in ion-exchange or complexed Refcoal: Only sodium fluoride treatment of Refcoal lowered the uranium concentration to 0.2 ppm. All the other ion-exchange or complexed methods listed in Table 4.12 were unable to lower the uranium concentration. The increase in concentration when this method is applied might be due to interference from within the instrumentation.

Hydrofluoric method was found to be the best method for uranium purification.

***Conclusions*:**

Calcium: Acid treatment and chlorination give better calcium purification.

Cobalt: Acid treatment with hydrofluoric acid and chlorination with both chlorine gas and fluorine were found to be the best methods for cobalt purification. These methods lower the cobalt concentration to less than 1 ppm. With some modification of these methods it may be possible to lower the cobalt concentration to less than 0.05 ppm.

Europium: The acid method (a mixture of hydrochloric acid and hydrofluoric acid), chlorination (chlorine gas and a mixture of chlorine gas and hydrofluoric acid) and the ion-exchange method (EDTA and sodium fluoride) lowered the europium concentration to less than 0.05 ppm. These could be the best methods for europium in further studies.

Gadolinium: The acid method lowers the concentration of gadolinium to less than 0.5 ppm. Hydrofluoric acid shows better results than all the other acids. The chlorination method is also one of the best methods for gadolinium purification. EDTA and sodium fluoride also show positive purification of gadolinium as compared with the other ion-exchange methods.

Lithium: Treatment of Refcoal with a mixture of hydrofluoric acid and hydrochloric acid lowers the lithium concentration to less than 1 ppm.

Sodium: Both the acid treatment and chlorination methods manage to reduce concentration of sodium marginally. A few of the ion-exchange methods lower the concentration, i.e. potassium cyanide, EDTA and ammonia solution treatment.

Silicon: Hydrofluoric acid is the best method for silicon purification.

Thorium and uranium: Hydrofluoric acid and chlorine gas are the only two treatments that lower the uranium and thorium concentrations to less than 0.05 ppm.

CHAPTER 6 GENERAL CONCLUSIONS

The methods of analysis give different results. The results obtained with ICP-MS differ from those obtained with ICP-OES. The sensitivity of the two types of instrumentation varies with the elements. The results obtained from the two preparation methods, i.e. microwave digestion and fusion, were also not the same, with the fusion results being lower than microwave digestion results.

The microwave digestion method works well for major and trace elements. The fusion method did not work very well for rare-earth elements because they do not dissolve in acids. The microwave digestion method works very well for rare-earth elements. The fusion method also works for major and trace elements. Analysis of boron was not possible with the fusion method because lithium metaborate was used as the flux.

Specific methods need to be applied for specific elements because some methods are sensitive to particular elements while others are not. The mode of occurrence in coal of the elements affects the purification and also the analysis. Some elements tend to occur in association with both the organic and inorganic parts of coal. Most of the elements occur in association with different minerals in coal, which makes their extraction complex.

The methods of purification show different degrees of success. Certain methods need to be applied for a specific group of elements, or for rare-earth minerals, metalloids, alkalis or trace elements. Water precipitation reduces the concentration of most of the elements in the Refcoal. Hydrofluoric acid works best for the purification of calcium, europium, sodium and thorium. Hydrochloric acid gives the best results for the purification of boron, calcium, cobalt, lithium, europium, gadolinium, sodium, silicon, uranium and thorium. A mixture of hydrofluoric and hydrochloric acid works for the purification of europium, lithium and sodium. Ascorbic acid works only for the purification of sodium.

Chlorination with chlorine gas works for the purification of boron, calcium, europium, gadolinium, sodium, uranium and silicon. Chlorination with HCH works for the purification of calcium and sodium. A combination chlorine and hydrofluoric acid works for the purification of cobalt, europium, sodium and silicon.

Only KCN, EDTA and ammonia solution show better purification in the ion-exchange or complexed methods; the rest give poor results when compared with other methods. Major contamination problems occur when the Refcoal is treated by ion exchange or is complexed. However, KCN works for sodium purification, EDTA for europium and sodium purification, and ammonia solution for sodium purification. Coking of Refcoal was done with the aim of volatilising some of the elements. In some cases the concentration rose instead of being reduced. The concentration of non-volatile elements increased during the conversion of Refcoal to coke at high temperature. The coking was done at 1 000 ºC, which is still below the boiling point of some undesirable elements. It may be best to use higher temperatures, above 2 000 ºC, for volatilising the undesirable elements. No method purifies cobalt to the expected level – this still remains a problem.

The best option may be to modify these methods in order to prepare nuclear-grade carbon graphite. The chlorination, hydrofluoric acid and hydrochloric acid methods show better purification for most of the elements and these are the methods that need to be modified. Specific instrumentation is needed for such studies because some instrumentation is particularly good with specific elements. On the other hand, methods such as X-ray diffraction (XRD), X-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA) are sensitive to yet other elements and could be able to give the best estimates for these elements.

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APPENDICES

Appendix 1

Table A1.1. Concentration of trace elements determined by ICP-OES (ppm)

Samples	Al	B	Ca	Co	Cu	Cr	Fe	Li	Mg	Mn	Ni	Si
Coal	5072.3	9.6	1839	4.15	2.1	6.6	1303.9	2.95	713	20.8	4	7 752
	4978.7	9.3	1800	3.99	1.9	5.9	1268.9	3.1	711	19.7	3.5	7633.6
Average	**5025.5**	**9.5**	**1819**	**4.1**	**2**	**6.25**	**1286**	**3**	**712**	**20.2**	**3.8**	**7693**
Standard Refcoal	418.05	6.3	86.95	2.6	0	8.5	31.3	0.15	16.7	0.3	7.05	428.55
	407.8	6	85.91	2.5	0.1	7.8	30.8	0.14	15.6	0.2	5.99	399.6
Average	**412.93**	**6.1**	**86.4**	**2.6**	**0.1**	**8.15**	**31.05**	**0.1**	**16**	**0.25**	**6.5**	**414.1**
Coke @ 600 °C	4608.25	7.9	120.5	5.5	-2.9	23.9	115.3	0.5	122	1.25	18.8	1276.2
	4588.17	7	122.6	4.9	2.5	23	110.6	0.6	121	1.33	17.9	1135.6
Average	**4598.2**	**7.4**	**122**	**5.2**	**-0**	**23.4**	**113**	**0.6**	**122**	**1.29**	**18**	**1206**
Coke @ 1 000 °C	13436.5	13	134	5.75	0.35	35.8	140.45	0.65	253	3.15	18.3	1720.8
	12277.6	13	129.7	5.43	0.41	33.8	139.6	0.56	250	2.98	16.3	1564.8
Average	**12857**	**13**	**132**	**5.6**	**0.4**	**34.8**	**140**	**0.6**	**251**	**3.07**	**17**	**1643**
Cl_2 Refcoal	250.55	4.9	58.05	2.25	2.25	9.55	83.9	0.1	8.3	0.7	4.3	534.2
	249.87	4.7	57.88	2.03	2.34	8.37	79.7	0.1	7.85	0.6	3.78	489.6
Average	**250.21**	**4.8**	**58**	**2.1**	**2.3**	**8.96**	**81.8**	**0.1**	**8.1**	**0.65**	**4**	**511.9**
Cl_2 Coke @ 600 °C	4166.9	8.8	88.05	4.05	-2.8	19.6	66.3	0.04	91.2	0.85	15.8	1413.1
	4211.3	9.1	87.91	3.99	2.56	18.7	65.5	0.03	90.3	0.7	16.1	1345.9
Average	**4189.1**	**9**	**88**	**4**	**-0**	**19.1**	**65.9**	**0**	**91**	**0.78**	**16**	**1379**
Cl_2 Coke @ 1 000 °C	16117.5	9.6	88.25	3.4	-4	44.5	91.25	0.65	437	1	14.7	2673.8
	15279.9	9.4	88.7	2.98	3.7	43.9	90.5	0.7	436	0.9	13.6	2559.6
Average	**15699**	**9.5**	**88.5**	**3.2**	**-0**	**44.2**	**90.88**	**0.7**	**437**	**0.95**	**14**	**2617**

Table A1.2. Concentration of trace elements determined by ICP-MS (microwave digestion) (ppm)

Sample	**B**	**Ca**	**Co**	**Eu**	**Gd**	**Li**	**Na**	**Si**	**U**	**Th**
Coal	9.05	569.97	6.33	0.02	0.10	3.94	272.51	14450.57	1.18	0.01
	9.10	570.01	5.81	0.01	0.09	3.01	271.00	14448.99	0.98	0.01
Average	**9.1**	**570**	**6.1**	**0.02**	**0.10**	**3.5**	**272**	**14450**	**1.1**	**0.01**
Standard	1.31		6.49	0.22	0.38	0.25	308.18	625.08		
Refcoal		82.18							1.22	0.06
	1.20	81.71	5.77	0.16	0.41	0.31	307.44	624.91	0.99	0.11
Average	**1.3**	**82**	**6.1**	**0.2**	**0.40**	**0.3**	**308**	**625**	**1.1**	**0.09**
Standard coke	1.46	164.06	9.19	0.13	0.79	0.58	384.46	994.09	1.75	0.15
	1.51	165.00	8.82	0.05	0.67	0.59	383.71	993.61	1.67	0.21
Average	**1.5**	**165**	**9.0**	**0.1**	**0.7**	**0.6**	**384**	**994**	**1.7**	**0.2**
HF Refcoal	0.79	35.39	4.57	0.04	0.25	<0.1	10.00	101.38	0.82	0.04
	0.90	34.60	4.49	0.03	0.31	<0.1	9.73	100.50	0.75	0.04
Average	**0.8**	**35**	**4.5**	**0.04**	**0.3**	**<0.1**	**10**	**101**	**0.8**	**0.04**
HF coke	1.05	21.37	5.98	0.01	0.02	0.45	18.02	194.80	1.04	0.02
	1.30	20.91	5.50	0.01	0.02	0.47	17.50	195.09	1.10	0.01
Average	**1.2**	**21**	**6**	**0.01**	**0.02**	**0.5**	**18**	**195**	**1.1**	**0.02**
Cl_2 Refcoal	0.73	21.58	5.21	0.02	0.09	0.23	<10	368.45	1.16	0.01
	0.69	20.99	4.70	0.02	0.08	0.25	<10	367.61	0.91	0.01
Average	**0.7**	**21**	**5**	**0.02**	**0.1**	**0.2**	**<10**	**368**	**1.0**	**0.01**
Cl_2 coke	0.49	53.92	5.95	0.09	0.51	<0.1	<10	259.65	1.07	0.08
	0.45	53.09	5.50	0.10	0.45	<0.1	<10	260.10	0.9	0.07
Average	**0.47**	**54**	**5.73**	**0.10**	**0.48**	**<10**	**<10**	**260**	**1.0**	**0.08**
HCH Refcoal	0.75	44.74	5.81	0.13	0.75	0.26	26.91	829.28	1.34	0.14
	0.69	45.43	6.42	0.14	0.81	0.31	26.52	830.01	0.91	0.11
Average	**0.7**	**45**	**6.1**	**0.1**	**0.8**	**0.3**	**27**	**830**	**1.13**	**0.1**
HCH coke	1.28	81.76	8.44	0.14	0.80	0.39	76.67	1124.88	1.91	0.15
	0.91	82.19	7.99	0.09	1.00	0.41	77.21	1125.12	0.99	0.1
Average	**1.1**	**82**	**8**	**0.1**	**0.9**	**0.4**	**77**	**1125**	**1.4**	**0.1**

Table A1.3. Concentration of trace elements determined by ICP-MS (ppm) [fusion method]

Sample	**Ca**	**Co**	**Eu**	**Gd**	**Li**	**Na**	**Si**	**U**	**Th**
Coal	3992.76	6.55	0.45	2.35	5.66	436.89	26479.37	2.72	4.78
	3993.41	7.23	0.51	2.14	6.1	437.11	26478.92	3.24	5.31
Average	**3993.09**	**6.89**	**0.48**	**2.25**	**5.88**	**437**	**26479.1**	**2.98**	**5.05**
Standard Refcoal	112.05	7.14	0.15	0.89	0.47	366.69	912.85	1.38	2.48
	109.92	6.99	0.19	1.01	0.51	359.91	899.85	0.93	1.99
	110.99	**7.07**	**0.17**	**0.95**	**0.49**	**363.3**	**906.35**	**1.16**	**2.235**
Standard coke	150.83	9.92	0.22	1.24	1.09	566.66	1328.16	1.92	3.5
	149.97	10.2	0.24	0.99	0.99	498.96	1236.25	2.11	4.1
Average	**150.4**	**10.06**	**0.23**	**1.12**	**1.09**	**532.81**	**1282.21**	**2.02**	**3.8**
Acid-treated									
	Ca	Co	Eu	Gd	Li	Na	Si	U	Th
HCl Refcoal	34.67	5.72	<0.05	0.09	0.41	15.12	930.85	0.76	0.09
	35.42	6.14	<0.05	0.14	0.35	14.94	889.36	1.31	0.08
Average	**35.05**	**5.93**	**<0.05**	**0.12**	**0.38**	**15.03**	**910.11**	**1.04**	**0.09**
HCl coke	164.72	9.34	<0.05	0.17	0.62	33.76	2102.03	1.3	0.19
	165.43	8.72	<0.05	0.24	0.59	32.89	2023.05	1.4	0.15
Average	**165.08**	**9.03**	**<0.05**	**0.21**	**0.61**	**33.33**	**2062.54**	**1.35**	**0.17**
HF Refcoal	50.81	0.24	<0.05	<0.05	-	2.4	10.26	<0.05	<0.05
	51.45	0.18	<0.05	<0.05	-	1.92	9.73	<0.05	<0.05
Average	**51.13**	**0.21**	**<0.05**	**<0.05**	-	**2.16**	**9.995**	**<0.05**	**<0.05**
HF coke	73.31	1.08	<0.05	0.15	-	7.54	82.84	<0.05	0.4
	72.94	0.91	<0.05	0.23	-	6.85	83.46	<0.05	0.37
Average	**73.13**	**1.00**	**<0.05**	**0.19**	-	**7.20**	**83.15**	**<0.05**	**0.39**
HF + HCl Refcoal	90.68	5.55	0.05	0.34	<0.1	5.6	522.42	0.32	1.36
	91.36	6.23	0.11	0.25	<0.1	5.52	499.24	0.25	0.98
Average	**91.02**	**5.89**	**0.08**	**0.30**	**<0.1**	**5.56**	**510.83**	**0.29**	**1.17**
HF + HCl coke	52.36	2.39	0.06	0.4	<0.1	9.48	634.14	0.34	1.58
	53.4	2.44	0.11	0.35	<0.1	8.91	570.52	0.26	1.2
Average	**52.88**	**2.42**	**0.09**	**0.38**	**<0.1**	**9.20**	**602.33**	**0.3**	**1.39**
Ascorbic acid Refcoal	49.6	6.66	0.13	0.69	-	29.94	1137.51	1.66	2.93
	50.33	7.24	0.14	0.71	-	30.1	1087.43	2.34	3.36
Average	**49.97**	**6.95**	**0.14**	**0.7**	-	**30.02**	**1112.47**	**2**	**3.15**
Ascorbic acid coke	184.71	11.14	0.22	1.14	-	60.85	2143.17	2.83	4.93
	185.37	10.87	0.15	1.34	-	61.41	1958.67	3.45	5.34
Average	**185.04**	**11.01**	**0.19**	**1.24**	-	**61.13**	**2050.92**	**3.14**	**5.135**

Sample	**Ca**	**Co**	**Eu**	**Gd**	**Li**	**Na**	**Si**	**U**	**Th**
Chlorinated Refcoal									
Cl_2 Refcoal	42.89	5.63	<0.05	<0.05	0.69	33.43	848.95	<0.05	<0.05
	39.67	6.02	<0.05	<0.05	0.71	32.97	789.76	<0.05	<0.05
Average	**41.28**	**5.83**	**<0.05**	**<0.05**	**0.7**	**33.2**	**819.36**	**<0.05**	**<0.05**
Cl_2 coke	48.12	6.67	<0.05	0.22	0.23	39.01	975.91	0.09	0.83
	46.95	7.41	<0.05	0.16	0.24	38.72	887.61	0.1	0.76
Average	**47.54**	**7.04**	**<0.05**	**0.19**	**0.24**	**38.87**	**931.76**	**0.10**	**0.80**

Table A1.3. (continued) Concentration of trace elements determined by ICP-MS (fusion method) (ppm)

Sample	**Ca**	**Co**	**Eu**	**Gd**	**Li**	**Na**	**Si**	**U**	**Th**
Chlorinated Refcoal									
Cl_2+HF Refcoal	296.73	<1.00	<0.05	0.17	-	2.81	22.76	1.08	2.06
	289.06	<1.00	<0.05	0.21	-	2.57	19.93	0.91	1.92
Average	**292.90**	**<1.00**	**<0.05**	**0.19**	-	**2.69**	**21.345**	**0.995**	**1.99**
Cl_2+HF coke	82.49	<1.00	<0.05	0.19	-	25.82	1158.71	1.25	2.37
	79.56	<1.00	<0.05	0.21	-	26.31	1028.39	0.98	1.95
Average	**81.03**	**<1.00**	**<0.05**	**0.2**	-	**26.07**	**1093.55**	**1.115**	**2.16**
HCH Refcoal	21.99	5.56	0.13	0.73	0.42	46.32	868.06	1.53	2.27
	18.67	6.01	0.14	0.65	0.38	45.83	766.15	1.61	2.01
Average	**20.33**	**5.79**	**0.14**	**0.69**	**0.4**	**46.08**	**817.11**	**1.57**	**2.14**
HCH coke	123.92	13.01	0.31	1.75	-	109.86	2238.39	3.61	5.34
	119.66	12.99	0.29	1.63	-	101.19	2196.41	4.01	4.74
Average	**121.79**	**13**	**0.3**	**1.69**	-	**105.53**	**2217.4**	**3.81**	**5.04**
Ion-exchange or complexed Refcoal									
	Ca	Co	Eu	Gd	Li	Na	Si	U	Th
Starch Refcoal	172.8	9.99	0.22	1.26	-	618.52	1205.86	2.13	3.66
	166.7	8.76	0.17	1.15	-	598.23	1136.49	1.96	3.45
Average	**169.75**	**9.38**	**0.20**	**1.21**	-	**608.38**	**1171.18**	**2.05**	**3.56**
Starch coke Refcoal	243.06	13.65	0.31	1.72	-	550.57	2038.36	2.79	4.96
	230.33	12.02	0.29	1.67	-	501.85	1879.52	2.65	4.61
Average	**236.70**	**12.84**	**0.30**	**1.70**	-	**526.21**	**1958.94**	**2.72**	**4.79**
Methanol Refcoal	245.18	10.31	0.24	1.34	-	223.45	1355.78	2.03	3.77
	237.31	9.65	0.24	1.31	-	201.62	1235.44	1.93	3.52
Average	**241.25**	**9.98**	**0.24**	**1.33**	-	**212.54**	**1295.61**	**1.98**	**3.65**
Methanol coke Refcoal	291.91	19.53	0.34	1.91	-	354.02	2149.12	3.02	5.44

Sample	Ca	Co	Eu	Gd	Li	Na	Si	U	Th
	290.72	18.53	0.27	1.76	-	344.67	1989.85	2.93	5.01
Average	**291.32**	**19.03**	**0.31**	**1.84**	-	**349.35**	**2069.49**	**2.98**	**5.23**
KCN Refcoal	151.41	8.22	0.22	1.27	0.61	67.28	1351.98	1.87	3.58
	149.72	7.51	0.21	1.53	0.59	66.95	1321.67	1.63	3.71
Average	**150.57**	**7.87**	**0.22**	**1.40**	**0.60**	**67.12**	**1336.83**	**1.75**	**3.65**
KCN coke Refcoal	148.92	10.4	0.27	1.54	5.84	85.62	1735.15	2.22	4.3
	149.37	9.85	0.25	2.11	6.31	84.96	1733.92	1.94	3.62
Average	**149.15**	**10.13**	**0.26**	**1.83**	**6.08**	**85.29**	**1734.54**	**2.08**	**3.96**
EDTA Refcoal	29.44	7.22	<0.05	0.22	1.17	77.99	1117.03	1.38	0.88
	28.51	6.72	<0.05	0.19	1.21	78.52	1116.83	1.27	0.76
Average	**28.975**	**6.97**	**<0.05**	**0.205**	**1.19**	**78.255**	**1116.93**	**1.325**	**0.82**
EDTA coke Refcoal	98.48	11.82	0.08	0.39	0.83	125.81	2060.74	2.43	1.59
	97.51	10.71	0.13	0.42	1.13	126.07	2058.52	1.73	2.1
Average	**98.00**	**11.27**	**0.105**	**0.405**	**0.98**	**125.94**	**2059.63**	**2.08**	**1.85**
NaF Refcoal	5.42	1.28	<0.05	0.15	0.06	2856.33	330.88	0.22	0.4
	4.52	1.36	<0.05	0.21	0.12	2854.55	331.52	0.21	0.5
Average	**4.97**	**1.32**	**<0.05**	**0.18**	**0.09**	**2855.44**	**331.2**	**0.22**	**0.45**
NaF coke Refcoal	265.94	13.12	0.31	1.7	0.67	14024.42	2054.91	2.58	4.66
	266.51	12.56	0.31	1.65	0.58	14124.31	2124.2	3.11	5.21
Average	**266.23**	**12.84**	**0.31**	**1.68**	**0.63**	**14074.37**	**2089.56**	**2.85**	**4.94**

Table A1.4 (continued) Concentration of trace elements determined by ICP-MS (ppm) [fusion method]

Sample	Ca	Co	Eu	Gd	Li	Na	Si	U	Th
Ion-exchange or complexed Refcoal									
NH_3 Refcoal	90.51	8.7	0.19	1.14	0.55	28.83	1895.08	1.71	3.06
	89.59	9.22	0.22	1.21	0.62	29.51	1901.34	2.3	2.96
Average	**90.05**	**8.96**	**0.21**	**1.18**	**0.59**	**29.17**	**1898.21**	**2.01**	**3.01**
NH_3 coke Refcoal	58.5	8.71	0.18	0.99	1.35	27.65	1161.87	1.55	2.82
	57.65	7.96	0.21	1.22	1.4	26.99	1163.2	2.34	3.52
Average	**58.08**	**8.34**	**0.20**	**1.11**	**1.38**	**27.32**	**1162.54**	**1.95**	**3.17**
Na_2SO_3 Refcoal	87.46	10	0.23	1.27	0.71	3284.76	1766.02	2.14	3.89
	86.21	9.9	0.22	1.31	1.2	3285.3	1765.5	2.51	4.37
Average	**86.84**	**9.95**	**0.23**	**1.29**	**0.96**	**3285.03**	**1765.76**	**2.33**	**4.13**
Na_2SO_3 coke Refcoal	81.99	11.78	0.28	1.57	10.47	3460.65	2274.54	2.53	4.69
	80.53	10.21	0.31	2.37	10.22	3459.92	2276.21	2.76	4.76

Sample	**Ca**	**Co**	**Eu**	**Gd**	**Li**	**Na**	**Si**	**U**	**Th**
Average	**81.26**	**11.00**	**0.30**	**1.97**	**10.35**	**3460.29**	**2275.38**	**2.65**	**4.73**
$NaNO_2$ Refcoal	150.15	11.14	0.27	1.53	0.54	2858.55	6369.76	2.34	4.23
	148.99	10.56	0.26	2.31	0.61	2799.87	6435.35	2.53	4.41
Average	**149.57**	**10.85**	**0.27**	**1.92**	**0.58**	**2829.21**	**6402.56**	**2.44**	**4.32**
$NaNO_2$ coke Refcoal	85.15	13	0.29	1.69	6.71	1959.24	1916.25	2.6	4.71
	84.36	12.57	0.32	2.47	7.22	1961.25	1915.11	3.28	5.41
Average	**84.76**	**12.79**	**0.31**	**2.08**	**6.97**	**1960.25**	**1915.68**	**2.94**	**5.06**
Na_2SO_3+$NaNO_2$ Refcoal	62.88	10.1	0.23	1.33	0.49	5703.04	1407.04	1.97	3.66
	63.54	9.65	0.31	1.43	0.52	5713.5	1410.22	2.57	4.61
Average	**63.21**	**9.88**	**0.27**	**1.38**	**0.51**	**5708.27**	**1408.63**	**2.27**	**4.14**
Na_2SO_3+$NaNO_2$ coke	66.39	13.42	0.31	1.79	8.01	6175.27	1992.69	2.64	4.88
	67.12	11.99	0.35	1.82	7.82	6169.25	1999.32	3.35	5.09
Average	**66.76**	**12.71**	**0.33**	**1.81**	**7.92**	**6172.26**	**1996.01**	**3.00**	**4.99**
Ice Refcoal	358.27	8.99	0.19	1.09	-	127.78	1112.56	1.84	3.11
	360.14	9.34	0.24	1.12	-	128.58	1113.44	2.26	2.99
Average	**359.21**	**9.17**	**0.22**	**1.11**	-	**128.18**	**1113.00**	**2.05**	**3.05**
Ice coke Refcoal	667.01	15.06	0.33	1.85	-	174.78	2111.54	3.09	5.29
	666.51	14.99	0.41	2.49	-	173.95	2122.37	2.99	4.78
Average	**666.76**	**15.03**	**0.37**	**2.17**	-	**174.37**	**2116.96**	**3.04**	**5.04**
5% Glycerol Refcoal	92.22	9.54	0.21	1.19	-	238.89	1201.51	1.83	3.35
	91.33	10.49	0.19	1.23	-	244.65	1211.94	1.78	2.75
Average	**91.78**	**10.015**	**0.2**	**1.21**	-	**241.77**	**1206.73**	**1.81**	**3.05**
5% Glycerol coke Refcoal	133.36	11.49	0.26	1.49	-	206.65	1936.49	2.28	4.19
	129.66	12.35	0.34	1.55	-	211.63	2021.86	2.34	3.75
Average	**131.51**	**11.92**	**0.3**	**1.52**	-	**209.14**	**1979.18**	**2.31**	**3.97**
Sugar Refcoal	119.64	9.93	0.23	1.29	-	230.35	1339.11	1.91	3.47
	120.33	10.02	0.22	1.41	-	228.79	1340.57	2.17	2.98
Average	**119.99**	**9.98**	**0.23**	**1.35**	-	**229.57**	**1339.84**	**2.04**	**3.23**
Sugar coke Refcoal	181.14	12.43	0.29	1.65	-	79.07	2142.6	2.44	4.48
	182.48	11.87	0.34	1.75	-	77.94	2213.5	2.52	4.54
Average	**181.81**	**12.15**	**0.32**	**1.70**	-	**78.51**	**2178.05**	**2.48**	**4.51**

Table A1.5. Progress of extraction (runs 1 and 2)

Run 1				Run 2		
Time	Mass, g	Absorbance	Cor. absorbance	Mass, g	Absorbance	Cor. absorbance
0	0.127	0.007	0.006	0.130	0.001	0.001
10	0.106	0.003	0.019	0.128	0.004	0.003
15	0.125	0.037	0.030	0.111	0.018	0.016
20	0.129	0.054	0.042	0.113	0.030	0.027
30	0.128	0.082	0.064	0.110	0.032	0.029
45	0.111	0.173	0.156	0.126	0.200	0.159
60	0.131	0.376	0.286	0.121	0.339	0.281
120	0.119	0.816	0.685	0.128	0.756	0.591
180	0.104	0.856	0.825	0.123	1.030	0.840
240	0.122	1.068	0.875	0.123	1.054	0.860
300	0.115	1.033	0.898	0.124	1.082	0.871
360	0.125	1.124	0.980	0.124	1.252	1.008

Table A1.6. (continued) Progress of extraction (run 3 and average corrected absorbance)

Run 3			
Mass	Absorbance	Cor. absorbance	Average Cor. absorbance
0.120	0.002	0.002	0.003
0.120	0.004	0.003	0.008
0.105	0.021	0.020	0.022
0.117	0.027	0.023	0.031
0.101	0.045	0.045	0.046
0.121	0.227	0.187	0.167
0.117	0.346	0.296	0.288
0.134	0.839	0.628	0.634
0.117	0.872	0.747	0.804
0.113	1.049	0.928	0.888
0.112	1.133	1.012	0.927
0.109	1.141	1.047	0.010

Appendix 2

Table A2.1. Analytical methods used in the analysis

Item	Method
Sample preparation	SABS 0135:part 1&2 – 1997
Moisture content	SABS Method 925
Ash content	SABS ISO 1171;1997
Volatile matter content	SABS ISO 562:1998
Total sulphur	Leco SC432 Instrumental method
Calorific value	CP500 Instrumental method
Swelling index	SABS ISO 501
Roga Index	SABS ISO 335
Coking property of coal: Ruhr dilatometer test	SABS Method 1072
Plastic property of coal determined by the constant-torque Gieseler plastometer	In house, based on ISO 1397
Ash fusion temperature	Based on SABS ISO 540:1995
Ash composition	XRD Method / ICP Method
Ultimate analysis	Leco – Instrumental
Form of sulphur	Wet chemistry method

Table A2.2. Physical properties of graphite [22]

Crystalline form	Hexagonal
Lattice parameters	A = 0.246 nm , c = 0.671 nm
Colour	Black
Density at 300 K, 1 atm	2.26 g/cm^3
Atomic volume	5.315 cm^3/mol
Sublimation point at 1 atm (estimated)	4 000 K
Triple point (estimated)	4 200 K
Boiling point (estimated)	4 560 K
Heat of fusion	46.84 KJ/mol
Heat of vaporisation to monoatomic gas	716.9 KJ/mol
Pauling electro-negativity	2.5

Table A2.3. Properties of nuclear-grade graphite [15]

Property	Anisotropic graphite	Isotropic graphite
Density	1.71 g/cm^3	1.86 g/cm^3
Resistance	735 $\mu\Omega$.cm	1 000 $\mu\Omega$.cm
Tensile strength	9 930 kPa	46 172 kPa
Coefficient of thermal expansion (CTE),10^{-6}/C with grain	2.2	5.3
Coefficient of thermal expansion (CTE),10^{-6}/C against grain	3.8	5.3
Anisotropy ratio (CTE ratio)	1.73	1
Total ash	740 ppm	400 ppm
Boron content	0.4 ppm	0.3 ppm

Table A2.4. Elements showing inorganic affinity in coal [9, 10, 27]

In clay minerals and feldspars	Al, Ba, Bi, Cr, Cs, Cu, Ga, K, Li, Mg, Na, Ni, P, Pb, Rb, Sn, Sr, Ta, Th, Ti, U, V, Y and rare-earth elements
In iron sulphides	As, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb, S, Sb, Se, Ti, W, and Zn
In carbonates	C, Ca, Co and S.[14,15]
In sulphates	Ba, Ca, Fe and S
In heavy minerals (tourmaline)	B
In several mineral phases	Co and W (carbonates and sulphides); Ni, Cu, Pb (clay minerals and sulphides); S (sulphides, sulphates and organic matter); C (carbonates and organic matter)

Table A2.5. Elements showing organic affinity in coal [9, 10, 27]

C, N, S, Be, B, Ge, V, W and Zr (boron exhibits partial association with tourmaline in the heavy fraction, and V with clay minerals).

Table A2.6. Abundance and elemental mode of occurrence in coal [4, 49, 35]

Element	Abundance (ppm)	Modes of occurrence	Level of confidence
Antimony	<0.1 – 40	Sulphides, pyrite	4
Arsenic	<1 – 250	As for S pyrite	8
Beryllium	<1 – 30	Clays? Organic association?	4
Boron	<1 – 500	Clays, organic association	-
Cadmium	<0.1 – 10	ZnS. Clays? Carbonates?	8
Chlorine	100 – 8000	Maceral moisture, NaCl	-
Chromium	1 – 100	Clays? $FeCr_2O_4$?, CrOOH	2
Cobalt	<1 – 50	Sulphides? Clays?	4
Copper	<1 – 200	Sulphides? Organic association?	-
Fluorine	<20 – 1 000	Fluorapatite, clays	-
Lead	<1 – 100	PbS, pyrite, PbSe	8
Manganese	5 – 1 000	Organic association, carbonates, other	8
Mercury	0.01 – 10	Sulphides? Hg? Org. association	6
Molybdenum	0.5 – 50	Pyrite, MoS_2? Org. association?	-
Nickel	<1 – 100	Sulphides, organic association?	2
Selenium	0.1 – 20	Organic Se, sulphides, etc.	8
Tin	0.1 – 20	Oxides, sulphides, organic association	-
Thalium	0.1 – 3	Sulphides	-
Thorium	<0.1 – 50	Monazite, zircon	-
Uranium	0.1 – 50	Org. association, various minerals	-
Vanadium	<1 – 300	Clays, organic association?	-
Zinc	1 – 300	ZnS, organic association?	-

Table A2.7. Concentration of trace elements in coal, Recoal and Refcoal gel treated with HCl, HF and chelating resins (TP260,TP208, TP214) (ppm) [4]

Elements	Coal	Refcoal	HCl treated	HF treated	Resin TP260	Resin TP208	Resin TP214
La	15.8	1.6	0.6	0.6	0.3	0.7	1.8
Br	4.1	0.7	2.6	3.2	1	2.2	1.3
Sm	2.7	0.6	0.1	0.1	0.05	0.4	0.3
U	2	0.1	1.5	1.4	nd	0.3	0.2
Hf	2.8	1.7	0.8	0.9	0.1	0.1	0.08
Tb	0.6	0.2	nd	nd	nd	nd	nd
Th	4.9	2.6	nd	2	0.6	0.7	1.24
Sc	5.7	2.7	0.6	0.1	0.09	0.08	0.08
Cs	1.1	0.3	nd	nd	0.02	0.04	0.04
Eu	0.6	0.08		nd	nd	nd	0.008
Co	8.7	6.9	2.79	5.9	4.8	4.3	4.49
Cr	11	7.2	3.07	6.3	4.7	4.2	3.68
Ta	0.6	0.4	0.42	0.51	0.5	0.6	0.3
Fe	3 400	433	100	40	10	50	50

Appendix 3

Table A3.1. ICP-MS analysis results (concentration in ppm) (fusion method)

Samples	**Li (7)**	**Be (9)**	**Na (23)**	**P (31)**	**Ca (44)**	**Ti (47)**	**Mn (55)**	**Fe (57)**	**Co (59)**	**Ni (60)**
Coal	5.661	1.333	267.085	122.115	1 284.809	892.963	16.221	1 525.379	5.622	16.035
Std Refcoal	0.474	0.647	296.226	11.820	82.570	647.925	0.625	88.727	5.751	16.762
Std Coke	1.096	0.896	350.871	17.258	136.653	899.142	0.902	107.031	7.876	23.384
Acid-treated Refcoal										
HCl Refcoal	0.411	0.080	12.918	4.041	22.398	716.803	0.196	32.759	4.267	14.911
HCl Coke	0.624	0.125	19.425	6.525	34.835	1 176.594	0.417	55.847	6.952	24.663
HF + HCl Refcoal	<0.1	0.001	3.383	1.360	<0.001	75.404	0.068	3.089	0.961	3.486
HF + HCl Coke	<0.1	0.016	6.894	0.985	8.339	437.127	0.303	10.194	4.992	18.242
Chlorinated Refcoal										
Cl_2 Refcoal	0.690	0.807	99.362	19.350	77.360	888.229	1.139	149.178	7.623	22.291
Cl_2 Coke	0.235	0.092	37.080	30.895	14.095	528.541	0.149	35.488	3.847	11.562
HCH Refcoal	0.416	0.474	34.808	12.321	34.447	573.526	0.589	80.564	4.815	14.139
Ion-exchange or complexed Refcoal										
NaF Refcoal	0.059	0.180	3 216.406	5.200	39.718	275.945	0.197	28.326	2.374	6.839
NaF Coke	0.668	0.579	–	18.296	150.962	847.188	0.943	129.914	7.866	22.755
NH_3 Refcoal	0.548	0.650	23.791	16.109	55.550	761.789	0.415	78.115	6.745	20.100

NH_3 Coke	1.352	1.324	1 10.041	30.782	167.509	1 422.465	1.353	154.715	12.476	37.928
KCN Refcoal	0.607	0.720	47.092	13.133	75.205	816.302	0.409	69.947	6.603	18.930
KCN Coke	5.839	0.866	176.995	16.899	119.970	1 050.944	0.615	90.281	8.297	24.174
Na_2SO_3 Refcoal	0.714	0.740	1 839.827	16.785	52.041	816.181	0.340	84.391	6.860	21.390
Na_2SO_3 Coke	10.470	0.723	1 359.536	16.102	88.672	828.896	0.542	85.119	6.612	20.569
$NaNO_3$ Refcoal	0.537	0.596	1 172.064	15.128	43.158	749.291	0.460	78.045	6.721	19.109
$NaNO_3$ Coke	6.712	1.148	1 453.404	26.240	104.134	1 266.815	0.925	132.231	11.449	32.398
Na_2SO_3+$NaNO_3$ Refcoal	0.495	0.626	3 428.057	15.844	44.679	814.854	0.478	81.963	7.049	20.587
Na_2SO_3+$NaNO_3$ Coke	8.007	1.281	5 573.942	30.961	98.847	1 558.187	1.279	166.898	13.635	40.300
EDTA Refcoal	1.173	0.515	170.864	31.943	88.428	1 489.792	0.714	92.835	11.575	37.052
EDTA Coke	0.833	0.394	140.463	22.935	55.742	1 076.263	0.352	67.273	8.243	26.184

Table A.3.1. (continued) ICP-MS analysis results (concentration in ppm) (fusion method)

Samples	**Cu (63)**	**Zn (66)**	**Ga (69)**	**Mo (95)**	**Te (128)**	**Tl (205)**	**Pb (208)**	**Bi (209)**	**U (238)**
Coal	7.926	4.459	7.541	2.336	0.027	0.202	1.710	0.250	1.472
Std Refcoal	2.603	3.196	2.630	0.127	0.001	0.001	0.307	0.028	1.118
Std Coke	7.918	5.667	5.935	0.201	0.001	<0.001	0.085	0.003	1.574
Acid-treated Refcoal									
HCl Refcoal	4.129	2.880	1.791	0.245	0.001	0.022	0.152	0.106	0.538
HCl Coke	6.547	4.909	3.062	0.527	0.001	0.015	0.050	0.388	0.868
HF + HCl Refcoal	0.657	1.160	<0.1	0.030	<0.001	<0.001	0.610	0.032	0.047
HF + HCl Coke	3.261	2.553	0.345	0.165	<0.001	<0.001	0.432	0.174	0.248

Chlorinated Refcoal									
Cl$_2$ Refcoal	3.631	5.495	6.726	0.224	0.001	0.002	0.259	0.007	1.863
Cl$_2$ Coke	2.265	3.407	<0.1	0.059	<0.001	0.017	0.181	0.087	0.622
HCH Refcoal	2.061	2.626	2.376	0.130	0.002	0.015	0.184	0.088	1.182
Ion-exchange or complexed Refcoal									
NaF Refcoal	0.677	1.127	0.864	0.053	<0.001	<0.001	0.004	<0.1	0.472
NaF Coke	2.665	6.747	3.655	0.183	0.002	<0.001	0.011	0.001	1.529
NH$_3$ Refcoal	3.060	4.297	3.741	0.093	0.003	0.025	0.430	0.094	1.407
NH$_3$ Coke	5.800	16.773	9.034	0.240	0.004	0.065	1.004	0.007	2.572
KCN Refcoal	4.053	3.130	3.155	0.112	0.002	0.004	0.685	0.008	1.372
KCN Coke	8.619	4.438	4.173	0.159	0.002	<0.001	0.070	<0.1	1.693
Na$_2$SO$_3$ Refcoal	2.816	4.783	3.356	0.127	0.002	<0.001	0.301	0.005	1.473
Na$_2$SO$_3$ Coke	13.224	4.890	3.389	0.133	0.001	<0.001	0.072	0.001	1.434
NaNO$_3$ Refcoal	3.114	4.726	3.216	0.084	0.001	<0.001	0.453	0.028	1.350
NaNO$_3$ Coke	23.640	8.548	6.308	0.149	0.003	0.001	0.043	0.038	2.259
Na$_2$SO$_3$+NaNO$_3$ Refcoal	2.001	4.639	3.063	0.122	0.001	<0.001	0.023	0.002	1.394
Na$_2$SO$_3$+NaNO$_3$ Coke	21.228	9.994	7.994	0.225	0.003	<0.001	0.004	0.003	2.599
EDTA Refcoal	2.312	7.808	6.051	0.234	0.003	0.020	0.179	0.013	2.200
EDTA Coke	1.969	6.384	4.184	0.162	0.004	0.038	0.185	0.033	1.607

Table A3.2. ICP-MS analysis results (concentration in ppm) (microwave digestion method)

Samples	**Li (7)**	**Be (9)**	**B (11)**	**Na (23)**	**Mg(24)**	**Al (27)**	**K (39)**	**Ca (44)**	**V (51)**	**Cr (52)**	**Mn (55)**	**Fe (57)**	**Co (59)**
Coal	3.939	1.239	9.053	272.506	40.846	1115.527	1.905	569.972	42.930	14.336	14.255	1072.359	6.333
Std Refcoal	0.251	0.477	1.313	308.183	5.833	416.131	0.422	82.179	24.073	15.188	0.834	105.277	6.492
Std Coke	0.580	0.677	1.456	384.461	19.424	635.232	0.612	164.061	35.455	22.397	0.909	102.659	9.188
Acid-treated Refcoal													
HF Refcoal	<0.100	0.022	0.788	10.000	1.568	34.376	<0.010	35.385	11.307	9.156	0.455	55.335	4.565
HF Coke	0.454	0.127	1.047	18.020	0.342	469.204	0.756	21.367	28.747	13.653	0.360	51.858	5.985
HCH Refcoal	0.258	0.393	0.750	26.907	23.849	538.109	0.477	44.743	23.406	14.217	0.642	89.636	5.805
Chlorinated Refcoal													
Cl_2 Refcoal	0.228	0.114	0.731	<10.000	1.574	537.475	0.534	21.581	24.390	11.434	0.279	44.340	5.214
Cl_2 Coke	<0.100	0.029	0.496	<10.000	2.008	47.016	0.027	53.915	15.128	11.924	0.131	24.102	5.952
HCH Refcoal	0.258	0.393	0.750	26.907	23.849	538.109	0.477	44.743	23.406	14.217	0.642	89.636	5.805
HCH Coke	0.394	0.572	1.285	76.676	25.915	695.814	0.696	81.756	34.447	21.417	1.196	158.828	8.448

Samples	Ni (60)	Cu (63)	Zn (66)	Ga (69)	As (75)	Se (82)	Rb (85)	Sr (88)	Mo(95)	Ag (107)	Cd (111)	Te (128)	Ba (137)
Coal	15.905	9.536	5.564	10.697	0.477	<0.200	0.193	25.028	2.565	0.359	0.882	<0.027	53.307
Std Refcoal	17.521	2.519	3.150	3.709	0.161	<0.200	0.520	20.070	0.139	0.326	0.067	<0.002	33.847
Std Coke	29.132	7.996	5.275	6.187	0.149	<0.200	0.640	29.421	0.206	0.456	0.079	<0.002	43.758
Acid-treated Refcoal													
HF Refcoal	14.929	2.004	0.703	1.540	0.915	<0.200	0.022	9.213	0.547	0.134	0.030	<0.002	37.696
HF Coke	16.097	7.330	2.188	3.045	0.161	<0.200	0.505	4.773	0.137	0.311	0.076	<0.002	4.986
Chlorinated Refcoal													
Cl_2 Refcoal	13.549	2.537	1.357	3.255	0.903	<0.200	0.666	14.001	0.102	0.276	0.075	<0.002	25.168
Cl_2 Coke	22.276	4.467	1.073	2.006	0.291	<0.200	0.049	12.043	0.768	0.170	0.044	<0.002	50.237
HCH Refcoal	14.748	3.096	2.519	4.499	0.092	<0.200	0.680	17.221	0.143	0.280	0.066	<0.002	34.336
HCH Coke	27.084	3.623	4.345	6.656	0.116	<0.200	0.733	20.402	0.274	0.407	0.073	<0.002	41.803

Table A3.2. (continued) ICP-MS analysis results (concentration in ppm) (microwave digestion method)

Samples	**Tl (205)**	**Pb (208)**	**Bi (209)**	**U (238)**	**Sc (45)**	**Y (89)**	**La (139)**	**Ce(140)**	**Pr (141)**	**Nd(146)**	**Sm (147)**	**Eu (153)**	**Gd (157)**
Coal	0.215	11.759	0.359	1.184	2.996	0.319	0.076	0.366	0.020	0.084	0.027	0.021	0.100
Std Refcoal	0.001	4.958	0.069	1.223	2.004	2.261	0.378	2.801	0.111	0.571	0.221	0.064	0.367
Std Coke	0.000	2.631	0.017	1.754	3.752	6.741	0.854	4.018	0.239	1.225	0.488	0.134	0.794
Acid-treated Refcoal													
HF Refcoal	0.003	3.049	0.037	0.821	0.260	1.516	0.341	1.287	0.082	0.384	0.129	0.042	0.247
HF Coke	0.019	1.698	0.013	1.035	0.167	0.087	0.027	0.309	0.009	0.034	0.010	0.004	0.015
Chlorinated Refcoal													
Cl_2 Refcoal	0.031	4.692	0.148	1.162	0.239	0.269	0.317	1.883	0.059	0.218	0.044	0.015	0.078
Cl_2 Coke	0.004	2.931	0.017	1.069	0.361	3.817	0.806	2.820	0.190	0.913	0.303	0.086	0.514
HCH Refcoal	0.022	4.745	0.098	1.344	2.772	6.342	1.346	3.037	0.291	1.426	0.493	0.128	0.750
HCH Coke	0.007	3.210	0.012	1.907	3.722	6.709	1.093	4.291	0.282	1.395	0.505	0.138	0.801

Samples	**Tb (159)**	**Dy (163)**	**Ho (165)**	**Er (167)**	**Tm (169)**	**Yb(172)**	**Lu(175)**	**Th(232)**	**Ru(101)**	**Rh(103)**	**Pd (108)**	**Sn (118)**	**Sb (121)**
Coal	0.009	0.073	0.017	0.061	0.011	0.094	0.014	0.265	0.001	0.002	0.762	1.402	0.426
Std Refcoal	0.064	0.454	0.098	0.304	0.047	0.329	0.048	0.499	<0.001	0.002	0.681	0.772	0.123
Std Coke	0.149	1.081	0.238	0.741	0.116	0.798	0.119	1.297	0.001	0.003	1.001	1.141	0.192

Acid-treated Refcoal													
HF Refcoal	0.036	0.243	0.054	0.167	0.025	0.170	0.026	0.537	0.001	0.001	0.237	0.876	0.567
HF Coke	0.002	0.016	0.004	0.012	0.002	0.017	0.003	0.132	0.001	0.001	0.773	1.257	1.450
Chlorinated Refcoal													
Cl_2 Refcoal	0.008	0.050	0.011	0.035	0.005	0.039	0.005	0.402	<0.001	0.001	0.576	0.938	1.071
Cl_2 Coke	0.083	0.579	0.125	0.388	0.059	0.396	0.062	1.218	0.001	0.001	0.290	1.041	0.670
HCH Refcoal	0.136	0.944	0.208	0.629	0.097	0.652	0.097	1.856	<0.001	0.002	0.633	0.780	0.132
HCH Coke	0.148	1.041	0.228	0.703	0.110	0.760	0.113	1.811	<0.001	0.002	0.877	1.077	0.205

Table A3.2. (continued) ICP-MS analysis results (concentration in ppm) (microwave digestion method)

Samples	**Te(128)**	**Hf (178)**	**Ir (193)**	**Pt (194)**	**Au (197)**	**Si (29)**	**P (31)**	**Ti (47)**	**Zr (90)**	**Hg (202)**
Coal	0.029	2.483	<0.001	0.031	0.015	14450.571	93.742	1003.572	75.981	0.020
Std Refcoal	0.001	2.152	<0.001	0.026	0.009	625.077	6.734	701.957	71.105	0.009
Std Coke	0.001	3.173	<0.001	0.038	0.013	994.096	10.726	1016.911	100.785	0.012
Acid-treated Refcoal										
HF Refcoal	<0.001	0.668	<0.001	0.009	0.006	101.379	1.000	490.362	23.904	0.006
HF Coke	0.001	2.147	0.002	0.027	0.010	194.800	11.250	873.660	72.930	0.007

Chlorinated Refcoal

Cl_2 Refcoal	0.001	1.618	0.002	0.020	0.007	368.454	9.228	734.404	62.707	0.006
Cl_2 Coke	<0.001	0.818	<0.001	0.011	0.007	259.655	1.000	640.828	30.964	0.007
HCH Refcoal	0.002	1.892	<0.001	0.023	0.011	829.284	7.713	653.661	61.373	0.006
HCH Coke	0.001	2.627	<0.001	0.032	0.015	1124.880	11.833	961.752	89.367	0.009