CHAPTER 1

GENERAL INTRODUCTION

1.1. Introduction

Eskom has embarked on a project to use Pebble Bed Modular Reactors (PBMRs) to generate electricity. A PBMR is a type of High-Temperature Gas Reactor (HTGR) which means that its core is gas–cooled, rather than water-cooled [1,2]. The nuclear technology, developed in the 1960s and 1970s, was extensively tested in Germany and elsewhere. The PBMR may offer South Africa an effective solution to some of the electricity-supply problems it currently experiences in areas far away from the coalfields. Eskom believes that it would create a market, both within South Africa and in the rest of the world, of 30 reactors per year within 12 to 15 years. The simplicity of the design enables low-cost electric power to be generated, while the simplicity of operation will allow the reactor to be operated effectively away from sophisticated centres.

The PBMR consists of a structure made up of synthetic graphite blocks (the reflectors), contained within a steel pressure vessel. Depending on their position within the structure, the blocks are of differing qualities, with the inner ones able to withstand the very high temperatures (up to 950 °C) and high neutron fluxes experienced during operation. The outer blocks are loaded with boron carbide, which acts as a neutron shield, to prevent activation of the steel shell.

The fuel consists of spheres of graphite (the "pebbles"), 60 mm in diameter, that contain many uranium dioxide beads, evenly distributed throughout. The uranium dioxide spheres are coated to contain the fission products. The coatings, applied by means of chemical vapour deposition, consist of, firstly, two

layers of carbon with differing porosities, then the main barrier layer of silicon carbide, and then a third carbon layer. The coated beads are mixed with a fine powder consisting of 75% natural graphite and 25% synthetic graphite, binder resin, and are then moulded into the spherical shape. After being hardened at about 1 900 °C, the pebbles are ready for use. The uranium used in the start-up fuel is 4% enriched and the equilibrium fuel has a uranium enrichment of 8% [2].

During normal operation, 440 000 pebbles, of which 310 000 contain uranium dioxide and 130 000 are pure graphite spheres that serve as additional nuclear moderators, are loaded into the top of the reactor and discharged at the bottom where their degree of "burn-up" is measured. The pebbles are then either returned to the reactor or, if fully "burned out", retained within the reactor building to allow most of the decay of the short-lived fission products to take place. To remove the heat generated by the nuclear reaction, helium gas at 450 °C is passed through the pressure vessel from the top. It passes between the fuel pebbles, and then leaves the bottom of the reactor vessel at about 900 °C. The hot gas then passes through a conventional gas turbine system to drive electric generators, giving a useful capacity of about 100 MW. The helium used as a coolant for the PBMR is not corrosive, has good heating properties (having a specific heat that is much greater than that of CO_2), does not condense and can therefore operate at any temperature, has a negligible neutron- absorption cross-section, and can be used in a direct cycle, driving a gas turbine with high efficiency [2]. The modular nature of the system would allow ten such reactor/generators to be built on a site, sharing services and a single control room.

The reactor is described as being inherently safe because the silicon carbide layer around the uranium oxide beads is able to contain essentially all the fission products up to a temperature of 2 000 °C [1,2]. If the coolant helium stopped flowing, the reactor would warm up to about 1 350 °C, at which point the negative coefficient of criticality would bring the nuclear chain reaction to a close. Fission products resulting from radioactive decay would continue to heat the fuel until, at a temperature of around 1 600 °C, the heat losses through the reactor shell would balance the heat production, and the core would begin

to cool. It is therefore impossible for the radioactivity of the fission products to be "lost". In addition, the thermal mass of the reactor core is such that temperature changes occur slowly, over several days, allowing problems to be solved under conditions that would not engender panic.

The graphite used for the construction of the reactor core contributes to the safety of the design due to its very high sublimation point, in an inert atmosphere, of more than 3 000 °C and its slow rate of oxidation, even at the operating temperature, in air. The graphite is required to be of high purity and physical (structural) integrity.

Graphite is chosen as a moderator in nuclear fission reactors because it is the most readily available material with a low thermal neutron-capture cross-section, allowing efficient use of the neutrons generated. The thermal neutron-capture cross-section is usually expressed in terms of an equivalent boron concentration by summing the concentrations of the individual impurities (elements), weighted by their thermal neutron-capture cross-sections. 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 include cesium, cobalt, hafnium, manganese, neodymium, praseodymium, scandium, selenium, silver and terbium. Low thermal neutron-capture cross-sections are associated with antimony, arsenic, copper, chromium, germanium, galium, iron, lanthanum, nickel, potassium, sodium, thorium, titanium, tungsten and vanadium. In this context, elements such as aluminum, barium, beryllium, bismuth, bromine, calcium, cerium, lead, magnesium, molybdenum, phosphorus, rubidium, silicon, strontium, sulphur, tin and zinc are unimportant [3].

Impurities such as lithium should not be present, as their reaction with neutrons gives rise to tritium, making the circulating coolant (helium) radioactive and thus spreading the radioactivity to the turbine part of the nuclear reactor plant. Elements that become activated by neutron capture to give medium-life

radioactive isotopes should also not be present, as the reactor would become highly active without rapid isotope decay and this would have an adverse effect on the dismantling process at the end of the reactor's life. Cobalt and rare earths are the most serious of these latter elements [4].

The final graphitisation step is carried out at temperatures in the range of 2 600 to 3 000 ºC in an Acheson furnace. At these temperatures carbon loses much of its load of impurities, except for carbide-forming elements, in particular boron, which tends to come off too slowly at higher temperatures. The lower the original load of impurities, the purer the final product will be. Various purification processes can be used to reduce the load of impurities in the original material. Very effective purification can be carried out using high-temperature chlorination [4 - 6]. In this case, gaseous chlorine and/or chlorine-containing compounds are introduced into the graphitising furnace for purification at temperatures around 2 300 ºC. The carbide-forming elements then form volatile halogen compounds. In another process, solid sodium fluoride is distributed in the graphitising furnace and vaporised during heating [7]. However, high-temperature purification increases the cost of production of graphite by 50 to 100%, and therefore avoiding the need for it would be very desirable.

The physical structure of the graphite is also crucial for efficient operation and long life. The graphite blocks must be highly isotropic to give the best dimensional stability under irradiation [8 - 10] and to obtain uniform thermal expansion in all directions. Essentially, all the graphites employed in fission reactors as moderators and most, but not all, graphites used in fusion systems are derived from blocks manufactured from petroleum or pitch cokes. Cokes employed to manufacture conventional nuclear graphite are classified as either needle cokes from petroleum, pitch cokes, Gilsonite pitch cokes from asphalt or Santa Maria cokes. Both needle cokes and pitch cokes yield anisotropic graphite blocks, while Gilsonite pitch cokes and Santa Maria cokes yield isotropic graphite blocks [10].

1.2. Aim of the study

High-ash coals are unsuitable for efficient use in carbonisation. Petroleum products currently satisfy this fuel application. At this point it is important to note that energy demands by the industrialised world are continuing to rise, while the rate of new oil discoveries is falling. Within the next 30 years, available petroleum supplies are likely to fail to meet the demand, and oil will no longer be able to serve as the world's major energy source. Coal, on the other hand, exists in relative abundance worldwide and if it can be adapted for use in existing plants that have been engineered for petroleum use, it can serve as an inexpensive substitute for, or successor to, the more expensive oil fuels in use today. However, in order to be used as an oil substitute, the coal must be cleaned of its mineral matter content so as to meet environmental pollution standards. This is the motivation for this study.

1.3. Contents of the study

The report consist of six chapters. Chapter one, already discussed above gives an overview of the purpose of this study. The second chapter gives the theoretical background of the coal matrix, methods of analysis, graphite manufacture and purification methods. Chapter three looks at the experimental methods. Chapter four looks at the experimental results, as well as the discussion of the results. Chapter five is a summary and the last chapter gives the references.

CHAPTER 2

LITERATURE SURVEY

2.1   COAL: THEORETICAL BACKGROUND

2.1.1 Introduction

Coal is a major fossil fuel resource. It is usually dark black in colour, although geologically younger deposits of brown coal have a brownish-red colour. The colour, lustre and fracture patterns vary with rank, type and grade. Coal is the result of combined biological, chemical and physical degradation of accumulated plant matter over geological ages. In many cases coal still contains recognisable source material and is composed mainly of the compressed and altered remains of terrestrial plant material such as wood, bark, roots, leaves, spores and seeds [11 - 13]. The relative amounts of remaining plant parts lead to different coal ranks, which are termed lignite, sub-bituminous, bituminous and anthracite. Other terms refer to the origin of the plant parts through maceral names such as vitrinite, liptinite and inertinite.

Coal consists mainly of carbon, hydrogen and oxygen, and contains lesser amounts of nitrogen and sulphur and varying amounts of moisture and mineral matter. A large amount of coal is burned directly in boilers to generate electricity or steam for industrial purposes. Small amounts of coal are used for transportation, space heating, firing of ceramic products, etc. The rest is essentially pyrolysed to produce coke, coal gas, ammonia, coal tar and light oil products, from which many chemicals are produced. Combustible gases and chemical intermediates are also produced by the gasification of coal, and different carbon products are produced by means of various heat treatments.

2.1.2 Coal structure

Coal is a heterogeneous solid containing many molecular subgroupings. The most prominent of these molecular subgroupings is the benzene ring. Condensed ring varieties, such as naphthalene, anthracene and larger-ring compounds also are abundant [14]. These subgroups are interlinked or bonded in an almost infinite variety of ways. Studies done in the past 30 years indicate that there may also be a significant number of straight-chain hydrocarbons subgroups. A representative coal molecule contains, besides carbon and hydrogen, elements such as oxygen, nitrogen and sulphur. Oxygen can be present in heterocyclic rings, or it can be part of a functional group, such as an acid or an aldehyde. The weight of oxygen diminishes from about 25% in lignites to near 0% in anthracite. Nitrogen and sulphur are also incorporated into the molecular structure in a manner similar to that of oxygen. However, there does not seem to be any correlation between element quantity and coal rank. The true structure of coal is at present unknown; most workers agree that the structure is so complicated and variable that it is impossible at this time to form an accurate model of it.

The chemical nature of coal and its diagenesis has been well documented [12]. Lignite, bituminous and anthracite coals represent three stages in the continuous process of coal formation ("coalification") which took place over millions of years. As the original plant materials, consisting largely of well-ordered polymers (e.g. cellulose and lignin) became degraded, lighter, hydrogen-rich compounds were formed and trapped leaving a macro-molecular residue depleted in hydrogen and rearranged as a completely disordered macro-molecular material. As coalification progressed, the aromatic character of the coal increased, with rings fusing and becoming cross-linked. Thus, the degree of condensation increases in the order: lignite, bituminous coal and anthracite. A large number of aromatic units indigenous to the original coals were identified in coal using GC-MS and high-resolution MS by Hayatsu et al. [15]. Of particular interest is the demonstrated chemical nature of organic nitrogen, oxygen and sulphur in coal. There had been a lack of reliable information about these important

elements which are troublesome in the process of converting coals to liquids or gases. The fact that no organic sulphur compounds were isolated from lignite suggests that sulphur has not yet been incorporated into stable aromatic systems and therefore may be easier to remove from lignite than from a higher rank coal.

2.1.3 Petrographic groups

Coal is an extremely heterogenous solid which is composed of organic entities, called macerals, and inorganic entities, called minerals. The organic entities make up most of the coal weight and consist mainly of carbon, with lesser amounts of hydrogen, oxygen, nitrogen and sulphur. The macerals and minerals occur in distinct associations, called lithotypes, and each lithotype has a set of physical and chemical properties which also affect the coal's behaviour. Coal macerals can be classified into three main groups, namely the vitrinite group, the liptinite group and the inertinite group.

2.1.3.1   The vitrinite group

Vitrinite is the most common, and therefore the most important, maceral group occurring in bituminous coals [12,13]. Three different submacerals are distinguished in vitrinite, namely telenite, collinite and vitrodetrinite. Telenite macerals are derived from plant cell walls. Telenite and vitrinite in general originate from tree trunks, branches, stems, leaves and roots. Collinite originates from the colloidal humic gel precipitated from humic solutions. Vitrodetrinite originates from plant or humic peat particles which were degraded at a very early stage. The density of vitrinite macerals varies with coal rank, but ranges from 1.3 to 1.8 g/cm^3. The carbon and hydrogen contents of vitrinite at any given rank are intermediate between those of inertinite and liptinite. In bituminous coal, the hydrogen content ranges from 4.5 to 5.5%, oxygen from 5 to 20% and carbon from 75 to 96%. In comparison with other maceral

groups, the reflectance of vitrinite is intermediate between that of the liptinite and inertinite macerals. Because the reflectance of the vitrinite macerals shows a more or less uniform increase with coal rank, reflectance measurements for the determination of coal rank are always taken exclusively on vitrinite macerals. The reflectance of vitrinite is also anisotropic, so that in most orientations a particle of vitrinite will display two maxima and two minima with complete rotation. The pore volume of the vitrinite is determined through the use of adsorption isotherms. It varies with rank from 0.05 cm^3/g for vitrinites with 71% carbon, to 0.03 cm^3/g for vitrinites with 94% carbon, apparently passing through a minimum of 0.025 cm^3/g at a carbon content of about 89%.

2.1.3.2   The liptinite group

The liptinite group consists of the submacerals sporinite, cutinite, resinite, alganite and liptodetrinite [12,13]. Sporinite consists of the skins of spores and pollen in lignite and bituminous coal. Cutinite originates from the cuticles that occur on leaves, needle shoots, stalks and thin stems. Resinite originates from the resins that are the products of the metabolism of plants. Alginite is not found in normal humic coals; it originates from certain types of algae. Liptodetrinite cannot be assigned with certainty to any of the other submacerals of the liptinite group. Liptodetrinite may consist of fragments or the degradation residue of spores, cuticles, resinous bodies or algae. In any given coal, the liptinite macerals have the lowest reflectance. The liptinite macerals are the most resistant to alteration or metamorphism in the early stages of coalification and hence the reflectance changes are slight up to the rank of medium volatile coal. In this rank range, the reflectance of the liptinite macerals increases rapidly until it matches or exceeds that of the vitrinite macerals in the same coal and thus, essentially, disappears. The liptinite macerals have the lowest density of any maceral group, ranging from slightly above 1.0 to around 1.25 g/cm^3. In coals of low rank, the liptinite macerals are distinguished from the vitrinite macerals by a higher hydrogen content. On carbonisation, they yield much tar and gas. The liptinite macerals can also have the highest carbon content in any given coal. These macerals are largely aliphatic in character,

although most do have aromatic components. The hydrogen content of these macerals in bituminous coals can range from 7 to 10%, the carbon content from 75 to 85% and the oxygen content from 5 to 18%.

2.1.3.3   The inertinite group

The inertinite macerals are derived from plant material, usually woody tissue, that has been strongly altered either before or shortly after deposition by forest fire charring or biochemical processes such as composting [12,13]. The inertinite macerals have the highest reflectance and the greatest reflectance range of all macerals. They are distinguished by their relative reflectance and the presence of cell texture. The density of the inertinite macerals is always higher than that of vitrinite and ranges from 1.35 to 1.60 g/cm^3. The inertinite macerals have the lowest hydrogen content of all the macerals, along with a very high carbon content, with values ranging from 2.75 to 4.25% hydrogen, 73 to 85% carbon and 13 to 25% oxygen. The inertinite macerals are fusinite, semifusinite, inertodetrinite and scleronite. Fusinite occurs in varying quantities in peat, brown coal and bituminous coal, and has a charcoal-like structure. It always has the highest reflectance and is distinguished by its cell texture, commonly being broken into small shards and fragments. Semifusinite also occurs in varying quantities in peat, brown coal and bituminous coal. It also has cell texture and the general features of fusinite, except that it has lower reflectance. Semifusinite has the largest range of reflectance of the various coal submacerals. It is also the most abundant of the inertinite macerals in most coals. Inertodetrinite occurs in varying quantities in trimacerites, durites and vitrinerites. Inertodetrinite exhibits variable reflectance within wide limits, but its reflectance is always higher than that of vitrinite. Macrinite is a relatively rare maceral which appears mostly in durites and clarodurites. It occurs as structureless ovoid bodies with the same reflectance as fusinite or semifusinite.

2.1.4 Mineral matter

The term *mineral matter* in coal refers to all inorganic material found in coal as mineral phases and also to all elements in coal that are considered inorganic. Coal contains almost all the elements of the periodic table in at least trace quantities, combined in all of the minerals found in the Earth's crust. Minerals in coal are classified by Stach et al. [12] as syngenetic and epigenetic. Syngenetic minerals come from the material inherent in all living matter or from material that was included in the coal during the biochemical changes associated with coalification, whereas epigenetic minerals were deposited in the cleats and cracks of the coal after the coalification process was complete. Table A1.1 in Appendix 1 lists some of the common minerals found in coal. The most common minerals in coal are the aluminosilicates or clay minerals, which include illite $[(OH)_8K(Mg,Al,Si).(Si_3Al_3)O_{10}]$, kaolinite $[Al_2Si_2O_5(OH)_4]$ and mixed-layer illite-montmorillonite.

2.1.4.1 Distribution and occurrence of mineral matter

Major elements in coals are present in the mineral rather than in the organic matter, but show no systematic change with factors such as rank, age, marine or non-marine roof rock, or origin from particular groups of plants such as lycopods or tree ferns [16,17]. Ren et al. [18] reported that the average concentrations of minor and trace elements in Chinese coals are higher in comparison with world averages. This, they proposed, is attributable to enrichment of various types, either rock-controlled, sedimentation-controlled, magmatic/hydrothermal-controlled, fault-controlled or groundwater-controlled.

Senior et al. [19] reported that trace elements in coal have diverse modes of occurrence that will greatly influence their behaviour during coal utilisation. The ranges for the concentrations and modes of

occurrence of elements considered to be of considerable significance in the environmental issues arising from coal utilisation are given in Table A1.2 in Appendix 1 [20,21]. Determining the mode of occurrence of an element is important because of the tremendous diversity of form exhibited by the elements found in coal. The mode of occurrence may vary from highly dispersed discrete forms, in which the elements are covalently bound in the organic matrix of the macerals, to discrete forms in which the elements are highly localised and concentrated in specific minerals [20,21]. Such differences in the mode of occurrence will greatly influence the behaviour of an element in many coal utilisation processes, notably its partitioning during coal cleaning by conventional processes, its susceptibility to oxidation upon exposure to air, and its fate during the process of combustion.

Although there is a large amount of information available on the trace elements in coal, little is known about the forms in which such trace elements occur, as indicated by the frequent question marks in Table A1.2 in Appendix 1. Trace elements in coal can occur basically in either organic or inorganic forms, and most trace elements are probably found in both combinations [14]. It is reported that alkaline-earth elements (Mg, Ca, Sr and Ba), Na and Br decrease with increasing coal rank [17]. Elements such as Fe, Ca, Zn, Mg, Si, Ti, etc. may occur predominantly in mineral species of these elements [17,20 - 25]. However, for many elements such as Hg, As, Sb, Pb, Cd, Co, Ni, etc., no specific mineral of the element may be present, but most elements are associated with the pyrite mineral [19 - 25].

Palmer and Lyons [25] reported the distribution of trace elements in the four most abundant minerals generally found in European and American bituminous coals, namely quartz, kaolinite, illite and pyrite. Quartz contributes little to the trace element mass balance, which suggests that the trace element content of coal can be explained mainly by the three major minerals: pyrite, kaolinite and illite. The concentration of trace elements in different minerals as reported by Palmer and Lyons [25] is given in Table A1.3 in Appendix 1. Hart and Leahy [26] reported the distribution of trace elements in the South

African coal occurring in the Witbank basin. They found that rare earth elements, together with the elements Th, Ta, Hf, Sc, Cs, U, As and Fe, are concentrated in the inorganic components of the coal, whereas Sb, Br and Co are associated with the organic matter. Laban and Atikin [27] suggested that the elements Ba, Co, Cr, Mn, Ni, Pb and Sr are associated with silicate, carbonate, sulphate and phosphate minerals, whereas the elements Cu, Mn, Ni, Pb and Zn are associated with pyrite minerals. An organic association is suggested for Cr, Br and Sr in lower rank coals [27].

Rare earth elements such as La, Ce, Sm, Eu and Lu are found to be associated primarily with the organic matter, while the elements Tb, Yb and Th are associated primarily with the inorganic matter [28]. Certain elements, i.e. Ge, B, B and Sb, are found primarily with the organic matter in coal, whereas Co, Ni, Cu, Cr and Se have intermediate organic affinities, which suggests a partial contribution from sulphide minerals in coal, but also suggests the presence of these elements in organometallic compounds as chelated species or as adsorbed cations. The existence of these elements in organometallic compounds such as porphyrins and corrins has been demonstrated [29 - 35]. It has been speculated that some of the major types of organometallic material include metal porphyrins, metal carbonyls, metallocene metal alkyls and metal chelates [29]. Unequivocal identification of these species in coal liquefaction products, however, has not been forthcoming. Although the coal liquefaction process was designed to remove the mineral matter, limited experimental evidence to date suggests that metal removal is not always complete [30]. The distribution of most elements in a THF-soluble portion of the solvent-refined coal suggests the existence of these elements as metal chelates or chemically bound metal species. Average concentrations for the trace elements are given in Table A1.4 in Appendix 1 [14]. The South African averages are given in Table A1.5 in Appendix 1 [36] and the data on Tshikondeni coal as reported by Morgan [4] is given by in Table A1.6 in Appendix 1.

2.2   TRACE ELEMENT ANALYSIS IN COAL

2.2.1   Introduction

Practically all available analytical techniques have been employed in the analysis of coal and coal-derived products. The analytical methods used in trace element analysis of coal and its ash can be separated into two categories. The first category includes methods that cannot be easily used for multi-element analysis on an individual sample. For this reason, many of these methods may require large quantities of sample if more than a few elements are to be determined. These methods include atomic absorption spectrometry, potentiometry, voltametry and absorption methods, and they require sample preparation for determining coal and fly ash matrices.

The methods in the second category include atomic emission spectrometry, X-ray fluorescence spectrometry, mass spectrometry and neutron activation analysis. These methods have multi-element analysis capabilities. The present trend is towards the use of multi-elemental instrumental procedures to quantitatively cover as many elements as are necessary. Such methods include instrumental neutron activation analysis(INAA), X-ray fluorescence spectrometry (XRFS), inductively coupled atomic emission(ICP-AES), and inductively coupled mass spectroscopy (ICP-MS). ICP-AES and ICP-MS require sample preparation to remove the organic matrix, whereas such preparation is not required with INAA and XRFS.

2.2.2 Sample preparation

Sample preparation can be carried out by either acid dissolution in open or closed systems, ashing or fusion. Wet decomposition in open systems has the advantage of being effective for both inorganic and organic material [37,38]. It often destroys or removes the sample matrix, thus helping to reduce or eliminate various types of interference. However, wet decomposition in an open vessel may give rise to systematic errors due to:

- contamination caused by reagents and container materials
- contamination from an external source
- losses of elements caused by adsorption on the surface of the vessel or reaction with the vessel material
- losses of elements by volatilisation
- incomplete digestion.

In the past decade, microwave-assisted dissolution of coal has been developed as a rapid and safe method of sample preparation which requires smaller amounts of acids and has the following advantages:

- no loss of volatile elements
- shorter reaction times and improved decomposition because of higher temperatures
- the reduction of blank values because of the smaller quantities of reagents added
- no contamination from external sources.

Numerous acids and acid mixtures, including HNO_3, HCl, HF, $HClO_4$, H_2SO_4, H_3BO_3, and H_2O_2 [42,43,45,46,48 - 57,59,63] have been used for coal sample preparation. Important restrictions may arise from safety considerations (HF and $HClO_4$), negative effects on instrument parts (HF and H_2SO_4), matrix effects (H_2SO_4 and H_3BO_3) and spectral interference in ICP-MS (HCl, $HClO_4$ and H_2SO_4) [59]. Smith and Arsenault summarised all the microwave-assisted dissolutions and digestion methods reported up to and including 1994 [42].

Dry ashing in open systems has the following disadvantages [37,38]:

- loss of volatile elements (e.g., Hg, B, Pb, Zn, Cd, Ca, In, Te, As, Sb, Fe, Cr and Cu)

- very slow ashing of some materials

- difficult dissolution of the ashed materials

- contamination from external sources.

The advantages of this sample preparation method are that no reagents are used and little operator attention is required.

Fusion methods enable resistant materials to be dissolved more easily after they have been fused [67]. Other problems that occur with both acid digestion and fusion include hydrolysis of refractory elements (e.g. Ta and W) if HF is not used and the low solubilities of the fluoride salts of Y, Pb, Ca, U and Hf [45,59]. Sample preparation in general creates opportunities for sample contamination. Sample contamination and/or loss can be minimised by limiting the number of steps needed to prepare the sample, working in a clean room environment and using well-washed glassware [37].

2.2.3   Coal standards

In earlier work, the standards used in the determination of trace elements in coal and coal-derived products were synthetic standards. These standards were produced by blending salts of the detectable elements together [41]. Most laboratories use the Standard Reference Materials (SRM) as standards for the determination of trace elements in coal and coal-derived products.

2.2.4 Analytical methods

The methods most frequently used for analysing trace elements in coal are instrumental neutron activation analysis, optical emission, atomic absorption, X-ray fluorescence and mass spectrometry, or a combination of these methods. Polarography has been used for the determination of trace elements in coal [39,41,77,78]. However, the polarographic method of analysis has not been extensively developed and applied to coal analysis because of the many analytical problems incurred with the complex matrix [41].

Colorimetric procedures, although quantitative, are usually specific only for a particular element, hence limiting. A variety of ultra-sensitive colorimetric methods are available for many elements that are suited to the trace element analysis of coal and coal-derived products. Phosphorus is the only element generally determined using a colorimetric method because the other elements may be more appropriately determined by other methods. This colorimetric method is capable of measuring phosphorus in microgram quantities [41,48].

2.2.4.1 Atomic absorption spectrometry (AAS)

Atomic absorption spectrometry (AAS) is based on the attenuation of a beam of electromagnetic radiation as a consequence of its interaction with and partial absorption by the analyte. Atomisation is carried out in a flame or an electrically heated surface. The sources of radiant energy usually employed in AAS include a hollow cathode lamp and electrodeless discharge lamps. Instruments for AAS consist of a source of radiant energy, a sample holder, a wavelength selector, a detector and a readout device [39]. AAS has been widely applied for the determination of trace elements in coal [18,23,41 - 51,54] because AAS instrumentation is the most widely available and cheapest among atomic spectroscopic

techniques. AAS is a highly sensitive method, particularly since new electrothermal atomisation procedures, e.g. graphite furnaces [39,41 - 46,50] and plasma units [41 - 43,45] were developed . In AAS, the sample in solution is atomised by a flame or other energy source, where it produces atomic vapour of the element being analysed for. Monochromatic light with the same wavelength as the required element is then passed through the sample 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. The method is suited for the accurate analysis of special elements because it does not provide information on more than two elements simultaneously. It is most applicable to metals because its sensitivity declines with increasing non-metallic character of the element. AAS is also less sensitive to elements that form refractory oxides. Atomic absorption techniques require sample dissolution by acid digestion [41- 43,45,46,48,50 - 52] and by fusion methods [41 - 43]. Samples may also be introduced as slurries [39,43,44].

2.2.4.2   Atomic emission spectrometry (AES)

Atomic emission spectrometry (AES) is based on the intensity of radiation emitted by atoms that are excited in the atomisation process. Atomisation is carried out in an arc, spark, plasma or flame. The heated sample serves as the source of radiant energy. The components of instruments for atomic emission spectrometry are a sample holder and source, a wavelength selector, a detector and a readout [39]. Atomisation using inductively coupled plasma (ICP) offers several advantages. First, atomisation is more complete and fewer interference problems caused by dissociation reactions are encountered. Ionisation interference is small or non-existent, perhaps because the large concentration of electrons from ionisation of the argon represses the ionisation of the sample components. Atomisation occurs in a chemically inert environment, which should enhance the lifetime of the analyte. In addition, and in contrast to arc, spark and flame sources, the temperature cross-section of the plasma is relatively uniform and, as a consequence, self-absorption and self-reversal effects are not encountered [39].

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is interesting because it offers the combination of multi-element capability, a wide dynamic range and low instrumental detection limits. ICP-AES has been widely applied for the simultaneous multi-element analysis of coal and coal-derived products [18,20,23,24,28,41 - 43,53 - 57,59,69]. The ICP-AES technique requires sample preparation because the sample must be introduced as a liquid. When ICP-AES is used for the analysis of coal and coal-derived products, the most time-consuming step in the procedure is dissolution of the sample. However, sample dissolution has become more efficient and faster with the advent of microwave techniques [39,42,54 – 57].

2.2.4.3   Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is based on the extraction of ions formed by a plasma for elemental analysis by mass spectrometry [39,41]. This allows the use of a single technique for determining most of the elements, as opposed to the necessity for using several different techniques and generally at detection limits lower than in ICP-AES. The mass spectrometer determines the ratio of mass to charge (m:e) of the gaseous ions. The rare earth elements are difficult to determine by ICP-AES owing to their inherently complex optical spectra. However, in ICP-MS this problem does not arise and these elements can be determined more readily. ICP-MS has been used for the simultaneous determination of a wide range of major, minor and trace elements in coal and coal-derived products [22,23,41,42,58-65]. Samples may be introduced in the form of a solution [41, 58 - 61,63,64] or a slurry [60 - 62], or laser ablation [60,65] may be used. The disadvantages of sample solution nebulisation include the need for dissolution procedures, which are time-consuming, complex, error-prone and hazardous, and may result in the loss of the more volatile analytes. Slurry atomisation-ICP-MS has potential as both a rapid screening technique and for full quantitative analysis for the determination of major and trace element components in coal, with minimum sample pretreatment. Laser ablation-ICP-MS is ideally suited to the rapid screening of element concentration ranges in coal if a 15 to 20%

accuracy is acceptable [60].

2.2.4.4   X-ray fluorescence spectrometry (XRFS)

The basis of the X-ray fluorescence technique lies in the relationship between the wavelength λ (or energy E) of the X-ray photons emitted by the sample element and the atomic number Z. The two main approaches to the analytical use of X-ray fluorescence spectrometry (XRFS) are wavelength-dispersive XRFS and energy-dispersive XRFS. The former approach uses the diffracting power of a single crystal to isolate narrow wavelength bands from the polychromatic beam of characteristic radiation excited from the sample; and the latter uses a proportional detector to isolate narrow energy bands from the polychromatic beam of characteristic radiation excited from the sample. The X-ray source in both wavelength and energy-dispersive XRFS is generally an X-ray tube. An energy-dispersive spectrometer consists of a polychromatic source, a sample holder, a semi-conductor detector and various electronic components required for energy discrimination [39,68]. In using these techniques, samples can be presented as finely pulverised powders or as fused solids [39,67]. XRFS is an attractive tool for the analysis of coal and coal-derived products [19,29,42,43,50,57,67 -71] because of its multi-element capability, excellent sensitivity down to the ppm level, and the minimal and non-destructive sample preparation requirements. It is rapid and can be automated for routine analysis. When used for analysis of coal samples, it has the advantage of preventing the volatilisation of elements that may be lost during ash preparation. However, certain problems are encountered in using XRFS as a quantitative tool. These stem from the absorption or enhancement of the actual fluorescence signal by constituent elements in the matrix of the specimen examined. In the case of XRFS analysis of trace metals in coal, the matrix effects are largely due to the mineral phases occurring in various amounts in various sources of coal [68,70]. As a result, matrix-matched standards are nearly impossible to produce synthetically.

2.2.4.5 Instrumental neutron activation analysis (INAA)

Instrumental neutron activation analysis (INAA) is based on the detection of radioactivity induced by neutron capture. The sample to be irradiated is placed into an irradiation capsule and transferred to the irradiation site and back. Thereafter, the gamma-ray spectra are recorded and counted. The gamma-ray spectra of all activated nuclei in the sample are usually measured using a Ge(Li) detector coupled to an analyser/computer. Data obtained from the Ge(Li) detector are stored in the analyser's memory and from an energy calibration of the detector system, the exact energy of each gamma-ray photopeak can be obtained; this enables positive identification of the radio nuclide to be made. The integrated area of each photopeak can be used to determine the quantitative amount of the radio nuclide present. Neutron activation methods offer several advantages, including high sensitivity, minimal sample preparation and ease of calibration. The major disadvantages of activation methods are their need for large and expensive instruments and special facilities for handling and disposing of radioactive materials. Another shortcoming is the long time required to complete analyses when long-lived radio nuclides are being used. INAA is suitable for the determination of most of the inorganic constituents of coal samples. Its sensitivity is adequate to allow the determination of some elements in concentrations down to 1 ppb. Elements determined by INAA include: Al, Ag, As, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, Ga, Hf, Hg, I, In, Ir, K, La, Lu, Mg, Mn, Mo, Na, Nd, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb and Zn [71,75,76]. Elements such as Co, Gd and the rare earth metals, which are of great concern for nuclear-grade carbon, can be satisfactorily determined by INAA. Boron cannot be determined satisfactorily by INAA because the product formed after irradiation, that is He, is not radioactive. INAA has been extensively applied in the analysis of coal and coal-derived products [16,18,19,22 - 28,42,52,54,57,71 - 76].

2.2.4.6   Comparison of analytical methods

Comparative studies on the different methods of coal analysis have been documented [80,81]. Because of the large number of elements that need to be analysed in coal and coal-derived products, multi-element techniques would appear to be the best option. The ICP-AES, ICP-MS, INAA and XRFS methods all have multi-element capabilities. The choice amongst the multi-element techniques depends on the sensitivity of the method, its speed, accuracy, cost and range of applicability. Because any particular analytical technique will be better suited to some elements than others for inherent reasons, a combination of methods is usually necessary to determine all the elements of interest. For example, elements such as boron, which have a very high neutron-capture cross-section, cannot be determined satisfactorily with INAA. The sensitivities of the different methods as reported by Roduskin et al. (for ICP-MS and laser ablation-ICP-MS) [58] and Dulka and Risby (for INAA, SSMS, CIMS, ICP-AES, NFAAS, XRFS and ASV) [80] are given in Table A1.7 in Appendix 1. The choice of analytical method also depends on the availability of instruments.

Assuming that the availability of instruments is not a limiting factor, the following conclusion can be made: In a process that requires rapid determination of the concentration of trace elements in coal, and where accurate results are not critical, XRFS would be a method of choice. In a process where the accurate determination of the concentration of a wide range of trace elements in coal, is important, ICP-MS would be a suitable method.

2.3   REFINED COAL

2.3.1   Introduction

Effective purification of coal by separating the inorganic mineral components from the organic components has long been the aim of coal technologists. Several chemical means of purification have been studied in recent years. Mineral matter in coal consists largely of aluminosilicate compounds, such as kaolinite ($Al_2Si_2O_5OH$) and clays (e.g. $(NaMg,Al)Si_4O_{10}(OH)_2$), in conjunction with quartz (SiO_2). The remainder of the mineral matter is made up of a large number of minerals which generally fall into five categories: carbonates, sulphites, phosphates, oxides and sulphides. Generally, aluminosilicates are extracted from a coal solution in alkali, by acid wash and through the removal of silica by treatment with hydrofluoric acid (HF). The separation of mineral matter by extracting the organic matter into a suitable organic solvent may also be used.

2.3.2   Extraction of mineral matter using sodium hydroxide

Stambaugh [82] reported the use of an alkaline solution comprising a sodium, potassium or ammonium hydroxide, and hydrosulphide or carbonate, followed by acid washing using formic, acetic, sulphuric or hydrochloric acid. The processes employing NaOH include those of Waugh and Bowling [83,84], Reggel et al. [85], Yang [86], Yang et al. [87], Mukherjee and Borthakur [88], Wang et al. [89], Çulfaz et al. [90], Bolat et al. [91] and Sharma and Gihar [92]. In these processes, coal is treated with aqueous NaOH at temperatures ranging from 100 °C to 350 °C. Under these conditions, aluminosilicate compounds react to form insoluble sodalite ($Na_8Si_6Al_6O_{24}$). This sodalite is fairly soluble in dilute mineral acids. This forms the basis for coal cleaning using a dilute alkali followed by washing with mineral acid. Yang et al. [87] reported a two-step acid-washing process. In this process the coal, after

NaOH treatment, is washed with either HCl or H_2SO_4, followed by washing with HNO_3. This process yields coal with an ash content of <0.1 to 1.0%. Wang and Tomita [93] demonstrated the use of calcium hydroxide followed by hydrochloric acid leaching. Calcium hydroxide reacts with kaolinite and quartz to form calcium-bearing hydrated silicates, such as tobermorite and hibschites, that can be dissolved in acid.

2.3.3 Extraction of mineral matter using hydrofluoric acid

The use of hydrofluoric acid (HF) for the dissolution of aluminosilicate compounds under ambient conditions and in a single leaching step has been reported [94 - 99]. HF is considered to have greater potential than NaOH as the main demineralising reagent in a process for producing ultra-clean coal, because it can penetrate further into the coal matrix and dissolve the aluminosilicates more completely than NaOH. HF is also able to dissolve most of the other minerals that occur in coal. The main concerns about the process using HF are the recycling of HF and the formation of insoluble fluorides, such as calcium fluoride (CaF_2), magnesium fluoride (MgF_2) and fluoroaluminate compounds such as $NaAlF_4$, $MgAlF_5$ and K_2NaAlF_6. A method for the recycling of the spent acid (HF) has been well documented by Lloyd et al. [98] and Kindig et al. [99]. A model for the determination of fluoride-complexed aluminium and silicon species, free fluoride (F^-), H^+ ions and molecular HF in solution when aluminosilicate compounds are treated with aqueous HF has been reported by Steel et al. [96]. The model elucidates the chemical mechanisms governing both the dissolution behaviour of mineral matter in coal towards aqueous HF, and the unwanted precipitation of various fluoride compounds, such as CaF_2, MgF_2, $NaAlF_4$ and $MgAlF_5$. According to the model, CaF_2, MgF_2, $MgAlF_5$ and $NaAlF_4$ will precipitate at 65 °C when the concentrations of Ca^{2+}, Mg^{2+}, Na^+ and F^- in solution are such that Equations 2.3.3.1 to 2.3.3.4 below are satisfied respectively.

$$[Ca^{2+}][\,F^-]^2 \geq 2.45 \times 10^{-10} \tag{2.3.3.1}$$

$$[Mg^{2+}][\,F^-]^2 \geq 2.63 \times 10^{-9} \tag{2.3.3.2}$$

$$[Mg^{2+}][\,AlF_5^{2-}] \geq 3.64 \times 10^{-6} \tag{2.3.3.3}$$

$$[Na^+][\,AlF_4^-] \geq 1.21 \times 10^{-5} \tag{2.3.3.4}$$

2.3.4 High-temperature solvent extraction of coal

The concept of refining coal was first developed in Germany during World War II, with the objective of producing low-ash electrode-grade coke. The process involves the dissolution of coal with a solvent at high temperatures and pressures, with or without hydrogen. The coal extract, known as solvent refined coal (SRC), can be used for the production of (a) low-ash, low-sulphur clean solid fuel from coal for use in boilers for power generation, (b) bituminous binder material for making briquettes and carbon blocks, (c) very low-ash carbon for making electrodes and carbon artefacts, and (d) a potential coking agent for making improved coke [100]. Anthracene oil, having a boiling range of 270 to 360 °C, was used as solvent to produce coal extracts with an ash content of 6 to 7% [100 - 103]. Natural solvents obtained by the hydrogenation of extracts (boiling range 230 to 400 °C) and synthetic solvents, consisting of 75% α-methyl naphthalene, 18% decalin and 7% tetralin, have also been used for the production of SRC [103]. In order to maintain the hydrogen level and the efficiency of the solvents, the dissolution in most cases is carried out under hydrogen pressure.

In brief, the process is as follows: The coal is crushed and dried, slurried with solvent, preheated and dissolved under pressure, with or without hydrogen. Undissolved coal, along with mineral matter, is separated by filtration and the solvent recovered by vacuum distillation. Table A1.8 in Appendix 1 lists the concentrations of the trace elements in SRC as given by Coleman et al. [30] and Table A1.9 in Appendix 1 those given by Filby et al. [104].

2.3.5 Low-temperature solvent extraction of coal

Solvent-extraction techniques using low-boiling organic solvents under mild conditions have since been developed. In these processes, the organic part of the coal is dissolved in a suitable solvent and separated from the insoluble inorganic portion, usually together with any part of the insoluble organic components. Solvent extraction results in a coal-derived extract containing the solvent-soluble organic portion of the coal, free of almost all mineral matter. The effectiveness of mixed solvents was recognised by Hombach [105]. Roy et al. [106] noted that N–methylpyrrolidinone (NMP) is particularly effective in swelling coal. Stiller et al. [107] identified a class of solvents that are capable of dissolving a large portion of the organic material in coal from the minerals and the fixed carbon matrix. These include tetramethyl urea (TMU), hexamethylphosphoramide (HMPA), dimethylacetamide (DMAA) and NMP. High degrees of dissolution of bituminous coal (50 to 70%) are found when refluxing similar solvents with the addition of alkaline [107 – 114]. The extent of extraction may be improved by first treating the coal with hydrogen-donating solvents such as tetralin and alcohol [107,115].

2.3.5.1 Extraction of coal with mixed solvents

Iino and Matsuda [116] have found that a carbon disulphide-pyridine mixture is efficient in the solvent extraction of bituminous coal at room temperature. Dimethylformamide, hexamethyl phosphoric triamide and dimethyl sulphoxide have also been found to give a high yield in combination with carbon disulphide. The extraction of bituminous coals using CS_2-N-methyl-2-pyrrolidinone (NMP) mixed solvent at room temperature was reported by Iino et al. [117] to give higher yields than CS_2-pyridine. The anthracites, subbituminous coals and lignites gave low extraction yields.

The process for the CS_2-NMP mixed solvent involved the extraction of the coal sample with CS_2-NMP

mixed solvent (1:1 by volume) under ultrasonic irradiation (38 kHz) for 30 min at room temperature. After centrifugation at 14 000 r/min for 60 min, the supernatant was separated by decantation. Fresh mixed solvent was then added to the residue in the centrifuge tube and the residue further extracted under ultrasonic irradiation for 30 min and then centrifuged. This procedure was repeated until the supernatant became almost colourless (usually three 30-min extractions and three 15-min extractions). The supernatant was filtered through a membrane filter paper with an average pore size of 0.8 μm. The coal extract, with relatively low ash values (<0.5%), was recovered by vacuum evaporation of the mixed solvent below 90 °C.

The extraction yield was determined from the weight of the residue using the following equation:

$$Extraction\,yield\left(wt\%daf\right) = \frac{[1 - (residue(g)\,/\,coal\,feed(g)] \times 100}{[-(ash(wt\%d.b.)\,/\,100)]}$$

where   daf   =   dry ash free

           wt%db   =   [(extract + residue)(g)/coal(g)] x 100

The presence of oxygen decreased the extraction yield for Upper Freeport coal [119]. The addition of aromatic amines [115,117], tetracyanoethylene [119], and various lithium and tetrabutylammonium salts [119] increased the extraction yield.

2.3.5.2   Extraction of coal with N-methylpyrrolidinone

Zondlo and co-workers [108 - 111] have developed a solvent-extraction process using N-methylpyrrolidinone (NMP) to produce extracts which may be suitable as precursors for the production of value-added carbon products. They reported that the dissolution of coal depends on several factors, such as solvent type and the physical and chemical properties of the solvent, and cannot be attributed to a simple diffusion-controlled process. Furthermore, solvent extraction is dependent on time and temperature and, to a lesser extent, on the particle size of the coal, the solvent-to-coal ratio,

and the oxygen and moisture content of the coal.

The process involved refluxing ground coal with NMP (at around 200 °C), using a solvent-to-coal ratio of 10:1, for one hour under a nitrogen atmosphere. After extraction, the mixture was cooled and the residue separated from the solution by centrifugation for 90 minutes at 30 °C and 4 000 r/min. After centrifugation, the supernatant was decanted and filtered, first through a coarse filter and then through a 0.2 micron Teflon filter. The refined coal was recovered either by evaporation of the solvent or by precipitation in water. Precipitation in water leads to a reduction in the quantity of the minerals, as indicated in Table A1.9 in Appendix 1. This is attributed to the fact that NMP solubilises some inorganic species in coal during the extraction process, which then crystallise during evaporation. The extraction efficiency was increased by hydrogenating the coal before extraction in NMP using hydrogen-donor solvents such as tetralin [109].

A technique has also been developed [111] for the beneficiation of the residue via specific gravity fractionation. It was shown that 70% of the residue can be separated into fractions containing less than 3.5% ash for a typical West Virginia bituminous coal using an organic liquid with a specific gravity of 1.5. This treatment enables the residue to serve as low-ash boiler fuel or as a suitable precursor for the manufacture of materials such as active carbons.

2.3.5.3   Extraction of coal with a polar aprotic solvent/alkali mixture

The Council for Scientific and Industrial Research (CSIR) [112] developed a coal solubilisation process which gives a refined coal solution referred to as the "Refcoal solution". The process involves mixing a polar aprotic solvent such as N-methylpyrrolidinone (NMP) or dimethylformamide (DMF) with an alkali (e.g. potassium hydroxide or sodium hydroxide) in solid or liquid form. The alkali needs to get into solution by means of a phase-transfer catalyst and the coal appears to act in this capacity. In brief,

the Refcoal process is as follows: 100 parts by mass of coal as received, 1 000 parts of either NMP or DMF, and 10 parts of either KOH or NaOH are mixed together in a water bath or oil bath-jacketed reactor and stirred for five hours under a nitrogen atmosphere. The progress of extraction is followed photometrically as follows: Small samples of the slurry are taken at suitable intervals. Each sample is immediately centrifuged for three minutes at 3 000 r/min. A 0.1 g portion of the supernatant is weighed into a 50 ml volumetric flask and made up to the mark with solvent. The absorbance at 600 nm is plotted against time to indicate the progress of extraction.

The degree of extraction is determined as follows: Coal, solvent and alkali, together with a small metal slug, are placed in some sealed stainless steel centrifuge tubes under nitrogen. The tubes are then gently mixed for 24 hours by tumbling them end over end. Thereafter, the extract is obtained by centrifugation and decantation. The residue is then washed once with fresh solvent, centrifuged and the washings decanted. The residue is then transferred into a pre-weighed sintered glass funnel, washed with water and dried to constant weight in a vacuum oven at 60 °C. The dried residue is then analysed for its carbon content and the degree of extraction calculated as:

$$\% Carbon = \frac{W_t \ of \ carbon \ in \ coal - W_t \ of \ carbon \ in \ residue}{W_t \ of \ carbon \ in \ coal}$$

The degree of extraction and the analysis for various coals in NMP have been reported by Morgan [120], and are given in Appendix 1, Table A1.10.

Under an inert atmosphere, the solution can stand for months, but it reacts readily with oxygen to form a rapid skin. Gelation occurs if the solution is exposed to the atmosphere. The solution gels if incompatible solvents such as water, methanol or traces of acids are added to it. The gel that is derived from the Refcoal solution is referred to as "Refcoal gel".

The refined coal can be separated from the solution by evaporation of the solvent or precipitation in

water. The separated refined coal from this process is referred to as "Refcoal". Recovery of Refcoal by precipitation at 0 °C was shown to be more effective in removing the bulk of the dimethylformamide from the Refcoal solution [121]. The ash level in the Refcoal is reported to be 0.2 to 0.5%, depending on the degree of centrifugation. This could be reduced to below 0.01% by acid washing [4]. The effect of extraction and acid washing on the impurity level as determined by laser ablation inductively coupled mass spectrometry as reported by Morgan [4] is shown in Table A1.6 in Appendix 1. These purification methods form the basis of this study.

2.4 GRAPHITE

2.4.1   Introduction

The existence of nuclear reactors is possible because the fission reaction induced by neutrons in the nuclei of fissile material such as,

$$^{235}_{92}U, \quad ^{239}_{94}Pu \quad \text{and} \quad ^{233}_{92}U,$$

leads to the release of more than one neutron. If the neutrons released are used to create a further fission, and if the concentration of the nuclei is sufficient, a self-sustaining reaction occurs, producing large quantities of heat in the core of the reactor. The reaction cross-section for fission by neutrons decreases with increasing neutron energy, and it is advantageous to slow down the neutrons emitted by the fission reaction and to utilise the heat produced. To control the amount of neutrons escaping from the core before they create a further fission, moderators are used in which neutron-nucleus collisions reduce the neutron energies without absorbing neutrons to an excessive degree and without themselves being split. Moderators used in nuclear reactors include H_2O, D_2O and graphite.Graphite is chosen as moderator in nuclear fission reactors because it is the most readily available material with low thermal neutron capture cross-section. The low thermal neutron capture cross-section allow efficient use of the neutrons generated. Graphite, not only acts as a moderator, but forms part of the reflector blocks contained within a steel pressure vessel of the reactor.

To utilise the heat released from the core, a coolant is used; the heat is transferred to the coolant, which expands the coolant, and the force of the expanding coolant can be used to drive a turbine generator to produce electricity. Helium gas is used as coolant for the pebble-bed reactor.

2.4.2   The physical structure and purity of graphite

The physical structure of the graphite is also important for efficient operation and long life. A highly graphitised structure, at the molecular level, is desirable to obtain a high thermal conductivity of the material [8 - 10]. The structure of perfect graphite crystal consists of covalently bonded sheets of hexagonal networks of carbon atoms with a spacing of 1.42×10^{-8} cm. These sheets are weakly bonded in ABAB.... stacking sequence, with a separation of 3.3535×10^{-8} cm. This is shown in Figure 2.1. An ABC ... stacking sequence is sometimes observed, associated with arrays of partial dislocations. The graphite crystallite can has two distinct dimensions: the crystal size L_a measured parallel to the basal plane and the dimension L_c measured perpendicular to the basal plane. In a coke-based nuclear graphite, typical values of L_a of $\sim 800 \times 10^{-8}$ cm and $L_c \sim 600 \times 10^{-8}$ cm, measured by X-ray methods, are found [8,9]. Typical properties of nuclear-grade graphite are given in Table A1.11 in Appendix 1.
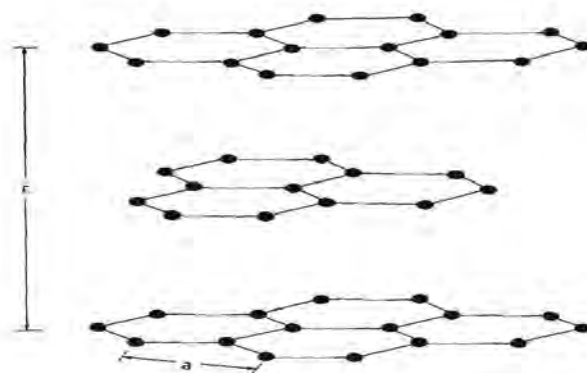

Figure 2.1: The graphite crystal lattice [9]

During irradiation, graphite undergoes considerable structural damage, which changes the properties of the graphite. The transfer of neutron energy to the nuclei of the solid materials creates lattice defects which modify the properties of these solids. A further process which is of significance in some conditions is the transmutation of nuclei by reaction with neutrons, the product of which may also significantly alter the material properties; examples are (n, p) and (n, α) reactions. Structural damage due to the neutron irradiation can be reduced by thorough selection of raw materials and by including a purification step in the manufacture of the graphite. Impurities have additive effect and are lumped

in terms of boron equivalent. The thermal neutron-capture [122], neutron-activated reactions [123], the boron equivalents (assuming a 1 ppm concentration for each element), and the type of decay of the radioactive products of some of the elements are given in Appendix 1. The boron equivalent is calculated as follows:

$$Boron \quad Equivalent = \frac{C_E \times M_B \times NC_E}{M_E \times NC_B} \times 10^4$$

where C_E is the concentration of the element

                 M_E is the molecular weight of the element

                 NC_E is the thermal neutron-capture cross-section of the element

                 M_B is the molecular weight of boron

                 NC_B is the thermal neutron-capture cross-section of boron.

2.4.3   Manufacture of graphite

Essentially, all the graphite employed in fission reactors as moderators and most, but not all, the graphite used in various applications in fusion systems is initially in the form of blocks manufactured from petroleum or pitch cokes. Cokes that are used to manufacture conventional nuclear graphite are classified as needle cokes from petroleum, pitch cokes, Gilsonite pitch cokes from asphalt and Santa Maria cokes. Both needle cokes and pitch cokes yield anisotropic graphite, while Gilsonite pitch cokes and Santa Maria cokes yield isotropic graphite. The graphite required as a moderator for nuclear reactors should have isotropic properties to give the best possible dimensional stability under irradiation [9,10]. Anisotropic graphite can be turned into 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 process of manufacture [10]. A typical raw coke contains ~ 10% volatiles, 0.1 to 2.2% ash and 0.1 to 4.3% sulphur [10]. The coke is broken down at the completion of the formation process and then

calcined at about 1 300 ºC to remove excess volatile matter and pre-shrink the coke to prevent excessive dimensional changes later in the process. Following the calcination process, the coke is crushed and ground to yield an appropriate particle size distribution for the chosen forming process and the size of the final artefact. The largest graphite bodies may have diameters up to 120 cm and lengths of 4 to 5 m, and may contain very large particles of coke. The usual size of graphite bricks for the nuclear industry is 1 m in length and about 20 - 50 cm in diameter, produced by extrusion or moulding, with particle sizes up to 0.1 cm. The selected particle size fraction is mixed with a pitch binder having the appropriate properties to produce a plastic mass suitable for the forming process. The mix of ground-up coke and binder pitch is then extruded, moulded or isostatically pressed into the desired shape, and the material is then baked to carbonise the binder pitch and produce the necessary rigidity in the artefact for handling. The heating cycle during baking, usually at temperatures in the range of 750 to 900 ºC, may take 30 to 70 days. The baking process may volatilise up to one-third of the binder pitch content, which shows a loss in density and an increase in permeability. To increase the density of the coke, multiple impregnations with fluid pitches are carried out after the baking process.

2.4.4 Graphite manufacture from refined coal

Cheaper high-rank bituminous coals, i.e. coking coals, which go through a fluid stage during coking, could be used as a substitute for the expensive petroleum coke in the manufacture of graphite. A coking coal is a coal that, when heated in the absence of air, will melt and foam on the evolution of volatile gases, resulting in a hard sponge-like mass of nearly pure carbon-coke. Coking and graphitising coals pass through a fluid stage during high-temperature heat treatment. The fluidity of the reaction system facilitates suitable mobility of the aromatic molecules in the system. The result is intermolecular dehydrogenative polymerisation to create aromatic lamellar molecules. These aromatic molecules rearrange themselves to create an intermediate anisotropic nematic liquid crystal phase, called the mesophase. This mesophase develops in the isotropic fluid matrix at a temperature between 350 and

500 °C. The mesophase stage grows and coalesces to give the anisotropic coke. The manufacturing process in the case of coal will require a purification step. The extraction of the original coal to yield a solvent-refined coal, called Refcoal, which is free of almost all of the mineral matter, serves as such a purification step. This purification through extraction of the original coal is much cheaper than the more effective high-temperature chlorination process.

The production of high-quality, high-purity, isotropic graphite from coal extracts has been reported [124]. Although hydrogenation before extraction substantially increases the amounts of coal that can be extracted, it also yields anisotropic graphite blocks undesirable for manufacturing nuclear graphite. Kgobane et al [125] noted that Refcoal recovered by precipitation forms better coke than Refcoal recovered by solvent evaporation. They further noted that Refcoal obtained by the extraction of coal in the presence of sodium sulphide at room temperature yields better graphite than that obtained by extraction at 90 °C. However, extraction at room temperature requires longer extraction periods.

2.5 GENERAL CHEMISTRY

2.5.1   Ion exchange

Ion-exchange is defined by Walton and Rocklin [126] as the reversible exchange of ions of similar charge, positive or negative, between a solution and an insoluble solid that is in contact with the solution. Ions are separated on the basis of ion-exchange reactions that are characteristic for each ion. Ion-exchange resins may be divided into one of three groups:

- cation exchange resins, which are usually an organic polymer with sulphonic acid functional groups

- anion exchange resins, which usually consist of an organic polymer with quaternary ammonium functional groups

- chelating ion-exchange resins.

The resin beads are spherical, small and uniform in size. In cationic resins, the sulphonic acid groups are the active resin sites used for the exchange. The $-SO_3^-$ anionic group is chemically bound to the resin. The H^+ counter-ions are free to move about and can be exchanged for another cation (say M^{2+}) as follows:

$$2R_s\text{-}SO_3^-H^+ + M^{2+} \rightleftharpoons (R_s\text{-}SO_3^-)_2M^{2+} + 2H^+$$
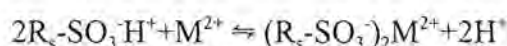
Separations of metal cations are based either on differences in their affinity for the cation-exchange resin or on selective complexation by the eluent. The affinity of an ion for a particular resin is measured by the distribution coefficient, D, which is defined by the following equation [127]:

$$D = \frac{amount\ of\ element\ in\ re\sin}{amount\ of\ element\ in\ soluion} \times \frac{volume\ of\ solution, \left(cm^3\right)}{weight\ of\ dry\ re\sin, \left(g\right)}$$

The value of this coefficient gives a measure of the volume of eluents required to elute a particular ion from a column. The larger the value of D for an ion, the more eluents will be required to elute that

particular ion. In general, the affinity of an ion-exchange resin increases with the charge on the ion. The distribution coefficient is determined experimentally. A measured mass of the resin is contacted with a solution of known strength until equilibrium is reached. The concentration of the desired ion in the remaining solution is then measured and the concentration of the ion absorbed onto the resin is determined by difference. The distribution coefficient depends on the composition of the solution, but is independent of the concentration of the solute. Distribution coefficients in aqueous hydrochloric acid-ethanol media have been reported by Strelow et al. [127]. They undertook fundamental studies of the distribution of the metal ions between ion-exchange resins and solutions. In their studies, they examined the distribution coefficients for cation-exchange resins in aqueous hydrochloric acid [128], aqueous hydrochloric acid media with macroporous resin [129], hydrochloric acid-methanol media with macro-porous resin [130], hydrochloric acid-acetone media [131], hydrochloric acid-acetone media with macro-porous resin [132], hydrochloric acid-thiourea media [133], hydrobromic acid-acetone media [134], perchloric acid media [135], nitric and sulphuric acid media [136] and tartaric acid and ammonium tartrate media [137]. They also reported distribution coefficients for anion-exchange resins in hydrobromic and nitric acid media [138], oxalic acid, with and without nitric and hydrochloric acid media [139] and sulphuric acid media [140].

The rate of ion exchange is governed by diffusion, either film diffusion in a layer of solution next to the exchanger or, more usually, particle diffusion within the exchanger bead itself. Boyd and Soldano [141] reported self-diffusion coefficients for cations in a sulphonated polystyrene exchanger and the effect of cross-linking measured by nominal divinyl benzene (%DVB) at 25 °C. They reported that the self-diffusion rate was lowered by increased cross-linking, and that the activation energies increased with cross-linking. Boyd and Soldano reported self-diffusion coefficients for cations in a hetero-ionic exchanger [142], water molecules [143] and anions [143,144].

The self-diffusion coefficients reported are in the order of 10^{-8} to 10^{-9} m.s^{-1}, which indicates that the

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diffusion of counter-ions in a gel-type cation exchanger is extremely slow. Compared with sulphonic acid resins, the chelating ion-exchange resins show superior selectivity in the sorption of various multivalent cations [145]. These resins can, therefore, be used to advantage in the removal and isolation of traces of heavy metals from relatively concentrated salt solutions. The uptake is very slow at pH 2, but increases rapidly when the pH of the outer solution is increased [145]. Chelating ion exchangers, also known as complexing or selectivity resins, are distinguished from resins of the ordinary type by three main properties, namely:

☞ The affinity of a particular metal ion for a functional group of the chelating resin depends mainly on the nature of this chelating group.

☞ The strength of the binding forces in chelating resins are much higher than in ordinary ion-exchange resins.

☞ The exchange process in a chelating resin is often slower than in, e.g., strongly acid or basic resins and is controlled either by a particle diffusion mechanism or a second-order chemical reaction.

The selectivity sequences for Lewatit TP 260 and Lewatit TP 208 respectively are [146]:

$UO_2^{2+} > Pb^{2+} > Cu^{2+} > Ni^{2+} > Cd^{2+} > Co^{2+} > Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+}$ > alkali metals;

$Cu^{2+} > VO^{2+} > UO_2^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+} > Fe^{2+} > Be^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+} >$ Na^+

The regeneration of the spent resins is preferably done by acid washing.

2.5.2 Specific elements

2.5.2.1   Iron

Iron has two principal oxidation states, +2 (ferrous) and +3 (ferric), both of which exist as ions in acid solution and as hydroxides in alkaline solution. Iron is available in coal mainly as pyrite, FeS or Fe_2S_3. Iron forms cationic octahedral, anionic tetrahedral and neutral complexes. The most important iron complex is the haem. Haemoglobin containing the iron in blood consists of haem bound to a protein called globin [147]. Haem (Figure 2.2) is an iron(II) complex of porphyrins, in which the six-coordinate iron atom is bonded to four nitrogen atoms from pyrrole rings in a plane, and to a nitrogen atom in globin perpendicular to this plane. Iron originates from the haem complex in coal [34].
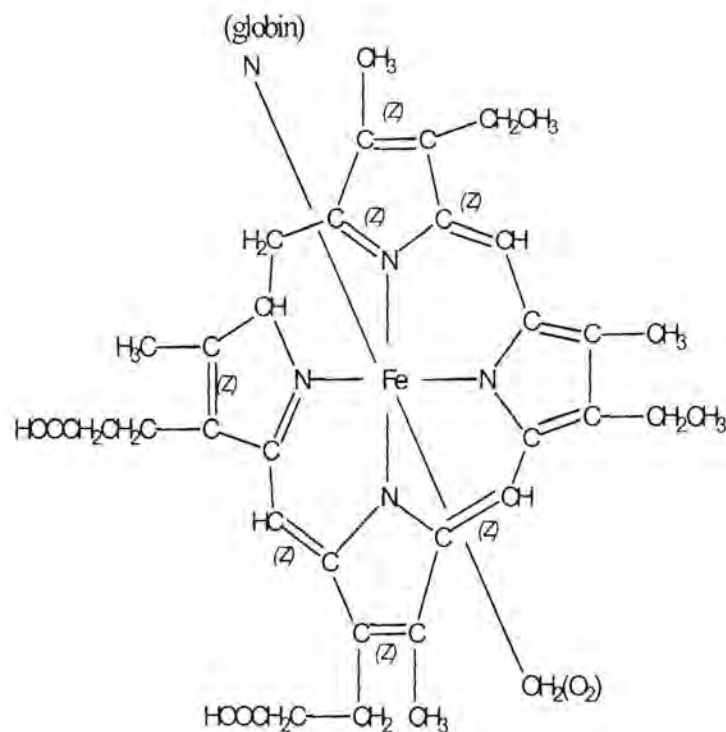

Figure 2.2: Structure of a heam complex

2.5.2.2   Cobalt

The main oxidation states of cobalt are +2 and +3. Cobalt is present as Co(II) in practically all of its simple compounds, whereas simple Co(III) compounds are almost nonexistent in nature. 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). Cobalt(III) complexes form an enormous number of octahedral complexes having the inert t_{2g}^6 configuration. As a result, they have been used for rate and mechanistic studies on octahedral substitution reactions [147]. Cobalt(III) has a greater affinity for nitrogen donors, especially ammonia (NH_3), amine, nitro ($-NO_2$), cyanide ($-CN$) and thiocyanide ($-NCS$) groups. The most important cobalt complex is the vitamin B_{12} complex (Figure 2.3).

Coal contains trace elements, which are in organic association with the coal macerals. These trace elements would therefore be extracted along with the organic components of the coal. Some of these organometallic compounds are porphyrins. Porphyrin complexes of nickel and vanadium (known as molecular fossils) are well known, being derived from the porphyrin structures in chlorophyl and haemoglobin present in the original plant and microbiological source [34]. Cobalt could have originated from vitamin B_{12}, where it is present complexed in the related corrin ring system. Battersby et al. [148] showed that Cu^{II}-porphyrins can be demetalated by combining a protic acid with a reagent that is expected to precipitate or complex the liberated metal ion. This was done by using either 1,2-ethanedithiol, or 1,3-propanedithiol or H_2S. Lewis et al. [149] reported the demetalation of nickel and cobalt from their corrin complexes using Battersby's method but employing 1.3-propanedithiol as complexing agent. However, it appears that applying this demetalation method to the vitamin B_{12} series does not work [150].
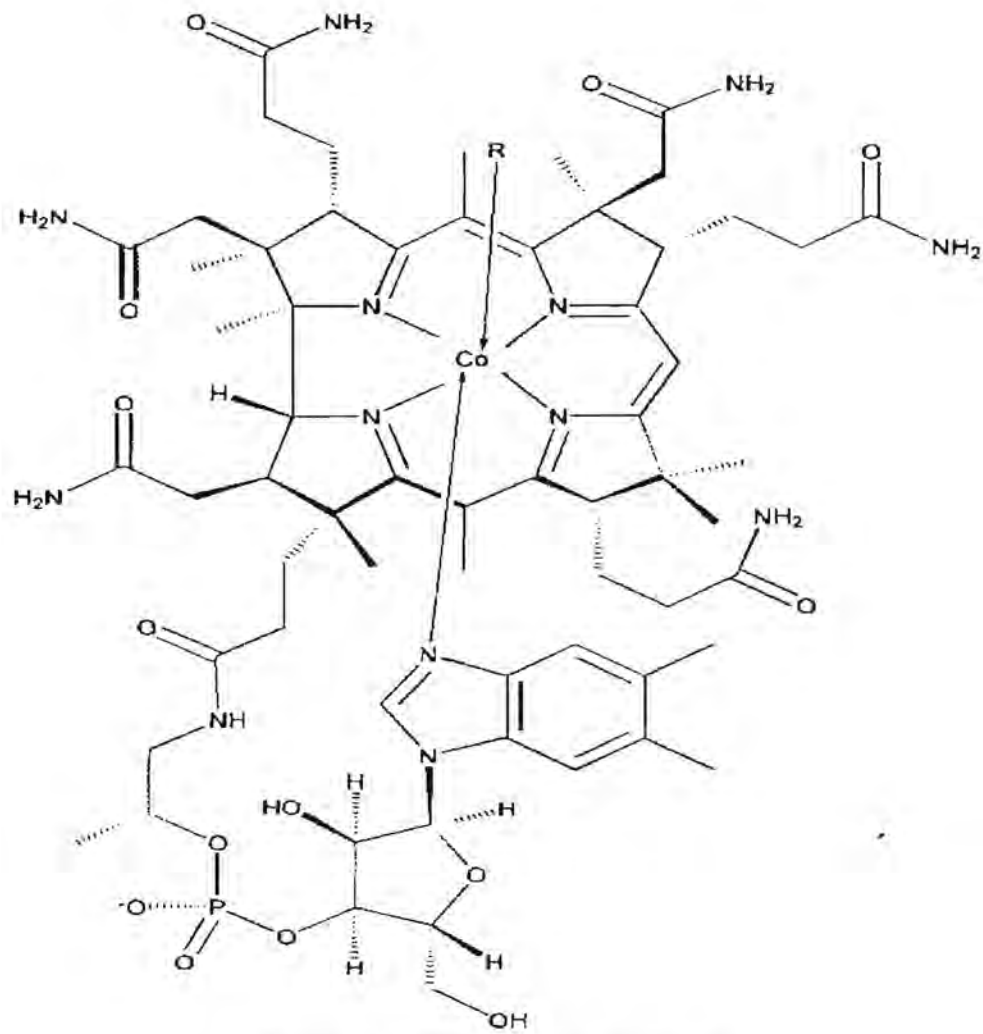
Figure 2.3:Structure of vitamin B$_{12}$

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1   Materials used

All the chemicals used were of analytical grades, unless indicated otherwise. The instruments used were:

- Spectronic Genesis 5 spectrophotometer

- Beckman GPR centrifuge operated at room temperature and a speed of 5 000 r/min

- LKB Bromma 2160 Midispin centrifuge operated at room temperature and 4 000 r/min

- Hettich EBA 3S centrifuge

- Clements GS 150 centrifuge.

The chelating resins used were:

- Bayer's Lewatit TP 260: aminomethylphosphonic acid in disodium form

- Bayer's Lewatit TP 208: Iminodiacetic acid in sodium form

- Bayer's Lewatit TP 214: Thiourea.

Their chemical and physical properties are give in Table 3.1 below.

Table 3.1: Chemical and physical properties of the chelating resins and sulphonic acid resins

[141]

		Lewatit TP 260	Lewatit TP 208	Lewatit TP 214	Sulphonic acid resin SP112
Bead size min. 90%, mm		0.4 – 1.25	0.4 – 1.25	0.4 – 1.25	0.315 - 1.25
Effective size, mm		0.55 ($\pm$ 0.05)	0.55 ($\pm$ 0.05)	0.55 ($\pm$ 0.05)	0.47 ($\pm$ 0.06)
Uniformity coefficient, max.		1.8	1.8	1.8	1.8
Bulk weight ($\pm$ 5%), g/L		770	790	700	840
Density, approx. g/ml		1.2	1.17	1.12	1.27
Water retention, % wt		60	55 – 60	43 – 48	45 - 50
Total capacity, min. eq/L		2.3	2.9	2.0	1.75
Volume change during exhaustion, approx. %				+5	7
Volume change (NaOH), max. %		-25	-40		
Stability	At temperature, °C	-20 up to 85	-20 up to 80	-20 up to 80	-20 up to 120
	In pH range	0 - 14	0 – 14	0 – 14	0 - 14
Storability	Product, min. years	2	2	2	2
	At temperature, °C	-20 up to 40	-20 up to 40	-20 up to 40	-20 up to 40

3.2 Coal studied

A froth floatation coal product from the Tshikondeni Mine in the Limpopo Province was used as received for this study. The particle size of the coal was approximately 0.5 mm. Its analyses are given in Tables 4.1 to 4.3 below, and its swelling number is 8.5.

3.3 Dissolution of coal with dimethylformamide-sodium hydroxide mixture

Coal was dissolved in a mixture of dimethylformamide and sodium hydroxide, using the procedure reported by Morgan [4,112,120]. To a 1 litre reactor with a hot oil jacket and operated at temperatures of 90 to 95 °C, 80 g of coal was charged together with 800 g of fresh dimethylformamide. The mixture was stirred at 700 r/min and allowed to reach operating temperature. At this stage 8 g of sodium hydroxide (CP, Associated Chemical Enterprises), in pearl form, was added. A slow stream of nitrogen was flushed into the dissolver to maintain an inert environment. The progress of extraction was monitored as follows: samples of about 2 cm^3 of the slurry were taken at suitable intervals. The samples

were centrifuged for five minutes at 4 000 r/min using the Hettich or Clements centrifuge. About 0.1 g of the supernatant solution was weighed accurately into a 50 cm³ volumetric flask and made up to the mark with dimethylformamide solvent. The absorbance at 600 nm was read using a Spectronic Genesis 5 spectrophotometer. The measured absorbance was then corrected to a 0.1g sample by multiplying by 0.1g and dividing by the accurate mass of the supernatant solution. The extraction period was four to five hours with the 1 litre reactor. The hot mixture of Refcoal solution and the inorganic components, together with the undissolved organic components of the coal, was transferred into a centrifuge bottle. The mixture was then centrifuged at room temperature and 3 000 r/min for 30 minutes, using the Beckman GPR centrifuge. After centrifugation, the supernatant (Refcoal solution) was separated from the residue by decantation.

3.4 Dissolution of coal with dimethylformamide-sodium hydroxide-sodium sulphide mixture

The same procedure as described in Section 3.3 above was followed. To a 1 litre reactor with a hot oil jacket and operated at temperatures of 90 to 95 °C, 80 g of coal, 800 g of fresh dimethylformamide and 8 g of sodium hydroxide, together with different amounts of anhydrous sodium sulphide ($Na_2S.\,x\,H_2O$) scales ((60 –62%), CP, PAL Chemicals) with $NaOH : Na_2S$ mole ratios of 8:1, 4:1, 2:1 and 1:1 was charged into the reactor and stirred for five to six hours.

3.5 Dissolution of coal with dimethylformamide–sodium sulphide mixture

The same procedure as described Section 3.3 above was followed. To a 1 litre reactor with a hot oil jacket and operated at temperatures of 90 to 95 °C, 80 g of coal was charged together with 800 g of fresh dimethylformamide. The mixture was stirred at 700 r/min and allowed to reach operating

temperature. At this stage anhydrous sodium sulphide ($Na_2S.\ x\ H_2O$) scales ((60 –62%), CP, PAL Chemicals) (6.3 g, 12.6 g and 25.2 g) was added. The mixture was then stirred for five to six hours.

3.6 Recovery of Refcoal

An amount of Refcoal solution (600 g) corresponding to 55 g of Refcoal solid was precipitated in cold (± 2 °C) distilled water (400 g) in a centrifuge bottle. The mixture was then centrifuged for ten minutes at room temperature and 3 000 r/min. The supernatant solution was replaced with an amount (400 g) of fresh distilled water and the Refcoal gel was re-suspended in the water by shaking the mixture for about ten minutes. The resulting mixture was again centrifuged for about ten minutes at room temperature and 3 000 r/min. The resulting Refcoal gel was washed with distilled water (twice with 400 cm^3) by re-suspending it in water, followed by centrifugation. The washed Refcoal gel was either used as is for subsequent experiments or dried in an oven at about 50 °C for at least 16 hours.

3.7 Extraction of mineral matter from Refcoal gel with hydrochloric acid and hydrofluoric acid

Refcoal gel (250 g,corresponding to 50 g of Refcoal solid), obtained as described in Section 3.6, was mixed with 32% hydrochloric acid (70 cm^3). The mixture of acid and Refcoal gel was heated under reflux for 12 hours. Thereafter the acid solution was separated from the Refcoal gel by centrifugation. The Refcoal gel was then washed with distilled water (twice with 500 cm^3), followed by centrifugation. Some of the resulting gel (40 g) was dried in an oven at about 50 °C for 16 hours. The remaining Refcoal gel (200 g) was then mixed with 40% hydrofluoric acid (67 cm^3) in a plastic container, after which the mixture was stirred with gentle heating in an oil bath set at 80°C for 6 hours. The Refcoal gel was then washed with distilled water (twice with 500 cm^3), followed by centrifugation. Some of

the resulting gel (40 g) was dried in an oven at about 50 ºC for 16 hours. The remaining Refcoal gel was then used as it was for subsequent experiments.

3.8   Extraction of trace elements from Refcoal gel with ammonium hydroxide solution

Refcoal gel (100 g, corresponding to 20 g of Refcoal solid), obtained as described in Section 3.6, was mixed with 25% ammonium hydroxide solution (33 cm^3). The mixture of ammonium hydroxide solution and Refcoal gel was stirred at room temperature for 12 hours. The ammoniac solution was then separated from the Refcoal gel by centrifugation. Thereafter the Refcoal gel was washed with distilled water (twice with 500 cm^3), followed by centrifugation. The resulting gel was dried in an oven at about 50 ºC for 16 hours.

3.9   Extraction of trace elements from Refcoal gel with sodium nitrite solution

Refcoal gel (100 g), obtained as described in Section 3.6, was mixed with sodium nitrite solution (5% w/v, 100 cm^3). The mixture of sodium nitrite solution and Refcoal gel was stirred with gentle heating for 12 hours. The sodium nitrite solution was then separated from the Refcoal gel by centrifugation. Thereafter the Refcoal gel was washed with distilled water (twice with 500 cm^3), followed by centrifugation. The resulting gel was dried in an oven at about 50 ºC for 16 hours.

3.10   Extraction of trace elements from Refcoal gel with chelating resins

Refcoal gel (100 g) with a pH of 3 to 4, obtained as described in Section 3.7, was mixed with chelating resin beads (15g). The mixture was stirred in an oil bath set at 80 °C for 48 hours. The resin beads and the Refcoal gel were then separated by filtering through a 150 μm screen. Thereafter the Refcoal gel was washed with distilled water (three times with 200 cm^3), and dried in an oven at about 50 °C for 16 hours.

3.11   Extraction of trace elements from Refcoal gel with sulphonic acid resins

Refcoal gel (100 g) with a pH of 3 to 4, obtained as described in Section 3.7, was mixed with sulphonic acid resin beads (15 g). The mixture was stirred in an oil bath set at 80 °C for 48 hours. The resin beads and the Refcoal gel were then separated by filtering through a 150 μm screen. The Refcoal gel was then washed with distilled water (three times with 200 cm^3), and dried in an oven at about 50 °C for 16 hours.

3.12   Extraction of trace elements from Refcoal gel with anionic resins

Refcoal gel (100 g), obtained as described in Section 3.8, was mixed with anionic resin beads (15 g). The mixture was stirred at room temperature for 48 hours. The resin beads and the Refcoal gel were then separated by filtering through a 150 μm screen. Thereafter the Refcoal gel was washed with distilled water (three times with 200 cm^3), and dried in an oven at about 50 °C for 16 hours.

3.13   Extraction of trace elements from Refcoal solution with chelating resins

Refcoal solution (200 g) was mixed with chelating resin beads (30 g). The mixture was stirred at 80 °C for 48 hours. The resin beads and the solution were then separated using a 150 μm screen. The Refcoal solution was precipitated in cold (± 2 °C) distilled water (200 g). The precipitated Refcoal was then filtered through a filter paper and washed with distilled water (three times with 200 cm^3). Thereafter the Refcoal was dried in an oven at about 50 °C for 16 hours.

3.14   Extraction of trace elements from Refcoal solution with sulphonic acid resins

Refcoal solution (200 g) was mixed with sulphonic acid resin beads (30 g). The mixture was stirred at 140 to 145 °C for 48 hours. The resin beads and the solution were then separated using a 150 μm screen. The Refcoal solution was precipitated in cold (± 2 °C) distilled water (200 g). The precipitated Refcoal was then filtered through a filter paper and washed with distilled water (three times with 200 cm^3). Thereafter the Refcoal was dried in an oven at about 50 °C for 16 hours.

3.15   Colorimetric determination of cobalt

Refcoal was first digested using the procedure given in the literature [142]. About 1 g of Refcoal was weighed accurately into a 250 cm^3 conical flask. An amount of 6 cm^3 of concentrated sulphuric acid was then added to the Refcoal and the mixture heated for about 30 minutes. Thereafter 10 cm^3 of concentrated nitric acid was added and the mixture heated to SO_3 fumes. Then a second 10 cm^3 of concentrated nitric acid was carefully added and the mixture was again heated to SO_3 fumes. Following this, three portions of 20 cm^3 30% H_2O_2 were carefully added, with the mixture being heated to SO_3 fumes after each addition. When the digestion was complete, all or almost all of the sulphuric acid was

fumed off. An amount of 4 cm^3 of concentrated nitric acid was then added and the mixture heated to dryness. After this, 20 cm^3 of distilled water and 5 cm^3 of concentrated hydrochloric acid were added and the mixture boiled until all residues had dissolved. Lastly, 10 cm^3 of distilled water was added, followed by cobalt, determined according to the procedure given by Claassen and Daamen [143].

A citric acid solution was made by dissolving 400 g of citric acid in distilled water, and the volume made up to 1 000 cm^3. A 2-nitroso-1-naphthol solution was prepared by dissolving 1 g of 2-nitroso-1-naphthol in 100 cm^3 of concentrated acetic acid. Activated carbon was added to this solution and the solution filtered before use. An amount of 1.1016 g of anhydrous CoCl$_2$ was weighed accurately into a 500 cm^3 volumetric flask. Then 5 cm^3 of concentrated hydrochloric acid was added to the flask and the volume made up to 500 cm^3 with distilled water to prepare a solution containing 1 000 ppm Co. From this solution, a series of dilutions was made to prepare calibration standards containing 0, 1, 2, 5,10, 15, 20, 50, 100, 150 and 200 μg Co.

A 10 cm^3 solution of each of the standards and samples was added to 10 cm^3 of the citric acid solution in 100 cm^3 beakers. The pH of the solution was adjusted to about 4 by the addition of 2 M hydrochloric acid or 2 M sodium hydroxide, using a pH paper as indicator. The solution was cooled to room temperature, and 10 cm^3 of 3% hydrogen peroxide was added, followed by 2 cm^3 of 2-nitroso-1-naphthol solution. The solution was allowed to stand at room temperature for 30 minutes. The solution was then transferred to a 100 cm^3 separating funnel, with the beaker being washed twice with 5 cm^3 of chloroform, which was then added to the separating funnel. Chloroform was then added to the separating funnel to a total volume of about 25 cm^3, and the mixture shaken vigorously for about 1 minute. After complete separation of the layers, the chloroform was drawn off into a 50 cm^3 volumetric flask and the extraction was repeated twice with 10 cm^3 of chloroform. The combined chloroform extracts were diluted to the mark with chloroform and mixed thoroughly. The chloroform solution was then transferred to a clean 100 cm^3 separating funnel, 20 cm^3 of 2 M hydrochloric acid solution was

added and the mixture was shaken well for about 1 minute. The chloroform solution was then drawn

off to a clean 100 cm^3 separating funnel, 20 cm^3 of 2 M sodium hydroxide solution was added and the

mixture was shaken well for about 1 minute. The chloroform solution was then drawn off to a clean

100 cm^3 separating funnel, 20 cm^3 of 2 M sodium hydroxide solution was again added and the mixture

was shaken well for about 1 minute. Finally, the chloroform solution was drawn through a small plug

of cotton wool in the stem of a funnel into a clean 50 cm^3 volumetric flask. The absorbances of both

samples and standards were measured at 529.9 nm using the Spectronic Genesis 5 spectrophotometer.