

Coal Purification

by

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Abstract

Coal is available in relative abundance worldwide and therefore can be used as an inexpensive precursor for the production of high purity carbon. High-purity carbon is required for the manufacture of pure graphite used as a moderator for nuclear reactors. High-purity coal suitable for the production of high-purity carbon is produced by treating the coal to remove the bulk of the mineral matter content. Purifying the coal before usage has some cost advantage since it could eliminate the need for expensive high-temperature purification during graphitisation.

The aim of this study was to reduce the inorganic mineral content of coal. For this purpose, Tshikondeni coking coal floatation concentrate was used which had an ash content of 9.4% by mass and a sulphur content of 0.81%. This coal was subjected to step-wise purification. The concentration levels of Ba, Co, Cr, Cs, Eu, Fe, Hf, La, Sc, Sm, Ta, Tb, Th, and U were determined by instrumental neutron-activation analysis.

The bulk of the minerals was removed by extracting the organic part of the coal into a polar aprotic solvent. The resulting solution was then centrifuged to separate the inorganic mineral matter and the undissolved organic matter from the solution. The coal material was recovered as a gel by precipitation with water and was then washed thoroughly with water to remove water-soluble products. The resulting coal material had an ash value of 1.7% by mass. At this stage of the purification process, the concentration levels of the elements Ba, Co, Cr, Cs, Eu, Fe, Hf, La, Sc, Sm, Ta, Tb, Th, and U were still high in relation to nuclear carbon. The purification value of these elements was below 20. Most of these elements are unimportant with respect to nuclear-grade carbon, but the elements cobalt (Co), which becomes activated by neutron capture, the rare-earth elements (e.g. europium [Eu] and samarium [Sm]), which are neutron absorbers and sodium (Na), which is an oxidation catalyst, are undesirable.

An attempt was made to purify the coal extracts by either treating the coal solution with chelating resins and sulphonic acid resins, or treating the gel with anion exchange resins in a form of beads. In the latter case, the coal solution is filtered to separate the purified coal from the resin beads, followed by precipitation with water to recover the coal material. The purification values for all the elements determined are below 20 for sulphonic acid resins and chelating resins. Improved reduction in tantalum (Ta) concentration is observed with anion resins which suggests that tantalum exists as an anion in the coal matrix whereas the rare-earth metals exist as cations.

Recovered coal gel was first treated with concentrated hydrochloric acid to remove the acid-soluble products. These include the ions that form insoluble fluorides, e.g. calcium ions. The resulting coal gel was then treated with concentrated hydrofluoric acid to remove the silicates. Finally, the acid-treated gel was treated with chelating resin beads and sulphonic acid resin beads, and then filtered

to separate the purified coal material from the resin beads.

Purification values above 20 for the elements Cs, Eu, Fe, La, Sc, Sm, and Tb were achieved when the coal gel was treated with acid. Treatment with chelating resins gave purification values of 20 and above for the elements Ba, Cs, Eu, Fe, Hf, La, Sc, Sm, Tb, Th and U, while treatment with sulphonic acid resins resulted in purification values of 20 and above for the elements Ba, Cs, Eu, Fe, Hf, La, Sc, Sm, Ta, Tb, Th and U.

Treating the gel with concentrated acid followed by sulphonic acid resins was found to be the best method for reducing the concentration of alkali metals (represented by cesium [Cs]) and rare-earth elements (e.g. europium [Eu] and samarium [Sm]). Treating the gel with acid followed by chelating resins was the second best method. Solvent extraction alone did not yield satisfactory results and neither did ion-exchange treatment of the coal solution. No significant purification of cobalt could be achieved, suggesting that this element is held strongly in organometallic complexes in the coal matrix as a result of which the rate of exchange with the resins is slow.

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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 CO₂), 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, gallium, 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 °C 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 °C. 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 heterogeneous 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/cm³. 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 cm³/g for vitrinites with 71% carbon, to 0.03 cm³/g for vitrinites with 94% carbon, apparently passing through a minimum of 0.025 cm³/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, alginite 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/cm³. 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/cm³. 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 ($\text{Al}_2\text{Si}_2\text{O}_5\text{OH}$) and clays (e.g. $(\text{NaMg,Al})\text{Si}_4\text{O}_{10}(\text{OH})_2$), 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 ($\text{Na}_8\text{Si}_6\text{Al}_6\text{O}_{24}$). 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 H₂SO₄, followed by washing with HNO₃. 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 (CaF₂), magnesium fluoride (MgF₂) and fluoroaluminate compounds such as NaAlF₄, MgAlF₅ and K₂NaAlF₆. 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 CaF₂, MgF₂, NaAlF₄ and MgAlF₅. According to the model, CaF₂, MgF₂, MgAlF₅ and NaAlF₄ will precipitate at 65 °C when the concentrations of Ca²⁺, Mg²⁺, Na⁺ and F⁻ in solution are such that Equations 2.3.3.1 to 2.3.3.4 below are satisfied respectively.

$$[\text{Ca}^{2+}][\text{F}^-]^2 \geq 2.45 \times 10^{-10} \quad (2.3.3.1)$$

$$[\text{Mg}^{2+}][\text{F}^-]^2 \geq 2.63 \times 10^{-9} \quad (2.3.3.2)$$

$$[\text{Mg}^{2+}][\text{AlF}_5^{2-}] \geq 3.64 \times 10^{-6} \quad (2.3.3.3)$$

$$[\text{Na}^+][\text{AlF}_4^-] \geq 1.21 \times 10^{-5} \quad (2.3.3.4)$$

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 CS₂-N-methyl-2-pyrrolidinone (NMP) mixed solvent at room temperature was reported by Iino et al. [117] to give higher yields than CS₂-pyridine. The anthracites, subbituminous coals and lignites gave low extraction yields.

The process for the CS₂-NMP mixed solvent involved the extraction of the coal sample with CS₂-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:

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

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:

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

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,



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 have 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.

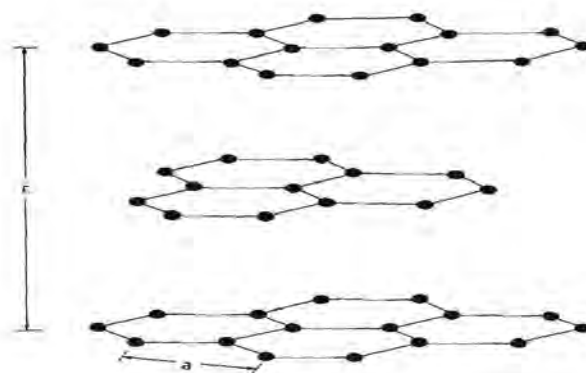


Figure 2.1: The graphite crystal lattice [9]

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:

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

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 °C 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 °C, 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

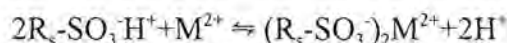
2.5.1 Ion exchange

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 $-\text{SO}_3^-$ 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:



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]:

$$D = \frac{\text{amount of element in resin}}{\text{amount of element in solution}} \times \frac{\text{volume of solution, (cm}^3\text{)}}{\text{weight of dry resin, (g)}}$$

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 $10^{-9}\text{m}\cdot\text{s}^{-1}$, which indicates that the

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]:

$\text{UO}_2^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} > \text{alkali metals};$

$\text{Cu}^{2+} > \text{VO}^{2+} > \text{UO}_2^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Be}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} > \text{Na}^+$

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].

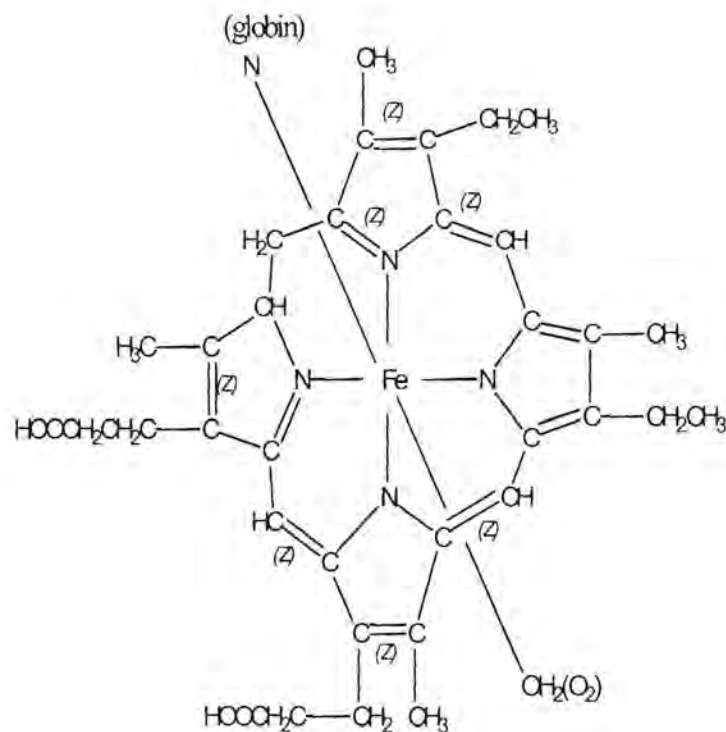


Figure 2.2: Structure of a haem complex

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 ($-\text{NO}_2$), cyanide ($-\text{CN}$) and thiocyanide ($-\text{NCS}$) 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 chlorophyll 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].

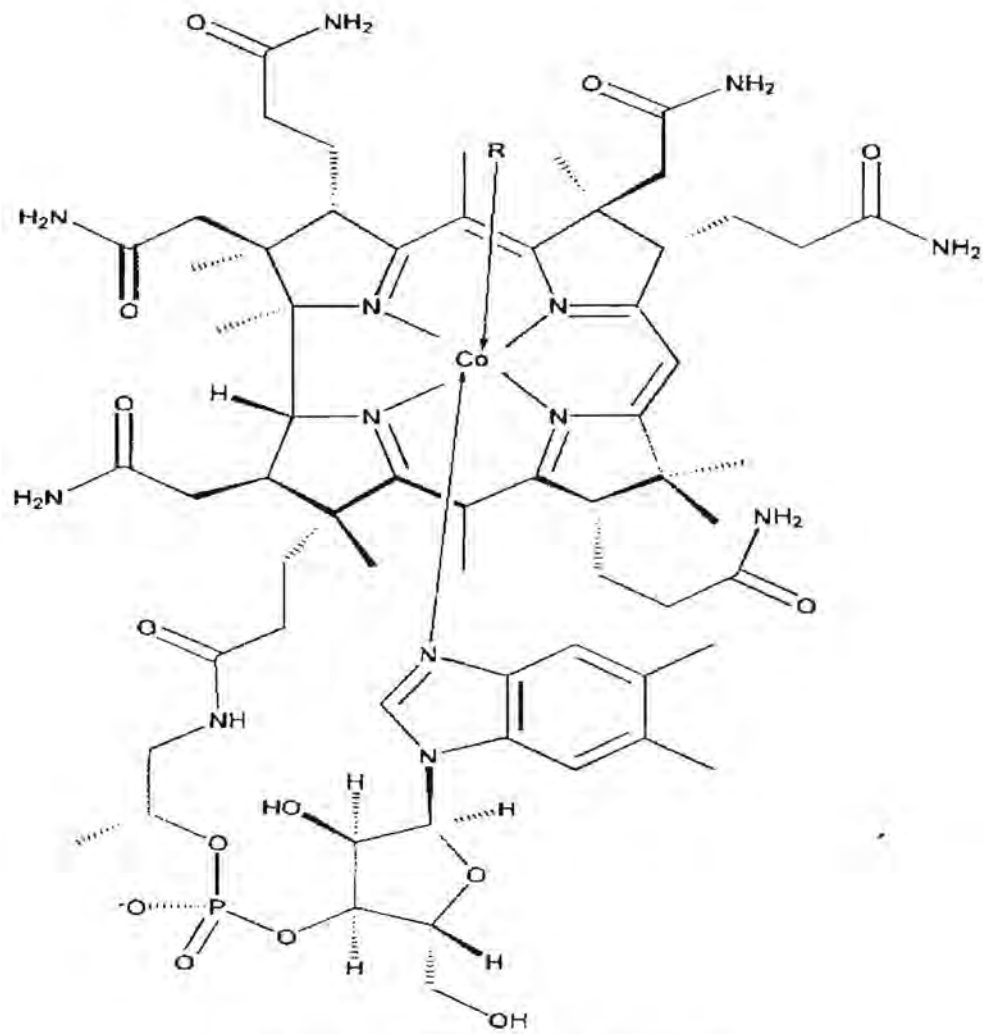


Figure 2.3: Structure of vitamin B₁₂

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
	In pH range	0 - 14	0 - 14	0 - 14
Storability	Product, min. years	2	2	2
	At temperature, °C	-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 cm³ 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 ($\text{Na}_2\text{S} \cdot x \text{H}_2\text{O}$) 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 ($\text{Na}_2\text{S} \cdot x \text{H}_2\text{O}$) 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 ($\pm 2^\circ\text{C}$) 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 °C 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 cm³). 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 cm³), followed by centrifugation. The resulting gel was dried in an oven at about 50 °C 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 cm³). 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 cm³), followed by centrifugation. The resulting gel was dried in an oven at about 50 °C 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 cm³), 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 cm³), 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 cm³), 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 cm³). 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 cm³). 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 cm³ conical flask. An amount of 6 cm³ of concentrated sulphuric acid was then added to the Refcoal and the mixture heated for about 30 minutes. Thereafter 10 cm³ of concentrated nitric acid was added and the mixture heated to SO₃ fumes. Then a second 10 cm³ of concentrated nitric acid was carefully added and the mixture was again heated to SO₃ fumes. Following this, three portions of 20 cm³ 30% H₂O₂ were carefully added, with the mixture being heated to SO₃ fumes after each addition. When the digestion was complete, all or almost all of the sulphuric acid was

fumed off. An amount of 4 cm³ of concentrated nitric acid was then added and the mixture heated to dryness. After this, 20 cm³ of distilled water and 5 cm³ of concentrated hydrochloric acid were added and the mixture boiled until all residues had dissolved. Lastly, 10 cm³ 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 cm³. A 2-nitroso-1-naphthol solution was prepared by dissolving 1 g of 2-nitroso-1-naphthol in 100 cm³ 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 CoCl₂ was weighed accurately into a 500 cm³ volumetric flask. Then 5 cm³ of concentrated hydrochloric acid was added to the flask and the volume made up to 500 cm³ 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 cm³ solution of each of the standards and samples was added to 10 cm³ of the citric acid solution in 100 cm³ 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 cm³ of 3% hydrogen peroxide was added, followed by 2 cm³ 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 cm³ separating funnel, with the beaker being washed twice with 5 cm³ 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 cm³, and the mixture shaken vigorously for about 1 minute. After complete separation of the layers, the chloroform was drawn off into a 50 cm³ volumetric flask and the extraction was repeated twice with 10 cm³ 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 cm³ separating funnel, 20 cm³ 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 cm³ separating funnel, 20 cm³ 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 cm³ separating funnel, 20 cm³ 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 cm³ volumetric flask. The absorbances of both samples and standards were measured at 529.9 nm using the Spectronic Genesis 5 spectrophotometer.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Coal studied

The Tshikondeni coal studied was submitted to Coal and Mineral Technologies (Pty) Ltd for proximate and ultimate analysis, major ash analysis and the determination of major petrographic characteristics. Table 4.1 lists the results for the proximate analysis on an air-dry basis and the ultimate analysis. Table 4.2 lists the major ash percentages. The major petrographic characteristics of Tshikondeni coal are shown in Table 4.3. The coal is classified as meta-bituminous (medium rank B), similar to the coal used by Stiller et al. [107 - 109], and has a vitrinite content of 93%.

Table 4.1: Proximate (air-dry-basis) and ultimate analysis of Tshikondeni coal

PROXIMATE ANALYSIS		ULTIMATE ANALYSIS (DRY ASH FREE)	
Moisture	0.9%	Carbon	90.86%
Ash	9.4%	Hydrogen	4.88%
Volatile matter	23.3%	Nitrogen	2.07%
Fixed carbon	66.4%	Oxygen (by difference)	2.19%
Total sulphur	0.81%		

Table 4.2: Ash analysis of Tshikondeni coal

SiO ₂	51.4%
Al ₂ O ₃	25.5%
Fe ₂ O ₃	6.00%
P ₂ O ₅	0.82%
TiO ₂	2.24%
CaO	5.05%
MgO	2.52%
K ₂ O	1.46%
Na ₂ O	0.36%
SO ₃	4.45%
TOTAL	99.79

Table 4.3: Major petrographic characteristics

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

4.2 Dissolution of coal and Refcoal recovery

Figure 4.1 is a plot of absorbance (section 3.3 above) versus time, showing the progress of the different extraction runs with sodium hydroxide and dimethylformamide only. The data for the different extraction runs are given in Appendix 2, Table A2.1. The extraction process shows S-shape progression nature of the CSIR-developed Refcoal process, as reported [4,112,120]. All the curves show an induction period of about 15 minutes, which is representative of the S-shape progression. The maximum absorbance was about 1.00; this is consistent with the literature report [112,120] which implies that the solution obtained was an 8% solution. The Refcoal is recovered from the solution either by evaporating the solvent or by precipitation in water. Recovery of Refcoal by precipitation is preferred because, as reported in the literature, this lowers the amount of ash in the Refcoal, furthermore, Refcoal recovered by precipitation forms better coke. Therefore, for the purpose of this study, the Refcoal was recovered by precipitation in water.

As reported, H_2S together with propane-triol aids in the demetalation of porphyrins. It was reasoned that a promising approach would be to introduce Na_2S into the extraction vessel during extraction to aid in complexing the metal ions released and thus precipitate them with the rest of the residue separated from the Refcoal solution. Not all the elements are likely to be associated with the porphyrin-type complexes, with nitrogen bonding to the central metal atom. Oxygen-loving elements such as boron, titanium, zirconium and tungsten are more likely to be associated with the polyhydroxy, or hydroxy-acid types of compound.

It was noticed that, on coking, the Refcoal derived from extraction with both sodium hydroxide and sodium sulphide hydrate swells better than the Refcoal derived from extraction with sodium hydroxide only. The better swelling implies that the Refcoal extracted with both sodium hydroxide and sodium sulphide goes through a more liquid phase, which suggests a better mesophase.

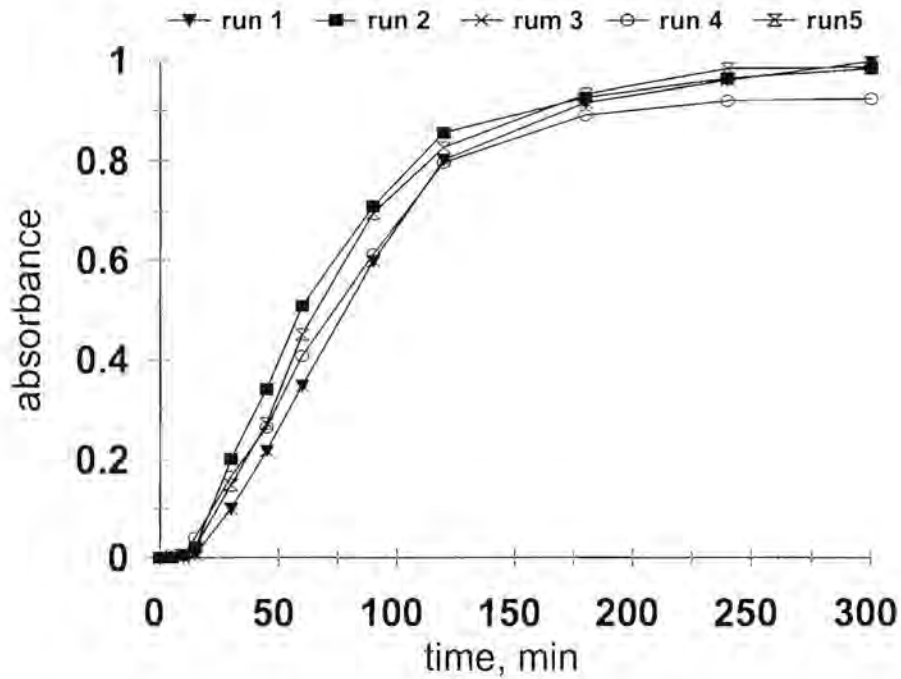


Figure 4.1: Progress of extraction with NaOH only showing reproducibility of the method. Mass ratio used is 100:10:1, DMF:Coal:NaOH

The swelling was determined at Coal and Mineral Technologies (Pty) Ltd by measuring the change in volume as the sample is taken from low temperature to about 500 °C in an inert atmosphere. Table 4.4 lists the swelling numbers for the Refcoal extracted with sodium hydroxide only and that extracted with both sodium hydroxide and sodium sulphide. Refcoal extracted with sodium hydroxide only gave a swelling number of 4.5, while Refcoal extracted with both sodium hydroxide and sodium sulphide gave swelling numbers of 9.0 and 9.5.

Table 4.4: Ash contents and swelling numbers of Refcoal

Mole ratio (NaOH:Na ₂ S)	Ash (%)	Total sulphur (%)	Swell (#)
1 : 0	1.7	0.72	4.5
2 : 1	1.2	0.78	9
4 : 1	7.4	1.03	9.5
8 : 1	5.6	1.78	9
1 : 1	3.3	1.12	9.5

Table 4.5: Percentage solids in Refcoal derived from the extraction with sodium sulphide

mass of Na ₂ S	with sodium hydroxide	without sodium hydroxide
6.3g	9%	6%
12.6g	6%	2%
25.2g	3%	2%

The better foaming during coking of Refcoal extracted using both sodium hydroxide and sodium sulphide prompted us to do optimisation experiments with different NaOH:Na₂S mole ratios. Figure 4.2 is a plot of absorbance versus time, showing the progress of extraction with the different doses of sodium sulphide used together with a fixed amount of sodium hydroxide. The amount of sodium sulphide used in these experiments was determined as a mole ratio to the amount of sodium hydroxide. The different data are given in Appendix 2, Table A2.2. The amount of sulphur increased, which could be the result of the added sulphide or could be due to insufficient washing during the Refcoal recovery. The ash content of the Refcoal extracted using both sodium hydroxide and sodium sulphide is higher than that obtained by extraction using sodium hydroxide only. This could be due to insufficient washing during the Refcoal recovery. In an industrial process where counter-current is employed to wash the Refcoal during the recovery process, both the ash and the sulphur content could be significantly

lowered. Table 4.5 lists the percentage solids in Refcoal solution obtained from the extraction with varying amounts of sodium sulphide, calculated according to the following equation:

$$\%Solids = \frac{\text{mass of dry solids}}{\text{mass of coal solution}} \times 100$$

The dry coal solids were obtained by precipitating a known amount of coal solution in water. The results show a decrease in the percentage solids from 9% to 3% in the Refcoal solution derived from extraction using both sodium hydroxide and sodium sulphide. As indicated in Figure 4.3, the smaller the amount of sodium sulphide used, the better the extraction. Extraction with smaller amounts of sodium sulphide, i.e. the 10:1, 8:1 and 4:1 NaOH:Na₂S mole ratios, gave better extraction of the coal. Extraction using larger amounts of sodium sulphide, i.e. a 1:1 NaOH:Na₂S mole ratio, gave poor extraction results. Figure 4.3 is a plot of absorbance versus time of the different runs for the 1:1 NaOH:Na₂S mole ratio. The detailed data are given in Appendix 2, Table A2.2. The curve showing the progress of this extraction goes through a maximum and then drops to an absorbance of about 0.200.

The drop in the absorbance may be due to moisture released by the sodium sulphide reagent, which inhibits the extraction of coal, as reported by Morgan [112,120], or may be due to some chemical reaction or back-precipitation of the dissolved coal. By comparison with the extraction using sodium hydroxide only (0:1 ratio, Figure 4.2), the extraction using both sodium hydroxide and sodium sulphide is faster at the beginning and gradually slows down. The increased rate of extraction could be a result of the dissolved sulphide at the beginning of the extraction process acting as a phase-transfer catalyst. The slowing down of the extraction rate may be due to a side-reaction releasing some inhibitors such as water and/or oxygen, which slow down the extraction, as reported in the literature [112,120].

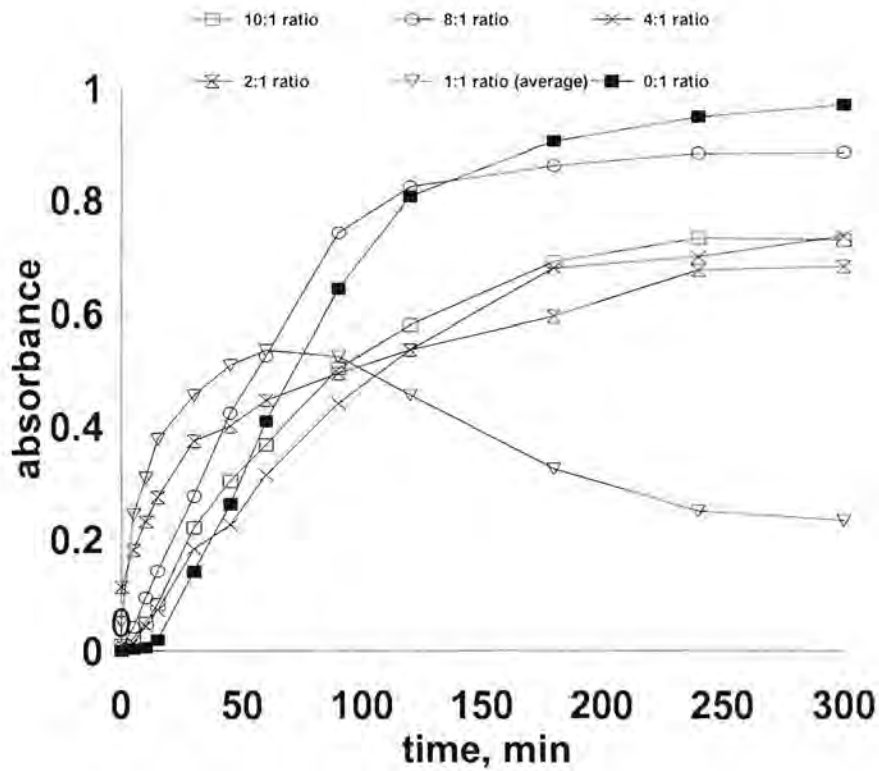


Figure 4.2: Progress of extraction with NaOH, showing different doses of Na₂S. Mass of DMF used: 800 g, mass of coal: 80 g, mass of NaOH: 8 g

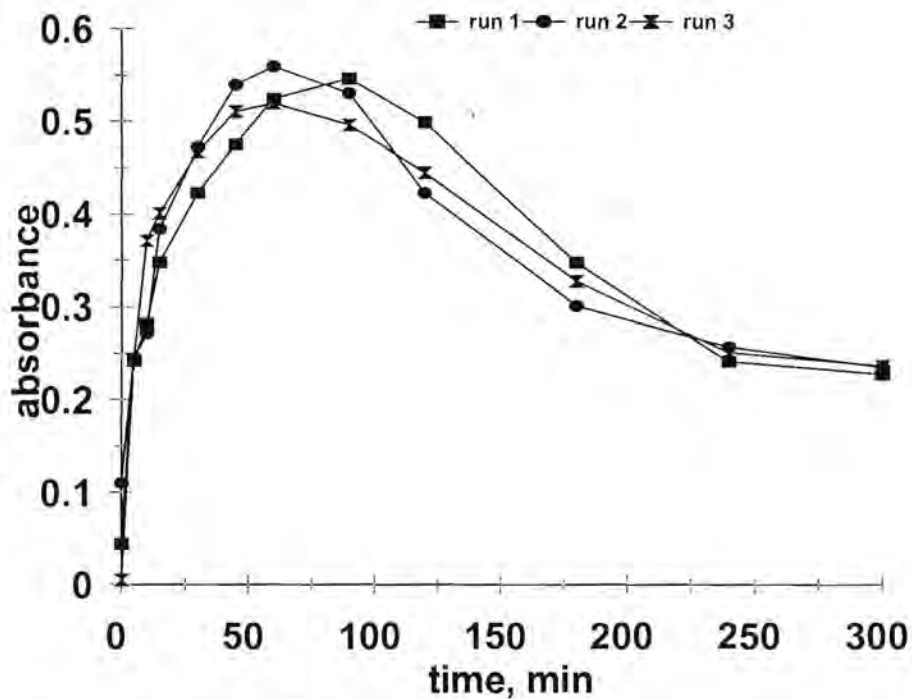


Figure 4.3: Progress of extraction showing bleaching effect of high doses of Na₂S. Mass of DMF:800 g, mass of coal: 80 g, mass of NaOH: 8 g and mass of Na₂S: 25.2 g

In order to minimise the impurities introduced into the Refcoal, we attempted the extraction of coal using dimethylformamide and sodium sulphide only. The same amounts of sodium sulphide used for the extraction using both sodium hydroxide and sodium sulphide were used for these experiments. Figure 4.3 is a plot of absorbance versus time, showing the progress of extraction without sodium hydroxide for the different doses of sodium sulphide (6.34 g, 12.61 g and 25.17 g). The detailed data are given in Appendix 2, Table A2.3. The results show a decrease in the percentage solids from 6% to 2% (Table 4.5) in the Refcoal solution derived from extraction using sodium sulphide only. Therefore, the resulting Refcoal solution was less than 8%. As indicated in Figure 4.5, the absorbance with the different amounts of sodium sulphide is less than 0.500, which is less than the absorbance of 1.00 for an 8% solution. This suggests that sodium sulphide alone is not suitable for extracting a reasonable amount of carbon from coal because the sulphide is a weaker nucleophile than the hydroxide. A strong nucleophile is required to extract a reasonable amount of carbon from coal. The extractions using large amounts of sodium sulphide (25.17 g), both those with sodium hydroxide and sodium sulphide and those with sodium sulphide only, gave the same results. For both the experiments, the curves (Figures 4.3 and 4.5) showing the progress of the extraction using a large amount of sodium sulphide go through a maximum and then drop to an absorbance of about 0.200. This shows that the behaviour was also reproducible for the extraction with sodium sulphide only (Figure 4.5). As mentioned before, this may be due to moisture released by the sodium sulphide, which inhibits the extraction of coal, as reported by Morgan [112,120], or may be due to some chemical reaction or back-precipitation of the dissolved coal.

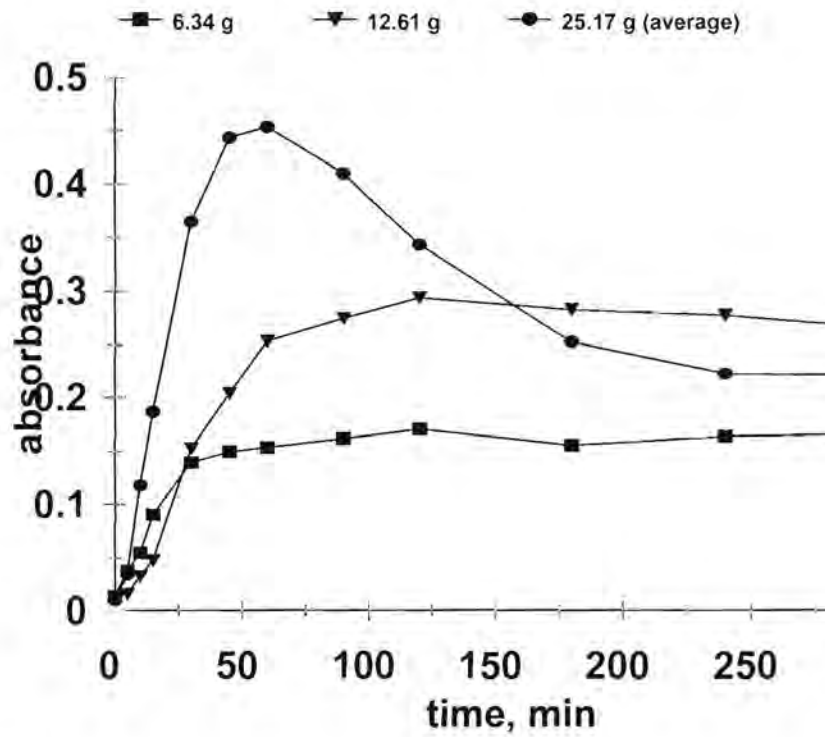


Figure 4.4: Progress of extraction without NaOH, showing different doses of Na₂S. Mass of DMF used: 800g, mass of coal: 80g

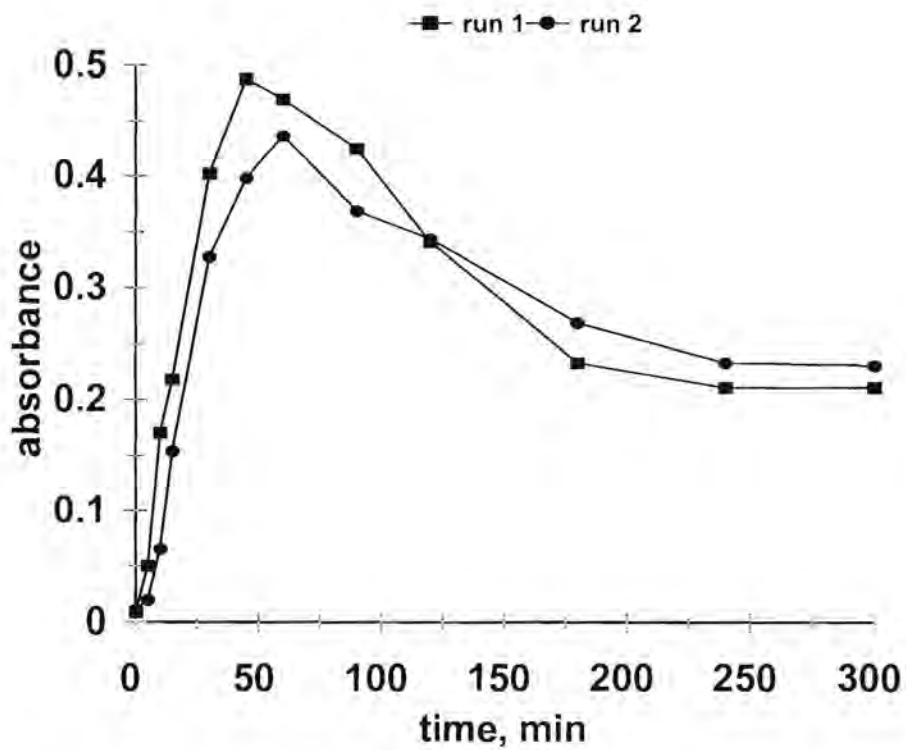


Figure 4.5: Progress of extraction without NaOH, showing bleaching effect of Na₂S. Mass of DMF: 800 g, mass of coal: 80 g and mass of Na₂S: 25.2 g

4.3 Trace element analysis

Trace element analysis of the original coal, unpurified Refcoal, acid-treated Refcoal and resin-treated Refcoal was done by means of ICP-AES and INAA. The dried samples of the original coal, unpurified Refcoal and purified Refcoal were submitted to Dr R. Hart of the Schonland Research Centre at the University of the Witwatersrand for analysis by INAA. Samples were also submitted to the National Energy Corporation of South Africa (NECSA) for analysis by ICP-AES. INAA and ICP-AES are very much standard techniques which were at our disposal. Table 4.6 lists the concentrations of trace elements as determined by ICP-AES. The concentrations are averages of two determinations. As indicated, the concentrations of most of the elements determined were less than the detection limits, but the cobalt concentrations were shown to be consistently higher. The high cobalt concentrations could probably be due to method error. ICP-AES is not suitable for determining the concentrations of trace elements in the unpurified Refcoal, acid-treated Refcoal and resin-treated Refcoal since these elements are present in concentrations lower than the detection limits for this method. The analysis of the trace elements for most of this work was therefore done by means of INAA. INAA is a good choice for this work because, with the exception of boron, trace elements which are easily activated by neutrons can be determined satisfactorily. A major disadvantage of this method, however, is the time it takes to analyse a set of samples. It took eight to twelve weeks before we could obtain the results of the samples submitted for analysis. Consequently, not many repetitive samples could be analysed for this work. The results of the analyses are shown in Appendix 2, Tables A2.1 to A2.4, as sample RC for the original coal, RCW for the unpurified Refcoal, RCA for the acid-treated Refcoal and RCR for the resin-treated Refcoal. Samples analysed for both unpurified and purified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, were only those with the 8:1 NaOH:Na₂S mole ratios.

Table 4.6: Concentrations of trace elements in Refcoal as determined by ICP-AES (ppm)

Element	DL	RCW	RCA1	RCA2	RCA3	RCR1	RCR2
B	19	< 19	< 19	< 19	< 19	< 19	< 19
Ca	3	20	< 3	< 3	< 3	< 3	< 3
Cd	1	< 1	< 1	< 1	< 1	< 1	< 1
Co	10	59	53	57	52	64	53
Cr	5	10	< 5	< 5	< 5	< 5	< 5
Cu	3	21	< 3	13	< 3	< 3	4
Dy	3	< 3	< 3	< 3	< 3	< 3	< 3
Eu	1	< 1	< 1	< 1	< 1	< 1	< 1
Fe	3	299	92	4	< 3	223	237
Gd	13	< 13	< 13	< 13	< 13	< 13	< 13
Mg	1	43	< 1	< 1	< 1	11	26
Mn	4	< 4	< 4	< 4	< 4	< 4	< 4
Mo	4	< 4	< 4	< 4	< 4	< 4	< 4
Ni	21	< 21	< 21	< 21	< 21	< 21	< 21
Sm	40	< 40	< 40	< 40	< 40	< 40	< 40
Sn	118	436	391	422	390	452	320
Ti	24	1161	1062	816	629	1162	1189
V	6	35	32	23	15	36	36
Zn	12	41	< 12	< 12	16	< 12	18

Note: DL = Detection limit; RCW = unpurified Refcoal; RCA = acid-treated Refcoal; RCR = chelating (TP260) resin-treated Refcoal

4.3.1 Trace element analysis of unpurified Refcoal

Table 4.7 and Table 4.8 list the concentrations of the elements Ba, Br, Co, Cr, Cs, Fe, Hf, La, Sc, Sm, Ta, Tb, Th and U, monitored for the original coal and unpurified Refcoal. The concentrations given are an average of at least two determinations as given in Appendix 3. Table 4.9 lists the extent of purification, calculated as a ratio of concentration in the original coal to concentration in the Refcoal.

for each of the elements monitored. The extent of purification is discussed below:

Barium: The barium concentration was lowered from 3 190 ppm in the original coal to 202 in unpurified Refcoal derived from the extraction with sodium hydroxide only. The barium concentration was lowered from 3 190 ppm in the original coal to 448 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. In both cases the leaching of barium is high, which suggests that barium is predominately in inorganic association in the original coal. Using barium as an indicator element for alkaline earth metals, we can conclude that these elements are predominantly in inorganic association in coal, and therefore can be easily separated from the organic component of the coal. This observation is consistent with those made in the literature [17,20 - 25]. Barium has a boron equivalent of 1×10^{-4} , which means that a concentration of 202 ppm is not a cause for concern with regard to nuclear graphite, since further purification of the Refcoal should be able to bring down the concentration to below 10 ppm.

Bromine: The bromine concentration was lowered from 4.1 ppm in the original to 0.7 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only. The bromine concentration was lowered from 4.1 ppm in the original to 0.9 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The high purification values for bromine in both cases suggests that bromine is predominately in inorganic association in the original coal, which is not consistent with literature report [26]. With respect to nuclear graphite, the amount of bromine in the coal is unimportant since this will easily come off the coal matrix during carbonisation.

Cesium: The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.3 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 1.1 ppm in the original coal to 0.11 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The purification value of 10 suggests that cesium occurs predominantly in

inorganic association in the coal. Cesium has been reported to occur predominantly in inorganic association in coal [26], which is consistent with the observations made here. If we use cesium as the indicator element, we can conclude that alkali metals are predominantly in inorganic association in the coal matrix, and therefore can be easily separated from the organic component of the coal. A purification value of 3.7, obtained from the unpurified Refcoal derived from the extraction with sodium hydroxide only, indicates a high recovery of cesium, which suggests contamination and/or analytical variations. Cesium has a boron equivalent of 3×10^{-3} . With respect to nuclear carbon, this does not pose a serious problem since at a concentration of less than 1 ppm, the boron equivalent will be less than 3×10^{-3} .

Cobalt: The concentration of cobalt was lowered from 8.7 ppm in the original coal to 6.9 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only. The concentration of cobalt was lowered from 8.7 ppm in the original coal to 4.8 ppm in untreated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. High recoveries of cobalt were observed; this suggests the presence of organometallic species, which are soluble in organic solvents. This is consistent with the observations reported [26]. In some experiments, the cobalt concentrations were higher in the unpurified Refcoal than in the original parent coal. The high cobalt concentration could be due to contamination or analytical variations. Since the concentration of cobalt drops with subsequent purification of the Refcoal, this observation suggests that the contamination occurred during extraction to prepare the unpurified Refcoal. The high recoveries of cobalt could have arisen from the stainless steel reactor vessel and its components, or the reagents used. Samples taken from the reactor lid, the stirrer blade, the stirrer, reactor blades, and reactor wall were sent to the Department of Metallurgy of the University of Pretoria for cobalt analysis by the transmission electron microscopy (TEM). As indicated in Figures A3.1 – A3.7 in Appendix 3, these samples did not show any presence of cobalt. Contamination from the reagents, dimethylformamide and sodium hydroxide, was also investigated. A concentration of 0.09 ppm was found for sodium hydroxide and 0.03 ppm for dimethylformamide. This

suggests that the contamination from the reagents was not too serious. Cobalt has a boron equivalent of 9×10^{-3} , which means that a concentration of less than 0.05 ppm is required, since cobalt forms stable carbides during carbonisation and therefore does not evaporate. Upon activation by neutrons, cobalt forms cobalt-60 which is more radioactive and has a longer half-life. For the coal to be employed in the manufacture of nuclear graphite, a purification method for cobalt will have to be developed.

Chromium: The concentration of chromium was lowered from 11.0 ppm in the original coal to 7.2 ppm in untreated Refcoal derived from the extraction with sodium hydroxide only. The concentration of chromium was lowered from 11.0 ppm in the original coal to 7.1 ppm in untreated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. High recoveries of chromium were observed; this suggests the presence of organometallic species, which are soluble in organic solvents. This is consistent with the observations reported [26]. In some experiments, chromium concentrations were higher in the unpurified Refcoal than in the original parent coal. The increase in concentration could be due to contamination. Chromium has a boron equivalent of 8×10^{-4} so a concentration of 7.2 ppm in the unpurified Refcoal is not a cause for concern with respect to nuclear graphite.

Europium: The concentration of europium was lowered from 0.6 ppm in the original coal to 0.08 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 0.6 ppm in the original coal to 0.1 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The purification values of 7.5 and 10 indicate a low recovery of europium, which suggests that europium occurs predominantly in inorganic association in the coal matrix. Europium has been reported to occur predominantly in organic association in the coal matrix [28], which is inconsistent with the observations made here. At this stage of purification, europium is a potential problem with respect to nuclear, since it has a very high boron equivalent (4×10^{-1}), therefore further purification is necessary to bring its concentration to below 0.005 ppm.

Hafnium: The concentration of hafnium was lowered from 2.8 ppm in the original coal to 1.7 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 2.8 ppm in the original coal to 1.9 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The low purification values indicate a high recovery of hafnium, which suggests that hafnium occurs predominantly in organic association in the coal matrix. Hafnium has been reported to occur predominantly in inorganic association in the coal matrix [26], which is inconsistent with the observations made here. The low purification values may also suggest a contamination problem. Hafnium has a high boron equivalent (8×10^{-3}), and therefore its concentration needs to be lowered to below 0.1 ppm for the coal to be used for the production of nuclear carbon. Further purification will, therefore, be necessary.

Iron: The concentration of iron was lowered from 3400 ppm in the original coal to 433 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only. The concentration of iron increased from 3400 ppm in the original coal to 4100 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, which suggests contamination or analytical variations. The increase in iron concentration in relation to Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide is probably due to the precipitation of iron ions as pyrite. The low purification value indicates a high recovery of iron, which suggests that iron occurs predominantly in organic association in the coal matrix. Iron has been reported to occur predominantly in inorganic association in the coal matrix [26], which is inconsistent with the observations made here. Since iron has a low boron equivalent (7×10^{-4}), it poses no serious problem with respect to nuclear carbon as with further purification its concentration can be brought to below 50 ppm.

Lanthanum: The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 1.6 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 15.8 ppm in the original coal to 4.8 ppm in unpurified Refcoal derived from the extraction with both sodium

hydroxide and sodium sulphide. The purification value of 10 indicates a low recovery of lanthanum, which suggests that lanthanum occurs predominantly in inorganic association in the coal matrix. However, the purification value of 3.3 indicates a high recovery of lanthanum, which suggests either that lanthanum occurs predominantly in organic association in the coal matrix or that there was a contamination problem when sodium sulphide was used. Lanthanum has been reported to occur predominantly in organic association in the coal matrix [27, 28]. Since lanthanum has a low boron equivalent (9×10^{-4}), it poses no serious problem with respect to nuclear carbon as with further purification its concentration can be brought to below 0.05 ppm.

Scandium: The concentration of scandium was lowered from 5.7 ppm in the original coal to 2.7 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 5.7 ppm in the original coal to 2.2 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The purification values of 2.1 and 2.6 indicate a high recovery of scandium, which suggests that scandium occurs predominantly in organic association in the coal. The low purification values of may also suggest a contamination problem.. Scandium has been reported to occur predominantly in inorganic association in the coal matrix [26], which is inconsistent with the observations made here. Since scandium has a high boron equivalent (9×10^{-3}), further purification will be necessary to bring the concentration down below 0.05 ppm in order for the coal to be suitable for use in the manufacture of nuclear carbon.

Samarium: The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.6 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 2.7 ppm in the original coal to 2.3 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The low purification values of 4.5 and 1.2 indicate a high recovery of samarium, which suggests that samarium occurs predominantly in organic association in the coal matrix. Samarium has been reported to occur predominantly in organic association in the coal matrix [27, 28],

which is consistent with the observations made here. The low purification values may also suggest a contamination problem. Samarium has a very high boron equivalent (5×10^{-1}), and therefore its concentration needs to be lowered to below 0.005 ppm for the coal to be used for the production of nuclear carbon. Further purification will, therefore, be necessary.

Tantalum: The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.5 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 0.6 ppm in the original coal to 0.3 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The low purification values of 1.2 and 2 indicate a high recovery of tantalum, which suggests that tantalum occurs predominantly in organic association in the coal matrix. Tantalum has been reported to occur predominantly in inorganic association in the coal matrix [26], which is inconsistent with the observations made here. The low purification values may also suggest a contamination problem. Tantalum has a low boron equivalent (2×10^{-3}), and therefore it poses no serious problem with respect to nuclear carbon since its concentration is less than 1 ppm..

Terbium: The concentration of terbium was lowered from 0.6 ppm in the original coal to 0.2 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only. The concentration of terbium increased from 0.6 ppm in the original coal to 0.7 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, which suggests contamination or analytical variations. The low purification value of 3 indicates a high recovery of terbium, which suggests that terbium occurs predominantly in organic association in the coal matrix. Terbium has been reported to occur predominantly in inorganic association in the coal matrix [28], which is inconsistent with the observations made here. Terbium has a low boron equivalent (2×10^{-3}), and therefore it poses no serious problem with respect to nuclear carbon since with further purification its concentration can be brought to below 0.05 ppm..

Thorium: The concentration of thorium was lowered from 4.9 ppm in the original coal to 2.6 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 4.9 ppm in the original coal to 1.7 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The low purification values of 1.9 and 2.9 indicate a high recovery of thorium, which suggests that thorium occurs predominantly in organic association in the coal matrix. Thorium has been reported to occur predominantly in inorganic association in the coal matrix [26, 28], which is inconsistent with the observations made here. The low purification values may also suggest a contamination problem. Thorium has a low boron equivalent (4×10^{-4}), and therefore it poses no serious problem with respect to nuclear carbon.

Uranium: The concentration of uranium was lowered from 2.0 ppm in the original coal to 0.4 ppm in unpurified Refcoal derived from the extraction with sodium hydroxide only, and from 2.0 ppm in the original coal to 1.3 ppm in unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The low purification values of 5 and 1.5 indicate a high recovery of uranium, which suggests that uranium occurs predominantly in organic association in the coal matrix. Uranium has been reported to occur predominantly in inorganic association in the coal matrix [26], which is inconsistent with the observations made here. The low purification values also suggest a contamination problem. Uranium has a very low boron equivalent (2×10^{-4}), and therefore it poses no serious problem with respect to nuclear carbon since with further purification its concentration can be brought to below 0.05 ppm.

Table 4.7: Average concentrations of elements in Tshikondeni coal and Refcoal derived from NaOH extraction, showing different stages of treatment (ppm)

Element	Coal	Unpurified Refcoal	HCl- treated	HF- treated	TP260- treated	TP208- treated	TP214- treated
Ba	3190	202	436	381	23.5	nd	13.5
Br	4.1	0.7	2.6	3.2	1.0	2.2	1.3
Co	8.7	6.9	5.5	5.9	4.8	4.3	4.5
Cr	11	7.2	5.0	6.3	4.7	4.2	3.7
Cs	1.1	0.3	0.03	nd	0.02	0.04	0.04
Eu	0.6	0.08	nd	nd	nd	nd	0.008
Fe	3400	1000	150	70	10	50	50
Hf	2.8	1.7	0.8	0.9	0.1	0.1	0.08
La	15.8	1.6	0.6	0.6	0.3	0.6	1.8
Sc	5.7	2.7	0.4	0.1	0.09	0.08	0.07
Sm	2.7	0.6	0.13	0.2	0.05	0.4	0.4
Ta	0.6	0.5	0.5	0.5	0.5	0.6	0.4
Tb	0.6	0.2	nd	nd	nd	nd	nd
Th	4.9	2.6	1.3	2	0.6	0.7	1.2
U	2.0	0.4	1.5	1.4	nd	0.3	0.2

Note: nd = undetected

Table 4.8: Average concentrations of elements in Tshikondeni coal and Refcoal derived from the NaOH-Na₂S extraction, showing different stages of treatment (ppm)

Element	Coal	Unpurified Refcoal	HCl-treated	HF-treated	TP260-treated	TP208-treated	TP214-treated
Ba	3190	448	327	324	491	159	217
Br	4.1	0.9	2.2	2.1	4.3	2.9	3.6
Co	8.7	4.8	2.4	5.1	3.4	2.4	3.9
Cr	11	7.1	4.0	5.4	3.5	4.4	4.0
Cs	1.1	0.1	0.03	0.08	0.03	0.03	0.03
Eu	0.6	0.06	0.01	0.05	0.005	nd	nd
Fe	3400	4100	100	nd	200	nd	100
Hf	2.8	1.9	0.6	1.3	0.06	0.2	0.05
La	15.8	4.8	0.7	0.5	0.03	0.7	0.04
Sc	5.7	2.2	0.5	0.5	0.05	0.2	0.05
Sm	2.7	2.3	0.06	0.1	0.03	0.03	0.05
Ta	0.6	0.3	0.5	0.6	0.5	0.6	0.3
Tb	0.6	0.7	nd	0.9	nd	nd	nd
Th	4.9	1.7	0.09	0.4	0.07	0.07	0.1
U	2.0	1.3	0.2	0.6	0.1	0.7	0.4

Note: nd = undetected

Table 4.9: Extent of purification of trace elements in Tshikondeni Refcoal

Element	NaOH-extracted					NaOH and Na ₂ S-extracted				
	RCW	HCl	TP 260	TP 208	TP 214	RCW	HCl	TP 260	TP 208	TP 214
Ba	16	7.3	136	>300	228	7.1	10	6	20	15
Br	5.9	1.6	2.7	2	3.2	4.6	2.6	<1	1.4	1.1
Co	1.3	1.6	1.6	2	1.9	1.2	3.6	2.6	3.6	2.2
Cr	1.5	2.2	2.1	2.6	3	1.5	2.8	3.1	2.5	2.8
Cs	3.7	37	18	28	28	11	16	37	37	37
Eu	7.5	>120	>120	>120	75	10	60	120	>12	>120
Fe	7.9	23	300	60	60	<1	34	15	>300	30
Hf	1.7	3.5	28	28	35	1.5	4.7	47	15	56
La	10	26	53	26	8.8	3.3	23	527	23	395
Sc	2.1	14	63	81	81	2.6	11	114	29	114
Sm	4.5	27	54	6.8	9	1.2	45	90	90	54
Ta	1.2	1.2	1.2	1	1.5	2	1.2	1.2	1	2
Tb	3	>56	>56	>56	>56	<1	>56	>56	>56	>56
Th	1.9	3.8	4.5	7	4.1	2.9	54	70	70	49
U	2.5	1.3	>20	6.7	10	1.5	10	20	3.3	5

Note: RCW = water-precipitated unpurified Refcoal; HCl = HCl-treated Refcoal; TP 260 = Lewatit TP 260 chelating resin-treated Refcoal; TP 208 = Lewatit TP 208 chelating resin-treated Refcoal; TP 214 = Lewatit TP 214 chelating resin-treated Refcoal

4.3.1.1 Conclusions

As seen in Table 4.7 and Table 4.8, Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide appears to be lower in cobalt but high in almost all the other elements determined. Therefore, future work should be directed towards the extraction of carbon from coal with as small an amount of sodium sulphide as possible in order to improve the foaming of the Refcoal during

carbonisation and, hopefully, improve the formation of mesophase. High amounts of sodium sulphide should be avoided. It will be necessary to develop a proper washing process for recovering the Refcoal from the Refcoal solution. The rare earth metals (La and Sm) are not consistent to each other, which could be attributed to contamination, analytical variations and/or that there was insufficient washing during the recovery of the Refcoal.

4.3.2 Extraction of trace elements from Refcoal gel with hydrochloric acid and hydrofluoric acid

It has been reported [147,148] that demetalation of porphyrins takes place when the metal complex is boiled in hydrochloric acid. Demetalation with hydrofluoric acid was also attempted by precipitating the Refcoal solution in concentrated hydrofluoric acid. Scanning electron microscopy (SEM) was used to determine qualitatively the extent of purification in the presence of acids. This is shown in Figure 4.6 for the unpurified Refcoal, in Figure 4.7 for the hydrofluoric acid-treated Refcoal, and in Figure 4.8 for the Refcoal treated with hydrochloric acid followed by hydrofluoric acid. The presence on the SEM micrograph of many bright spots against a dark carbon background (Figure 4.6), indicates more impurities. The analysis of the energy-dispersive spectrometer (EDS) showed that the unpurified Refcoal contains more titanium-rich impurities. For the Refcoal treated with hydrochloric acid only, the micrograph shows fewer bright spots than for the unpurified Refcoal. EDS analysis of the hydrofluoric acid-treated Refcoal, showed that these impurities contain compounds consisting mainly of Na, Al and F, which suggests the presence of insoluble compounds such as NaAlF_4 . This is consistent with the observation made by Steel et al. [94,95]. The Refcoal treated with hydrochloric acid followed by treatment with hydrofluoric acid shows even fewer bright spots on the SEM micrograph, which demonstrates that the number of impurities has been reduced. EDS analysis showed that these impurities contain compounds consisting mainly of Ca and F, which suggests the presence of insoluble compounds such as CaF_2 . The presence of compounds such as NaAlF_4 was not observed, which suggests that the

treatment of Refcoal with hydrochloric acid removes most of the insoluble fluoride-forming ions from the coal matrix. Consequently, most of the samples prepared were first treated with hydrochloric acid, followed by hydrofluoric acid.

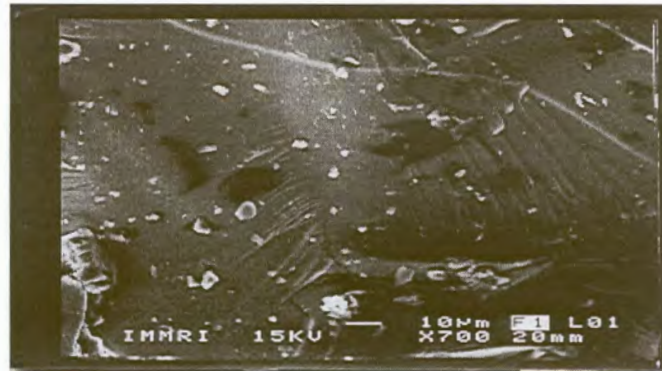


Figure 4.6: SEM micrograph of showing unpurified Refcoal

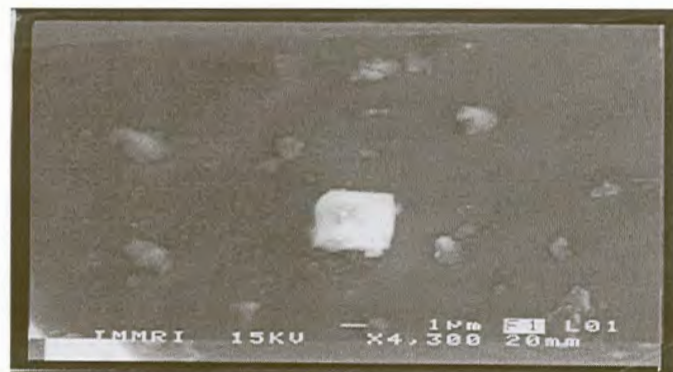


Figure 4.7: SEM micrograph of Refcoal treated with HF



Figure 4.8: SEM micrograph of Refcoal treated with HCl followed by HF

To minimise the formation of dimethylamine from dimethylformamide as a result of reaction with

hydrochloric acid, the Refcoal solution was first precipitated from water to form a gel containing less DMF, followed by treatment with the acids. Table 4.7 and Table 4.8 respectively list the average concentrations of the elements monitored in the acid-treated Refcoal samples for the extractions using sodium hydroxide only and those for the extractions using both sodium hydroxide and sodium sulphide. The purification experiments conducted using hydrochloric and hydrofluoric acid were initial experiments and were not optimised. The concentrations given are an average of at least two determinations as given in Appendix 3. Table 4.9 lists the extent of purification, calculated as the ratio of concentration in the original coal to that in the Refcoal, for each of the elements monitored. Purification of the elements monitored is discussed below.

Barium: The concentration of barium was lowered from 3 190 ppm in the original coal to 436 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. This concentration was then lowered to 381 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of barium increased from 202 ppm in unpurified Refcoal to 436 ppm and 381 ppm respectively in the hydrochloric acid-treated Refcoal and hydrofluoric acid-treated Refcoal, which suggests contamination, or analytical variations. The increase in concentration with respect to the hydrofluoric acid-treated Refcoal is probably due to the precipitation of insoluble barium fluoride. The concentration of barium was lowered from 3 190 ppm in the original coal to 327 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The concentration of 327 ppm in the hydrochloric acid-treated Refcoal was then lowered to 324 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. No significant purification was achieved in proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid treated Refcoal. With respect to the unpurified Refcoal no barium purification was achieved with acid treatment. This may be either because of the precipitation of barium fluorides, or an indication that the washing method used, although similar, was ineffective.

Bromine: The concentration of bromine was lowered from 4.1 ppm in the original coal to 2.6 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. This concentration was then increased to 3.2 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of bromine increased from 0.7 ppm in unpurified Refcoal to 3.2 ppm in both the hydrochloric acid-treated Refcoal and hydrofluoric acid-treated Refcoal, which suggests bromine contamination by the acids. The concentration of bromine was lowered from 4.1 ppm in the original coal to 1.6 ppm and 1.7 ppm respectively in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with hydrochloric acid and hydrofluoric acid. The concentration of bromine increased from 0.9 ppm in unpurified Refcoal to 1.6 ppm and 1.7 ppm in the hydrochloric acid-treated Refcoal and hydrofluoric acid-treated Refcoal respectively, again suggesting bromine contamination by the acids. Therefore, using either hydrochloric acid or hydrofluoric acid introduces bromine into the sample. The extent of contamination appears to be lower with the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. Contamination by bromine is, however, not a problem with regard to the manufacture of nuclear carbon, since bromine will easily volatilise during carbonisation. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

Cesium: The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.03 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with hydrochloric acid. This concentration was then lowered to a concentration that is close to the detection limit after treatment with hydrofluoric acid. The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.03 and 0.08 ppm respectively in the Refcoal derived from the extractions with both sodium hydroxide and sodium sulphide, after treatment with both hydrochloric acid and hydrofluoric acid. From the high purification values of 37 and 16 it can be concluded that acid treatment is suitable for the leaching

cesium out of the original coal and/or Refcoal. Cesium was used as an indicator element for alkali metals, which suggests that sodium, which is a catalyst for oxidation, and which is added during extraction could be removed. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, which may be due to contamination, analytical variations and inefficient washing of the Refcoal.

Cobalt: The concentration of cobalt was lowered from 8.7 ppm in the original coal to 5.5 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of 4.8 ppm in the hydrochloric acid-treated Refcoal then increased to 5.9 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only, which suggests contamination or analytical variations. The concentration of cobalt was lowered from 8.7 ppm in the original coal to 2.4 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The concentration of 2.4 ppm in the hydrochloric acid-treated Refcoal then increased to 5.1 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, again suggesting contamination. No significant cobalt purification is achieved when proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal for both the Refcoal derived from the extraction with sodium hydroxide only and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

Chromium: The concentration of chromium was lowered from 11.0 ppm in the original coal to 5.0 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of 5.0 ppm in the hydrochloric acid-treated Refcoal then increased to 6.3 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only, which suggests contamination. The concentration of chromium was lowered from 11.0 ppm in the original coal

to 4.0 ppm and 5.4 ppm respectively in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with hydrochloric acid and hydrofluoric acid. This observation suggests a strong organic association for chromium. In relation to the unpurified Refcoal, no significant chromium purification is achieved with acid treatment. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no chromium purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

Europium: The concentration of europium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with both hydrochloric acid and hydrofluoric acid. The europium concentration was lowered from 0.6 ppm in the original coal to 0.01 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The concentration of 0.01 ppm in the hydrochloric acid-treated Refcoal then increased to 0.05 ppm in the hydrofluoric acid-treated Refcoal, which suggests contamination or analytical variations. However, acid treatment was found to be suitable for leaching europium out of the original coal and/or Refcoal. In proceeding from hydrochloric acid-treated to hydrofluoric acid-treated Refcoal, no purification was achieved for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, which may be due to contamination, analytical variations and inefficient washing of the Refcoal.

Hafnium: The concentration of hafnium was lowered from 2.8 ppm in the original coal to 0.8 ppm and 0.9 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after hydrochloric acid and hydrofluoric acid treatment respectively. The concentration of hafnium was lowered from 2.8 ppm in the original coal to 0.6 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after hydrochloric acid. The concentration of 0.6 ppm then increased to 1.3 ppm in hydrofluoric acid-treated Refcoal, which suggests contamination when sulphide is used.

No significant hafnium purification is achieved when proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal for both the Refcoal derived from the extraction with sodium hydroxide only and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

Iron: The concentration of iron was lowered from 3400 ppm in the original coal to 150 ppm and 70 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with both hydrochloric acid and hydrofluoric acid respectively. In proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal, no significant iron purification was achieved. The concentration of iron was lowered from 3400 ppm in the original coal to 100 ppm after treatment with hydrochloric acid and to a concentration that is close to the detection limit in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. In proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal a purification value greater than 10 was observed, therefore a significant purification was achieved. Acid treatment was, therefore, found to be sufficient to leach out iron from the coal and/or Refcoal.

Lanthanum: The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 0.6 ppm after hydrochloric acid treatment, and then lowered to 0.2 ppm after hydrofluoric acid treatment in the Refcoal derived from the extraction with sodium hydroxide only. In proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal an increase in concentration to 0.2 ppm was observed, which suggests contamination. The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 0.7 and 0.5 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after hydrochloric acid and hydrofluoric acid treatment respectively. Again, in proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal an increase in concentration to 0.2 ppm was observed, which suggests contamination. The high purification values indicate that acid treatment is sufficient to leach out lanthanum from the coal and/or

Refcoal, therefore further purification is not necessary. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

Scandium: The concentration of scandium was lowered from 5.7 ppm in the original coal to 0.4 and 0.1 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with hydrochloric acid and hydrofluoric acid respectively. The concentration of scandium was lowered from 5.7 ppm in the original coal to 0.5 ppm for both the hydrochloric acid and hydrofluoric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. With regard to the Refcoal derived from the extraction with sodium hydroxide only, no further purification is necessary, although a further purification step is necessary for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

Samarium: The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.1 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. This concentration then increased to 0.2 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only, which suggests contamination. The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.06 ppm for the hydrochloric acid and 0.1 ppm for the hydrofluoric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The purification values below 20 indicate that acid treatment is not sufficient to leach out samarium from the coal and/or Refcoal. Therefore, further purification is necessary to bring the concentration of samarium down to about 0.005 ppm. In proceeding from hydrochloric acid-treated

Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

Tantalum: The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.5 ppm for the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of 0.5 ppm in the hydrochloric acid-treated Refcoal then remained at 0.5 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.5 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with both hydrochloric acid and hydrofluoric acid. The concentration of tantalum increased from 0.3 ppm in unpurified Refcoal to 0.5 ppm in both hydrochloric acid and hydrofluoric acid-treated Refcoal, again suggesting contamination. The low purification values indicate a high recovery of tantalum, which suggests that acid treatment does not leach out tantalum from the coal and/or Refcoal. No significant tantalum purification is achieved when proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid-treated Refcoal for both the Refcoal derived from the extraction with sodium hydroxide only and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

Terbium: The concentration of terbium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit for both the hydrochloric acid and hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of terbium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit after hydrochloric acid treatment of the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. This concentration was then increased to 0.9 ppm in the hydrofluoric acid-treated Refcoal, which suggests contamination. The high purification values observed, indicate that acid treatment is

sufficient to leach out terbium from the coal and/or Refcoal and therefore further purification is not necessary. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

Thorium: The concentration of thorium was lowered from 4.9 ppm in the original coal to 1.3 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of 1.3 ppm in the hydrochloric acid-treated Refcoal then increased to 2.0 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with sodium hydroxide only, which suggests contamination. The concentration of thorium was lowered from 4.9 ppm in the original coal to 0.09 ppm in hydrochloric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The concentration of 0.09 ppm in the hydrochloric acid-treated Refcoal then increased to 0.4 ppm in the hydrofluoric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The low purification values indicate a high recovery of thorium, which suggests that acid treatment is not sufficient to leach out thorium from the coal and/or Refcoal, but further purification is not necessary since thorium is the nuclear fission product. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

Uranium: The concentration of uranium was lowered from 2.0 ppm in the original coal to 1.5 ppm and 1.4 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with hydrochloric acid and hydrochloric acid respectively. The concentration of uranium was lowered from 2.0 ppm in the original coal to 0.4 ppm in the hydrochloric acid-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The concentration of 0.2 ppm in the hydrochloric acid-treated Refcoal then increased to 0.6 ppm in the hydrofluoric acid-treated Refcoal,

again suggesting contamination. The low purification values indicate a high recovery of uranium, which suggests that acid treatment is not sufficient to leach out uranium from the coal and/or Refcoal and therefore further purification is necessary. In proceeding from hydrochloric acid-treated Refcoal to hydrofluoric acid-treated Refcoal, no purification was achieved for both the Refcoal derived from the extraction with sodium hydroxide only, and the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

4.3.2.1 Conclusions

The observations made above lead to the following conclusions:

- ⇒ The concentrations of the elements fluctuate for the different stages of purification, i.e. in moving from the original coal to the unpurified Refcoal, to the hydrochloric acid-treated Refcoal and to the hydrofluoric acid-treated Refcoal. Fluctuations in concentrations suggest a serious contamination problem, or inefficiency in the washing method that was used. Analytical errors cannot be ruled out. The fluctuations in concentrations, however, do not affect the major conclusions with regard to the acid-washing process as a Refcoal purification method.
- ⇒ With regard to the original coal, the degrees of purification after acid treatment of the Refcoal derived from the extraction with sodium hydroxide only are as follows:
 - ⇒ High purification, with purification values of 20 and above, is observed for Cs, Eu, Fe, La, Sm and Tb.
 - ⇒ Values between 5 and 15 are observed for Ba and Sc.
 - ⇒ Purification values below 5 are observed for Br, Co, Cr, Hf, Ta, Th and U.

- ⇒ The degrees of purification after acid treatment of the Refcoal derived from the extraction with sodium hydroxide and sodium sulphide are as follows:
- ⇒ High purification, with purification values of 20 and above, is observed for Eu, Fe, La, Sm, Tb and Th.
 - ⇒ Purification values of between 15 and 20 are observed for Cs.
 - ⇒ Values between 5 and 15 are observed for Ba, Sc and U.
 - ⇒ Purification values below 5 are observed for Br, Co, Cr, Hf and Ta.
- ⇒ For the hydrochloric acid-treated Refcoal, the samples derived from the extraction with both sodium hydroxide and sodium sulphide appear to be lower in the rare earths than the samples derived from the extraction with sodium hydroxide only. The hydrofluoric acid-treated samples also show a similar trend, which suggests that sodium sulphide is necessary for the demetalation of the metal complex in the coal matrix. Both the hydrochloric acid and hydrofluoric acid-treated samples show an increase in the concentration of Br, which suggests contamination by the acids. Contamination with Br is not serious for the Refcoal to be used for the production of nuclear graphite because Br will easily be lost during carbonisation of the Refcoal. With the exception of iron, the hydrofluoric acid-treated samples appear to have a serious contamination problem, therefore no significant purification was achieved in proceeding from the hydrochloric acid-treated Refcoal to the hydrofluoric acid treated Refcoal. Acid treatment of the Refcoal gel was carried out under very harsh conditions only. Therefore future work must examine the optimum concentration of the acid required to obtain better purification. The contamination problem also needs to be addressed. Although purification values below 5 are demonstrated for Br, Co, Cr, Hf and Th at this stage of the purification, Br, Cr, Hf and Th are not a problem with respect to nuclear graphite, the only real problem is Co.

4.3.3 Extraction of trace elements from Refcoal solution with chelating resins

Table 4.10 lists the average concentrations of the trace elements monitored in the Refcoal samples derived from treating Refcoal solution with chelating resins. The purification experiments conducted were initial experiments and were not optimised. The concentrations given are an average of at least two determinations as given in Appendix 3. Table 4.11 lists the extent of purification, calculated as a ratio of concentration in the original coal to concentration in the Refcoal, for each of the elements monitored. The extent of purification is discussed below::

Barium: The concentration of barium was lowered from 3 190 ppm in the original coal to 87 ppm, 636 ppm and 82 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260 and Lewatit TP 214 chelating resins respectively. With regard to the unpurified Refcoal, an increase in concentration occurred from 202 ppm in the unpurified Refcoal to 636 ppm in the Refcoal from the extraction with sodium hydroxide only, treated with Lewatit TP 208 chelating resins, which suggests contamination. The concentration of barium was lowered from 3 190 ppm in the original coal to 686 ppm, 897 ppm and 516 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With regard to the unpurified Refcoal, an increase in concentration occurred from 486 ppm in the unpurified Refcoal to 686 ppm, 897 ppm and 516 ppm in Refcoal treated with Lewatit TP 260, TP 208 and Lewatit TP 214 chelating resins respectively, which suggests contamination. Purification appears to be better for the Refcoal derived from the extraction with sodium hydroxide only than for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

Bromine: The concentration of bromine was increased from 4.1 ppm in the original coal to 6.3 ppm and 6.9 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit

TP 260 and Lewatit TP 214 chelating resins respectively, which suggests contamination. The concentration of bromine was lowered from 4.1 ppm in the original coal to 0.4 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 208 chelating resins. The concentration of bromine was increased from 4.1 ppm in the original coal to 5.6 ppm and 7.4 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 260 and Lewatit TP 214 chelating resins respectively, which suggests contamination. The concentration of bromine was lowered from 4.1 ppm in the original coal to 3.2 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 208 chelating resins. For all the samples analysed, no significant bromine purification was demonstrated.

Cesium: The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.09 ppm, 0.07 ppm and 0.1 ppm respectively in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins. The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.2 ppm, 0.04 ppm and 0.1 ppm respectively in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins. It appears that the Lewatit TP 208 and Lewatit TP 214 chelating resins give better purification for cesium than the Lewatit TP 260 chelating resin. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only.

Cobalt: The concentration of cobalt was lowered from 8.7 ppm in the original coal to 4.9 ppm, 5.6 ppm and 5.2 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of cobalt was lowered from 8.7 ppm in the original coal to 7.4 ppm, 6.2 ppm and 6.2 ppm respectively in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after

treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins. For all the samples analysed, no significant cobalt purification was demonstrated.

Chromium: The concentration of chromium was lowered from 11.0 ppm in the original coal to 6.1 ppm, 6.8 ppm and 9.0 ppm respectively in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 260 and Lewatit TP 208 and Lewatit TP 214 chelating resins. The concentration of chromium was lowered from 11.0 ppm in the original coal to 8.5 ppm, 8.8 ppm and 6.4 ppm respectively in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins. An increase in chromium concentration was observed from 7.1 ppm in the unpurified Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, to 8.5 ppm and 8.8 ppm after treatment with Lewatit TP 260 and Lewatit TP 208 chelating resins respectively, which suggests contamination. For all the samples analysed, no significant chromium purification was demonstrated.

Europium: The concentration of europium was lowered from 0.6 ppm in the original coal to 0.2 ppm, 0.04 ppm and 0.2 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of europium was lowered from 0.6 ppm in the original coal to 0.04 ppm, 0.2 ppm and 0.2 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that the Lewatit TP 260 chelating resin gives better purification for europium than the Lewatit TP 208 and Lewatit TP 214 chelating resins. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Hafnium: The concentration of hafnium was lowered from 2.8 ppm in the original coal to 1.5 ppm, 2.2

ppm and 1.5 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With regard to the unpurified Refcoal, an increase in concentration occurred from 1.7 ppm in the unpurified Refcoal to 2.2 ppm in Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 208 chelating resins, which suggests contamination. The concentration of hafnium was lowered from 2.8 ppm in the original coal to 1.7 ppm and 1.5 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260 and Lewatit TP 208 chelating resins respectively. The concentration of hafnium was increased from 2.8 ppm in the original coal to 4.1 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 214 chelating resins, which suggests contamination. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Iron: The concentration of iron was lowered from 3400 ppm in the original coal to 200 ppm, 100 ppm and 150 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating respectively. The concentration of iron was lowered from 3400 ppm in the original coal to 200 ppm, 300 ppm and 100 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Lanthanum: The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 2.4 ppm, 0.7 ppm and 1.6 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The

concentration of lanthanum was lowered from 15.8 ppm in the original coal to 2.5 ppm, 1.6 ppm and 2.7 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Scandium: The concentration of scandium was lowered from 5.7 ppm in the original coal to 2.4 ppm, 1.7 ppm and 2.7 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of scandium was lowered from 5.7 ppm in the original coal to 2.5 ppm, 2.0 ppm and 1.4 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Samarium: The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.8 ppm, 0.5 ppm and 1.3 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. An increase in samarium concentration was observed from 0.6 ppm in the unpurified Refcoal derived from the extraction with sodium hydroxide only, to 0.8 ppm and 1.3 ppm after treatment with Lewatit TP 260 and Lewatit TP 214 chelating resins respectively, which suggests contamination. The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.7 ppm, 0.5 ppm and 0.6 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant

difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Tantalum: The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.4 ppm, 0.2 ppm and 0.5 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.5 ppm, 0.4 ppm and 0.5 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that the Lewatit TP 208 chelating resin gives better purification for tantalum than the Lewatit TP 260 and Lewatit TP 214 chelating resins. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Terbium: The concentration of terbium was lowered from 0.6 ppm in the original coal to 0.1 ppm, 0.2 ppm and 0.1 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of terbium was lowered from 0.6 ppm in the original coal to 0.1 ppm in all the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Thorium: The concentration of thorium was lowered from 4.9 ppm in the original coal to 2.3 ppm, 2.4 ppm and 2.4 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment

with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of thorium was lowered from 4.9 ppm in the original coal to 2.7 ppm, 2.2 ppm and 2.6 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Uranium: The concentration of uranium was lowered from 2.0 ppm in the original coal to 1.4 ppm, 1.1 ppm and 1.2 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With regard to the unpurified Refcoal derived from the extraction with sodium hydroxide only, an increase in uranium concentration was observed from 0.4 ppm in the, to 1.4 ppm, 1.1 ppm and 1.2 ppm after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively, which suggests contamination. The concentration of uranium was lowered from 2.0 ppm in the original coal to 1.2 ppm, 0.7 ppm and 1.5 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Table 4.10: Average concentration of elements in Tshikondeni Refcoal derived from treating Refcoal solution with chelating resins (ppm)

Element	Coal	NaOH-extracted				NaOH and Na ₂ S-extracted			
		RCW	TP 260	TP 208	TP 214	RCW	TP 260	TP 208	TP 214
Ba	3190	202	87	636	82	448	686	897	516
Br	4.1	0.7	6.3	0.4	6.9	0.9	5.6	3.2	7.4
Co	8.7	6.9	4.9	5.6	5.2	4.8	7.4	6.2	6.2
Cr	11	7.2	6.1	6.8	9.0	7.1	8.5	8.8	6.4
Cs	1.1	0.3	0.09	0.07	0.1	0.1	0.20	0.04	0.1
Eu	0.6	0.08	0.18	0.04	0.2	0.06	0.04	0.20	0.1
Fe	3400	1000	200	100	150	4100	200	300	100
Hf	2.8	1.7	1.5	2.2	1.5	1.9	1.7	1.5	4.1
La	15.8	1.6	2.4	0.7	1.7	4.8	2.5	1.6	2.7
Sc	5.7	2.7	2.4	1.7	2.7	2.2	2.5	2.0	1.4
Sm	2.7	0.6	0.8	0.5	1.3	2.3	0.7	0.5	0.6
Ta	0.6	0.5	0.4	0.2	0.5	0.3	0.5	0.4	0.5
Tb	0.6	0.2	0.1	0.2	0.1	0.7	0.1	0.1	0.1
Th	4.9	2.6	2.3	2.4	2.4	1.7	2.7	2.2	2.6
U	2.0	0.4	1.4	1.1	1.2	1.3	1.2	0.7	1.5

Note: nd = undetected; RCW = water-precipitated unpurified Refcoal; TP 260 = Lewatit TP 260 chelating resin-treated Refcoal; TP 208 = Lewatit TP 208 chelating resin-treated Refcoal; TP 214 = Lewatit TP 214 chelating resin-treated Refcoal

Table 4.11: Extent of purification of trace elements in Tshikondeni Refcoal

Element	NaOH-extracted				NaOH and Na ₂ S-extracted			
	RCW	TP 260	TP 208	TP 214	RCW	TP 260	TP 208	TP 214
Ba	16	37	5	39	7.1	5	4	6
Br	5.9	<1	10	<1	4.6	<1	1.3	<1
Co	1.3	1.8	1.6	1.7	1.2	1.2	1.4	1.4
Cr	1.5	1.8	1.6	1.2	1.5	1.3	1.2	1.7
Cs	3.7	12	16	10	11	5.5	28	10
Eu	7.5	3.3	15	3	10	15	3	3
Fe	7.9	15	30	20	<1	15	10	30
Hf	1.7	1.9	1.3	1.9	1.5	1.6	1.9	<1
La	10	6.6	23	10	3.3	6.3	10	5.9
Sc	2.1	2.4	3.4	2.1	2.6	2.3	2.9	4.1
Sm	4.5	3.4	5.4	2.1	1.2	3.9	5.4	4.5
Ta	1.2	1.5	3	1.2	2	1.2	1.5	1.2
Tb	3	6	3	6	<1	6	6	6
Th	1.9	2.1	2	2	2.9	1.8	2.2	1.9
U	2.5	1.4	1.8	1.7	1.5	1.7	2.9	1.3

Note: RCW = water-precipitated unpurified Refcoal; TP 260 = Lewatit TP 260 chelating resin-treated Refcoal; TP 208 = Lewatit TP 208 chelating resin-treated Refcoal; TP 214 = Lewatit TP 214 chelating resin-treated Refcoal

4.3.3.1 Conclusions

The above observations can be summarised as follows for Refcoal derived from the extraction with sodium hydroxide only and Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide treated with Lewatit TP 260 chelating resins:

- ☞ High purification, with purification values of 20 and above, is observed for Ba.

- ☞ Purification values of between 15 and 20 are observed for Fe.
- ☞ Values between 5 and 15 are observed for Cs, La and Tb.
- ☞ Purification values below 5 are observed for Br, Co, Cr, Eu, Hf, Sc, Sm, Ta, Th and U.

The above observations can be summarised as follows for Refcoal derived from the extraction with sodium hydroxide only and Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide treated with Lewattit TP 208 chelating resins:

- ☞ High purification, with purification values of 20 and above, is observed for Fe and La.
- ☞ Values between 5 and 15 are observed for Ba, Br, Cs, Eu and Sm.
- ☞ Purification values below 5 are observed for Co, Cr, Hf, Sc, Ta, Tb, Th and U.

The above observations can be summarised as follows for Refcoal derived from the extraction with sodium hydroxide only and Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide treated with Lewattit TP 214 chelating resins:

- ☞ High purification, with purification values of 20 and above, is observed for Ba and Fe.
- ☞ Values between 5 and 15 are observed for Cs and La.
- ☞ Purification values below 5 are observed for Br, Co, Cr, Eu, Hf, Sc, Sm, Ta, Tb, Th and U.

Treatment of Refcoal solution with chelating resins did not remove rare earth metals to any significant extent. Low purification of Sm, Th and U may be due to contamination or analytical variations. Alkali metals, represented by Cs, together with Fe appear to be the only elements removed completely when the Refcoal solution is treated with chelating resins. A serious contamination problem occurs when the Refcoal solution is treated with chelating resins, suggesting. No significant difference in purification between the Refcoal solution derived from the extraction with sodium hydroxide only and that derived

from the extraction with both sodium hydroxide and sodium sulphide was observed, as shown in Table 4.10.

4.3.4 Extraction of trace elements from Refcoal gel with chelating resins

The average concentrations of the trace elements monitored in the Refcoal samples derived from treating Refcoal gel are listed in Table 4.7 for the extraction with sodium hydroxide only, and in Table 4.8 for the extraction with both sodium hydroxide and sodium sulphide. The purification experiments conducted were initial experiments and were not optimised. The concentrations given are an average of at least two determinations as given in Appendix 3. Table 4.9 lists the extent of purification, calculated as a ratio of concentration in the original coal to concentration in the Refcoal, for each of the elements monitored. The extent of purification is discussed below:

Barium: The concentration of barium was lowered from 3190 ppm in the original coal to 23.5 ppm and 13.5 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260 and Lewatit TP 214 chelating resins respectively. The concentration of barium was lowered from 3 190 ppm in the original coal to a concentration that is close to the detection limit in Lewatit TP 208 chelating resin-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of barium was lowered from 3 190 ppm in the original coal to 490 ppm, 158 ppm and 217 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With regard to hydrofluoric acid-treated Refcoal, an increase in concentration occurred from 324 ppm in hydrofluoric acid-treated Refcoal to 490 ppm in the Lewatit TP 260 chelating resin-treated Refcoal, which suggests contamination. It appears that the Lewatit TP 208 chelating resin gives better purification for barium than the Lewatit TP 260 and Lewatit TP 214 chelating resins. Purification appears to be better for the Refcoal derived from the extraction with sodium hydroxide only than for that derived from

the extraction with both sodium hydroxide and sodium sulphide.

Bromine: The concentration of bromine was lowered from 4.1 ppm in the original coal to 1.0 ppm, 2.2 ppm and 1.3 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of bromine increased from 4.1 ppm in the original coal to 4.3 ppm in Lewatit TP 260 chelating resin-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, which suggests contamination. The concentration of bromine was lowered from 4.1 ppm in the original coal to 2.9 ppm and 3.6 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With respect to hydrofluoric acid-treated Refcoal, an increase in concentration occurred from 1.7 ppm in hydrofluoric acid-treated Refcoal to 4.2 ppm, 2.9 ppm and 3.6 ppm in the Refcoal treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively, which suggests contamination. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and the extent of purification in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Cesium: The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.2 ppm, 0.04 ppm and 0.04 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of cesium was lowered from 1.1 ppm in the original coal to 0.03 ppm in all the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that the Lewatit TP 208 and Lewatit TP 214 chelating resins give better purification for cesium than the Lewatit TP 260 chelating resin. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for that derived from the extraction with sodium

hydroxide only.

Cobalt: The concentration of cobalt was lowered from 8.7 ppm in the original coal to 4.8 ppm, 4.3 ppm and 4.5 in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of cobalt was lowered from 8.7 ppm in the original coal to 3.4 ppm, 2.4 ppm and 3.9 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed. For all the samples analysed, no significant cobalt purification was demonstrated.

Chromium: The concentration of chromium was lowered from 11.0 ppm in the original coal to 4.7 ppm, 4.2 ppm and 3.7 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of chromium was lowered from 11.0 ppm in the original coal to 3.5 ppm, 4.4 ppm and 4.0 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. For all the samples analysed, no significant chromium purification was demonstrated. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Europium: The concentration of europium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit in Lewatit TP 260 and Lewatit TP 208 chelating resin-

treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of europium was lowered from 0.6 ppm in the original coal to 0.008 ppm in Lewatit TP 214 chelating resin-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of europium was lowered from 0.6 ppm in the original coal to 0.005 ppm in Lewatit TP 260 chelating resin-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. The concentration of europium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit in Lewatit TP 208 and Lewatit TP 214 chelating resin-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only. It appears that Lewatit TP 208 chelating resin gives better purification for europium than Lewatit TP 260 and Lewatit TP 214 chelating resins. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only.

Hafnium: The concentration of hafnium was lowered from 2.8 ppm in the original coal to 0.1 ppm, 0.1 ppm and 0.08 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of hafnium was lowered from 2.8 ppm in the original coal to 0.06 ppm, 0.2 ppm and 0.05 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that the Lewatit TP 214 gives better purification for europium than the Lewatit TP 208 and Lewatit TP 260 chelating resins. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Iron: The concentration of iron was lowered from 3400 ppm in the original coal to 10 ppm in Lewatit TP 260 chelating resin-treated Refcoal coal and to 50 ppm in both Lewatit TP 208 and Lewatit TP 214 chelating resin-treated Refcoal derived from the extraction with sodium hydroxide only. The concentration of iron was lowered from 3400 ppm in the original coal to 200 ppm and 100 ppm in both Lewatit TP 208 and Lewatit TP 214 chelating resin-treated Refcoal and to a concentration that is close to the detection limit in Lewatit TP 208 chelating resin-treated Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide. It appears that Lewatit TP 208 chelating resin gives better purification for iron than Lewatit TP 260 and Lewatit TP 214 chelating resins for the Refcoal derived from the extraction with sodium hydroxide only. Purification appears to be better for the Refcoal derived from the extraction with sodium hydroxide only than for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide.

Lanthanum: The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 0.3 ppm, 0.6 ppm and 1.8 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With regard to the hydrofluoric acid-treated Refcoal, there was an increase in the lanthanum concentration for the chelating resin-treated Refcoal, which suggests contamination. The concentration of lanthanum was lowered from 15.8 ppm in the original coal to 0.03 ppm, 0.1 ppm and 0.04 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that the Lewatit TP 260 chelating resin gives better purification for lanthanum than the Lewatit TP 208 and Lewatit TP 214 chelating resins. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only.

Scandium: The concentration of scandium was lowered from 5.7 ppm in the original coal to 0.09 ppm, 0.08 ppm and 0.08 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With regard to the hydrofluoric acid-treated Refcoal, there was an increase in scandium concentration for the Lewatit TP 260 chelating resin, which suggests contamination. The concentration of scandium was lowered from 5.7 ppm in the original coal to 0.05 ppm, 0.2 ppm and 0.05 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that Lewatit TP 214 chelating resin gives better purification for scandium than Lewatit TP 260 and Lewatit TP 208 chelating resins. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only.

Samarium: The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.05 ppm, 0.4 ppm and 0.3 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. With respect to the hydrofluoric acid-treated Refcoal, there was an increase in samarium concentration for the Lewatit TP 208 and Lewatit TP 214 chelating resins, which suggests contamination. The concentration of samarium was lowered from 2.7 ppm in the original coal to 0.03 ppm, 0.03 ppm and 0.04 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It appears that Lewatit TP 260 chelating resin gives better purification for samarium than Lewatit TP 208 and Lewatit TP 214 chelating resins. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only.

Tantalum: The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.5 ppm, 0.6 ppm and 0.3 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of tantalum was lowered from 0.6 ppm in the original coal to 0.5 ppm, 0.6 ppm and 0.3 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Terbium: The concentration of terbium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit for all the Refcoal derived from the extraction with sodium hydroxide only, treated Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins. The concentration of terbium was lowered from 0.6 ppm in the original coal to a concentration that is close to the detection limit for all the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, treated Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins. No significant difference between the extent of purification in the Refcoal derived from the extraction with sodium hydroxide only and that in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide was observed.

Thorium: The concentration of thorium was lowered from 4.9 ppm in the original coal to 1.1 ppm, 0.7 ppm and 1.2 ppm in the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of thorium was lowered from 4.9 ppm in the original coal to 0.07 ppm, 0.07 ppm and 0.1 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. It

appears that Lewatit TP 208 chelating resin gives better purification for thorium than Lewatit TP 260 and Lewatit TP 214 chelating resins. Purification appears to be better for the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide than for the Refcoal derived from the extraction with sodium hydroxide only.

Uranium: The concentration of uranium was lowered from 2.0 ppm in the original coal to a concentration that is close to the detection limit for the Refcoal derived from the extraction with sodium hydroxide only, after treatment with Lewatit TP 260 chelating resins. The concentration of uranium was lowered from 2.0 ppm in the original coal to 0.3 ppm and 0.2 ppm in the Refcoal derived from the extraction with sodium hydroxide only, treated with Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. The concentration of uranium was lowered from 2.0 ppm in the original coal to 0.1 ppm, 0.6 ppm and 0.4 ppm in the Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide, after treatment with Lewatit TP 260, Lewatit TP 208 and Lewatit TP 214 chelating resins respectively. Purification appears to be better for the Refcoal derived from the extraction with sodium hydroxide only than for that derived from the extraction with both sodium hydroxide and sodium sulphide.

4.3.4.1 Conclusions

The above observations are summarised below:

With regard to the original coal, the degree of purification of the Refcoal gel treated with chelating resins is as follows for the extraction with sodium hydroxide only:

- ☞ High purification, with purification values of 20 and above, is observed for Ba, Cs, Eu, Fe, Hf, La, Sc, Sm, Tb and U.
- ☞ Purification values below 5 are observed for Br, Co, Cr, Ta and Th.

The degree of purification of the Refcoal gel treated with chelating resins is as follows for the extraction with both sodium hydroxide and sodium sulphide:

- ☞ High purification, with purification values of 20 and above, is observed for Ba, Cs, Eu, Fe, Hf, La, Sc, Sm, Tb, Th, and U.
- ☞ Purification values below 5 are observed for Br, Co, Cr and Ta.

Precipitating Refcoal solution in water, followed by treating the resulting gel with acids and finally with chelating resins, appears to remove the elements Ba, Cs, Eu, Fe, Hf, La, Sc, Sm, Tb, Th and U. This suggests that these elements are either present as cationic ions in the coal matrix or are mainly present in inorganic association with the coal matrix. Elements such as cobalt, chromium and tantalum show little or no purification. This suggests that these elements are either strongly held in organometallic compounds in the coal matrix or are present as anionic ions in the coal matrix. The cobalt concentration appears to be lowered if the Refcoal gel derived from the extraction with both sodium hydroxide and sodium sulphide is first treated with acids, followed by resins. The elements Ba, Cs, Eu, Fe, Hf, La, Sc, Tb and Th are removed better with the chelating resin Lewatit TP 208, the elements Cs, Eu, Fe, La, Sm, Tb and U are removed better with the chelating resin Lewatit TP 260 and the elements Ba, Cs, Fe, Hf, La, Sc, Sm, Tb and Th are removed better with the chelating resin Lewatit TP 214. The chelating resin Lewatit TP 208 appears to be more effective than the other two chelating resins, i.e. Lewatit TP 260 and Lewatit TP 214, in lowering the amount of impurities in the Refcoal gel and or solution. Lewatit TP 208 is the sodium form of the iminodiacetic acid resin, which suggests that most of the elements that are removed by this resin are cations.

4.3.5 Extraction of trace elements with sulphonic acid resins

Initial experiments were conducted to determine whether sulphonic acid resins could be used in a Refcoal purification process. The experiments involved treating Refcoal solution and Refcoal gel with the resins, as explained in the procedure. Table 4.12 below lists the average concentrations of the elements monitored in the Refcoal samples derived from treating the Refcoal solution with the resins, usually at 140 to 145 °C, and in the samples derived from treating the Refcoal gel with the resins, usually at about 80 °C. The concentrations given in Table 4.12 are averages of two determinations. The Refcoal gel was obtained by precipitating the Refcoal solution in distilled water, followed by treatment with hydrochloric acid and hydrofluoric acid, as explained before.

For the Refcoal samples derived from treating the Refcoal gel with sulphonic acid resins, the degree of purification in relation to the original coal is as follows, for the Refcoal gel derived from the extraction with sodium hydroxide only:

- ⇒ High purification, with purification values of 20 and above, is observed for Cs, Eu, Fe, Hf, La, Sc, Sm, Tb, Th and U.
- ⇒ Purification values below 5 are observed for Br, Co, Cr and Ta.

The degree of purification in relation to the original coal is as follows, for the Refcoal gel derived from the extraction with both sodium hydroxide and sodium sulphide:

- ⇒ High purification, with purification values of 20 and above, is observed for Cs, Eu, Fe, Hf, La, Sc, Sm, Ta, Tb, Th and U.
- ⇒ Purification values below 5 are observed for Br, Co and Cr.

The samples derived from treating the Refcoal solution with the sulphonic acid resins did not show any

purification for the rare earth elements and cobalt. However, tantalum, which did not show any purification with chelating resins, appears to be lowered for the both the Refcoal solution and the Refcoal gel derived from the extraction with sodium hydroxide only. The use of sulphonic acid resins appears to give better than the chelating resins for cobalt which may be because of the high temperature to which the resins can be taken. Sulphonic acid resins are cheaper than chelating resins, therefore future work should look into the application of the sulphonic acid resins in place of the chelating resins.

Table 4.12: Concentrations of trace elements in Refcoal derived from Refcoal gel and Refcoal solution treated with sulphonic acid resins (ppm)

Element	Refcoal extracted with NaOH only		Refcoal extracted with NaOH and Na ₂ S	
	Derived from treating Refcoal solution	Derived from treating Refcoal gel	Derived from treating Refcoal solution	Derived from treating Refcoal gel
Br	1.6	0.8	10.6	4.5
Co	5.6	1.5	4.9	2.5
Cr	10.1	2.1	-	3
Cs	nd	nd	0.2	nd
Fe	300	nd	100	nd
Hf	2.2	0.07	1.7	0.07
La	1.9	nd	3.3	0.09
Sc	3	0.04	2.4	0.07
Sm	1.06	0.02	0.9	0.03
Ta	0.2	0.2	0.6	nd
Tb	0.2	nd	0.1	nd
Th	2.2	0.1	2.6	0.1
U	1.3	nd	1.4	-

Note: - = not determined; nd = undetected

4.3.6 Extraction of cobalt with ammonia hydroxide solution, sodium nitrite solution and anion exchange resins

Initial experiments were conducted to investigate the effect of ammonium and sodium nitrite on cobalt. As it was reported in the literature that cobalt(III) ions have greater affinity for NH_3 and NO_2^- , we reasoned that treating the Refcoal solution with these compounds would complex the cobalt(III) ions present in the coal matrix. The results of these experiments are listed in Table 4.13 below. The concentrations given in Table 4.13 are averages of two determinations. The samples obtained by treating with *ammonium hydroxide* the Refcoal gel derived from the extraction with sodium hydroxide only, and the Refcoal gel derived from the extraction with both sodium hydroxide and sodium sulphide, did not show any lowering of the cobalt concentration, which suggests that cobalt is present in a more stable complex in the Refcoal. The samples obtained by treating with *sodium nitrite* the Refcoal gel derived from the extraction with sodium hydroxide only, and the Refcoal gel derived from the extraction with both sodium hydroxide and sodium sulphide, did show some lowering of the cobalt concentration, which suggests that the nitrite ion (NO_2^-) forms a complex with the cobalt that is more stable than the complex in which cobalt exists in the coal. The Refcoal derived from treating the Refcoal gel extracted with sodium hydroxide only with ammonia solution, followed by anionic resins, shows some purification for most of the elements, with the cobalt concentrations in particular being reduced from 7.45 ppm to 4.29 ppm.

The lowering of the cobalt concentration appears to be better with the Refcoal gel derived from the extraction with both sodium hydroxide and sodium sulphide, treated in the same way. In this case, the cobalt concentration is reduced from 7.52 ppm to 3.70 ppm. This suggests that sodium sulphide aids in the demetalation of cobalt from its complex in the Refcoal, and future work should be directed towards the use of sodium sulphide in the extraction and purification of coal. Just as observed with the chelating

resins, the anion resins also introduced some bromine into the sample. Tantalum, which did not show any purification with chelating resins, appears to be lowered with anion resins. This suggests that tantalum is in anionic form in the Refcoal and for this reason could not be removed by the chelating resins. The rare earth metals did not show any purification with anion resins, which suggests that they are present in cationic form in the Refcoal.

Table 4.13: Concentrations of trace elements in Refcoal derived from Refcoal gel treated with NH₃, NaNO₂ and anion resins (ppm)

Element	Refcoal extracted with NaOH only			Refcoal extracted with NaOH and Na ₂ S		
	NH ₃ -treated	NaNO ₂ -treated	Resin-treated	NH ₃ -treated	NaNO ₂ -treated	Resin-treated
Br	1.1	1.8	12.6	1.5	2.3	14.4
Co	7.8	6.3	4.3	7.2	7.8	3.7
Cr	9.4	6.4	5.9	7.2	7.5	6.3
Cs	0.2	0.1	0.05	0.2	0.1	0.1
Eu	0.2	0.2	nd	0.2	0.08	0.1
Hf	2.7	2	0.8	2.4	0.9	1.1
La	3.1	2.6	1.13	2	2.1	0.8
Sc	3.9	2.9	0.03	3.2	1.3	1.6
Sm	0.8	0.8	0.4	0.7	0.7	0.3
Ta	0.5	0.6	0.6	0.5	0.2	0.2
Th	2.4	2.6	0.1	2.7	1.2	1.5
U	1.2	2.8	1.3	1.2	3.8	1.4

Note: nd = undetected

4.3.7 Colorimetric determination of cobalt

The analysis of coal is normally done by either ICP-AES, ICP-MS, INAA or XRF to obtain reasonable and acceptable data. These instruments are, however, very expensive and not every institution can afford its own. The University of Pretoria did not have such instruments at the time of this work. Samples had to be sent to the University of the Witwatersrand for analysis, which usually took about six to eight weeks before results were obtained. The only instruments available at the University of Pretoria that could be used for this work were the AA and UV/VIS. We therefore selected cobalt as an indicator element, and its rapid determination by the colorimetric method using a UV/VIS spectrophotometer was investigated. The calibration curve (Figure 4.9) obtained using the published method showed that the method could indeed be used successfully for the determination of cobalt. However, determinations using representative samples (Table 4.14) gave inconsistent results. This could be attributed to a number of factors. First, the digestion method, which employs an open vessel, is not reproducible as we had thought, leading to some samples being digested completely and others not. Secondly, contamination from the atmosphere, the vessel and the reagents used could be the cause of the inconsistency. Furthermore, the loss of analyte, due to volatilisation during digestion and to incomplete extraction of the cobalt complex into the chloroform solution, could be the cause of the low concentration values obtained in some samples. Finally, because of the complex matrix we are dealing with in coal and because the level of impurities is not well known, interference from elements such as iron, nickel, tin, copper and the platinum group metals cannot be ruled out.

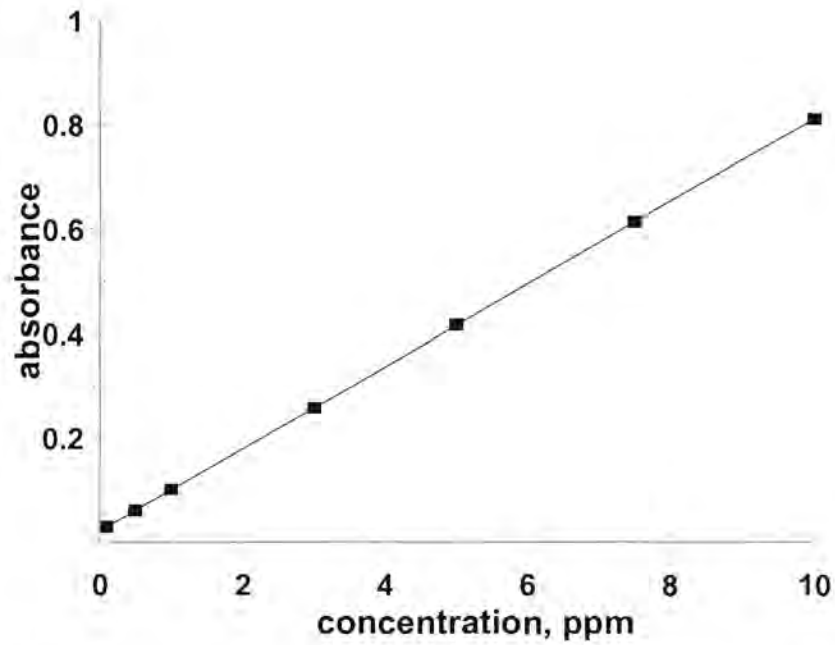


Figure 4.9: Calibration curve for the colorimetric determination of cobalt

Table 4.14: Cobalt concentration in Refcoal as determined by colorimetric method

Sample	RCO	RCB	RCR6	RCR9	RCR13	RCR14	RCR15
Concentration, ppm	6.3	6.6	2.1	17.3	15.4	7.2	6.2
	4.3	10.8	8.5	12.9	12.5	5	10.8
	6.1	15.6	1.7	5.8	16.6	5.8	6.7
	4.3	7.3	3.5				
	0.8	7.7	9.7				
	2.1	7.3	3.1				
	5.6	2.1					
	2.3	15.1					
	3.6	9.8					
Average	3.9	9.1	4.8	12	14.8	6	7.9
Standard deviation, δ	1.8	4	3.1	4.7	1.7	0.9	2.1

CHAPTER 5

GENERAL CONCLUSIONS

The Refcoal derived from the extraction with both sodium hydroxide and sodium sulphide appears to be lower in cobalt but higher in almost all the elements determined. Future work should be geared towards the extraction of carbon from coal with as little as possible amount of sodium sulphide to improve the coking of the Refcoal. High amounts of sodium sulphide should be avoided. A proper washing process for the recovery of the Refcoal from the Refcoal solution needs to be developed.

Refcoal solution treated with chelating resins did not remove rare earth metals as well as cobalt but tantalum appears to be lowered. There is no significant difference in terms of impurities between the Refcoal solution derived from the extraction with both sodium hydroxide and sodium sulphide treated with resins, and the Refcoal solution derived from the extraction with sodium hydroxide only also treated with the resins.

The hydrochloric acid treated Refcoal samples derived from the extraction with both sodium hydroxide and sodium sulphide appear to be low in the rare earth and cobalt than the Refcoal samples derived from the extraction with sodium hydroxide only. The hydrofluoric acid treated samples also show a similar trend, which suggests that the sodium sulphide is necessary for the demetalation of the metal complex in the coal matrix. Future work has to be geared towards this approach. Both hydrochloric acid and hydrofluoric acid treated samples show an increase in the concentration of Br, which suggests contamination by the acids. A similar increase in Br concentration is demonstrated when the Refcoal solution is treated with chelating resins which also suggests contamination by the resins.

Good purification is demonstrated for all the elements determined except for cobalt, chromium and tantalum if the Refcoal is first precipitated in water, followed by successive treatment with concentrated hydrochloric acid, concentrated hydrofluoric acid and chelating resins. Chromium and tantalum are not a problem with respect to nuclear carbon, the only real problem is cobalt. The Lewatit TP 208 chelating resins appear to be working better than the other two chelating resins, that is Lewatit TP 260 and Lewatit TP 208 chelating resins. The use of sulphonic acid resins appears to be even better than the Lewatit chelating resins as shown in Table 5.1 below.

Table 5.1 Concentration of trace elements in Refcoal derived from treating Refcoal gel with sulphonic acid resins and Lewatit TP 208 chelating resins (ppm)

Element	Coal	Refcoal extracted with NaOH only			Refcoal extracted with both NaOH and Na ₂ S		
		Unpurified Refcoal	Lewatit TP 208 resins	Sulphonic acid resins	Unpurified Refcoal	Lewatit TP 208 resins	Sulphonic acid resins
Br	4.1	0.7	2.2	0.8	0.9	2.9	4.5
Co	8.7	6.9	4.3	1.5	4.8	2.4	2.5
Cr	11	7.2	4.2	2.1	7.1	4.4	3
Cs	1.1	0.3	0.04	nd	0.1	0.03	nd
Fe	3400	1000	50	nd	4100	nd	nd
Hf	2.8	1.7	0.1	0.07	1.9	0.2	0.07
La	15.8	1.6	0.6	nd	4.8	0.7	0.09
Sc	5.7	2.7	0.08	0.04	2.2	0.2	0.07
Sm	2.7	0.6	0.4	0.02	2.3	0.03	0.03
Ta	0.6	0.5	0.6	0.2	0.3	0.6	nd
Tb	0.6	0.2	nd	nd	0.7	nd	nd
Th	4.9	2.6	0.7	0.1	1.7	0.07	0.1
U	2	0.4	0.3	nd	1.3	0.7	

Note: nd = undetected

CHAPTER 6

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APPENDICES

APPENDIX 1

Table A1.1: Minerals in coal [12,98]

Mineral group	Mineral constituents	Chemical formulae
Silicates (clay minerals)	Kaolinite (S)	$Al_2Si_2O_5(OH)_4$
	Illite (S, E)	$(OH)_8K(Mg,Al,Si)_3(Si_3Al)_3O_{10}$
	Chlorite (S, E)	$(Mg, Fe, Al)_6(AlSi_3)_4O_{10}(OH)_8$
	Feldspar	$(K, Na)_2O \cdot Al_2O_3 \cdot 6SiO_2$
	Zircon	$ZrSiO_4$
	Kyanite	$Al_2O_3 \cdot SiO_2$
	Staurolite	$(2FeO \cdot 5Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O)$
	Topaz	$(AlF)_2O \cdot SiO_4$
	Tourmaline	$H_5Al_3(BOH)_2 \cdot Si_4O_{19}$
	Muscovite (S)	$KAl_2(AlSi_3)O_{10}(OH)_2$
	Pyrophyllite	$Al_2Si_4O_{10} \cdot (OH)_2$
	Garnet	$3CaO \cdot Al_2O_3 \cdot 3SiO_2$
	Hornblende	$CaO \cdot 3FeO \cdot 4SiO_2$
	Epidote	$4CaO \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$
	Biotite	$K_2O \cdot MgO \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$
	Pernnite	$5MgO \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$
	Augite	$CaO \cdot MgO \cdot 2SiO_2$
	Montmorillonite (S)	$(AlMg)_8 \cdot (Si_4O_{10})_3(OH)_2$
	Mixed-layer illite-montmorillonite (S)	
	Paegioclaste (S)	$(Na, Ca)Al(SiAl)Si_2O_8$

Note: S = Syngenetic; E = Epigenetic

Table A1.1(continue): Minerals in coal [12,98]

Mineral group	Mineral constituents	Chemical formulae
Carbonates	Calcite (S, E)	CaCO ₃
	Dolomite (S, E)	CaMg(CO ₃) ₂
	Aragonite (S, E)	CaCO ₃
	Ankerite (S, E)	CaCO ₃ · (Mg, Fe, Mn)CO ₃
	Siderite (S)	FeCO ₃
	Mixed-layer Siderite-Ankerite	
Chlorides	Sylvite	KCl
	Halite	NaCl
Oxides	Quartz (S, E)	SiO ₂
	Diaspore	Al ₂ O ₃ ·3H ₂ O
	Lepidocrocite	Fe ₂ O ₃ ·3H ₂ O
	Hematite (S)	Fe ₃ O ₄
	Magnetite	Fe ₂ O ₃
	Rutile (S)	TiO ₂
Sulphates	Gypsum (E)	CaSO ₄ · 2H ₂ O
	Jarosite (E)	KF ₃ (OH) ₆ (SO ₄) ₂
	Barite	BaSO ₄
	Themadite (E)	Na ₂ SO ₄
Sulphides	Pyrite (S, E)	FeS ₂
	Marcasite (S, E)	FeS ₂
	Sphalerite (S, E)	ZnS
	Galena (E)	PbS
Phosphates	Apatite (S)	9Ca ₃ P ₂ O ₃ CaX ₂ (X = OH, F, Cl)

Note: S = Syngenetic; E = Epigenetic

Table A1.2 Abundance and elemental mode of occurrence in coal [20,21]

Element	Abundance (ppm)	Modes of occurrence	Level of confidence
Antimony	< 0.1 - 40	Sulfides, pyrite	4
Arsenic	< 1 - 250	As for S in 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 ₂ O ₄ ?, CrOOH	2
Cobalt	< 1 - 50	Sulfides?, clays?	4
Copper	< 1 - 200	Sulfides?, organic association?	-
Fluorine	< 20 - 1000	Fluorapatite, clays	-
Lead	< 1 - 100	PbS, pyrite, PbSe	8
Manganese	5 - 1000	Org. association, carbonates, other	8
Mercury	0.01 - 10	Sulfides?, Hg?, org. association?	6
Molybdenum	0.5 - 50	Pyrite, MoS ₂ ?, org. association?	-
Nickel	< 1 - 100	Sulfides, organic association?	2
Selenium	0.1 - 20	Organic Se, sulfides, etc.	8
Tin	0.1 - 20	Oxides, sulfides, org. association	-
Thallium	0.1 - 3	Sulfides	-
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 A1.3. Trace element content in major minerals, ppm[25].

Coal bed/ Region	Quartz							Kaolinite	Illite	Pyrite	
	Upper Banner Coal				Fire clay coal			West- phalian Region	Ruhr	Pittsburg no. 8	Upper Freeport
As	< 0.5	< 0.3	< 0.3	< 0.2	< 0.5	< 0.7	< 3	0.52	2.35	227	1210
Ba	950	550	< 60	630	<130	< 120	<400	159	840	< 300	< 200
Br	1.4	< 0.3	< 0.3	0.61	2.03	0.8	6.9	14.5	4.61	ND	ND
Ce	< 2	< 1	< 2	< 0.6	5.8	18	42	73	143	3.2	< 2
Cr	< 5	< 2	< 5	< 1	< 7	< 7	< 27	8.8	167	39	4.2
Co	< 0.6	< 0.3	< 0.5	< 0.2	< 1	< 1	< 4	0.943	12.4	13.8	23.1
Cs	0.52	0.2	< 0.4	0.078	0.44	< 0.5	1.8	1.99	27.4	< 0.6	0.19
Fe (%)	<0.03	<0.021	<0.03	<0.01	<0.01	<0.06	0.22	0.287	1.46	46.6	46.6
Eu	0.33	0.15	< 0.2	0.178	< 0.4	< 0.4	< 1	0.157	1.6	0.058	0.092
Hf	0.56	0.16	0.65	0.157	0.73	0.5	2.7	8.88	5.21	0.24	< 0.3
K (%)	0.7	0.56	0.058	0.52	< 0.1	< 0.1	< 0.4	0.146	5.64	0.02	0.02
La	0.41	0.5	0.26	0.271	2.26	10.2	17.7	36.4	88.7	1.64	1.31
Lu	<0.04	<0.02	<0.02	<0.01	0.063	<0.06	< 0.2	0.81	0.558	0.19	< 0.09
Na (%)	0.155	0.118	0.014	0.112	0.011	0.012	0.037	0.425	0.665	0.0249	0.027
Nd	< 8	< 5	< 7	< 3	< 11	< 10	< 30	28.4	42	< 40	< 30
Ni	< 60	< 22	< 40	< 13	< 80	< 80	< 290	< 26	36	ND	ND
Rb	25	11.5	< 19	10.5	< 30	< 30	< 100	7.5	273	< 50	12
Sb	< 0.2	< 0.2	0.076	<0.08	< 0.2	< 0.2	< 0.6	0.28	0.82	2.49	2.49
Sc	0.05	0.026	0.027	0.022	0.106	0.076	0.86	11.2	24.5	0.55	0.546
Se	< 6	< 2	< 5	< 1	< 5	< 9	< 13	< 3	< 7	45	32.2
Sm	< 0.6	0.041	0.029	0.018	0.438	0.96	2.51	11.03	10.21	0.16	0.194
Sr	< 230	74	< 220	54	< 500	< 400	<1200	< 110	189	< 300	< 100
Ta	< 0.5	< 0.3	< 0.4	< 0.1	< 0.8	< 0.9	< 3	9.9	2.06	< 0.4	< 0.3
Tb	< 0.2	< 0.08	< 0.1	<0.04	< 0.2	< 0.3	< 0.2	2.05	0.82	< 0.6	< 0.4
Th	0.77	1.2	0.6	0.22	1.1	3	6.9	59.6	20.7	0.46	0.46
U	< 0.4	< 0.2	< 0.3	< 0.1	< 0.4	< 0.5	< 1	25.3	4.25	2	ND
W	< 0.6	< 0.3	< 0.3	< 0.2	< 0.6	< 0.8	< 2	8.8	5.25	ND	ND
Yb	< 0.3	< 0.1	< 0.1	< 0.1	<0.3	< 0.4	< 1	7.3	4.7	< 2	< 0.5
Zn	< 12	< 5	< 0.9	< 3	< 20	< 18	< 80	23	36	18	37

Note: ND = not determined

Table A1.4. Average concentrations of elements in coal [14]

Element	U.S. average	Worldwide average	Element	U.S. average	Worldwide average
<i>Concentration (%)</i>					
Aluminium, Al	1.4	1.0	Potassium, K	0.18	0.01
Calcium, Ca	0.54	1.0	Silicon, Si	2.6	2.8
Iron, Fe	1.6	1.0	Sodium, Na	0.06	0.02
Magnesium, Mg	0.12	0.02	Sulfur, S	2.0	2.0
Manganese, Mn	0.01	0.005	Titanium, Ti	0.08	0.05
Phosphorus, P	-	0.05			
<i>Concentration (ppm)</i>					
Antimony, Sb	1.1	3.0	Lithium, Li	20	65
Arsenic, As	15	5.0	Lutetium, Lu	0.08	0.07
Barium, Ba	150	500	Mercury, Hg	0.18	0.012
Beryllium, Be	2.0	3	Molybdenum, Mo	3	5
Bismuth, Bi	0.7	5.5	Neodymium, Nd	37	4.7
Boron, B	50	75	Nickel, Ni	15	15
Bromine, Br	2.6	-	Niobium, Nb	4.5	-
Cadmium, Cd	1.3	-	Praseodymium, Pr	2.7	2.2
Cerium, Ce	7.7	11.5	Rubidium, Rb	2.9	100
Cesium, Cs	0.4	-	Samarium, Sm	0.42	1.6
Chlorine, Cl	207	1000	Scandium, Sc	3	5
Chromium, Cr	15	10	Selenium, Se	4.1	3
Cobalt, Co	7	5	Silver, Ag	0.20	0.50
Copper, Cu	19	15	Strontium, Sr	100	500
Dysprosium, Dy	2.2	-	Tellurium, Te	0.1	-
Erbium, Er	0.34	0.6	Terbium, Tb	0.1	0.3
Europium, Eu	0.45	0.7	Thorium, Th	0.1	-
Fluorine, F	74	-	Thulium, Tm	1.9	-
Gadolinium, Gd	0.17	1.6	Tin, Sn	1.6	-
Galium, Ga	7	7	Tungsten, W	2.5	-
Germanium, Ge	0.71	5	Uranium, U	1.6	1.0
Hafnium, Hf	0.60	-	Vanadium, V	20	25
Holmium, Ho	0.11	0.3	Ytterbium, Yb	1	0.5
Iodine, I	1.10	-	Yttrium, Y	10	10
Lanthanum, La	6.1	10	Zinc, Zn	39	10
Lead, Pb	16	25	Zirconium, Zr	30	-

Table A1.5. Average concentrations of elements in South African coals, ppm [36]

Element	Witbank- Heidelberg	Ermelo- Belfast- Piet Retief	South Rand	Ellisras	Orange Free State	Natal
Arsenic, As	8.1	7.8	12	5.5	13.3	7.3
Barium, Ba	243.1	220.6	512	83.5	371.2	280.9
Beryllium, Be	1.8	2.6	3	2.5	2.2	3.6
Cadmium, Cd	0.12	0.12	0.1	0.15	0.15	0.27
Chlorine, Cl	41.8	42.7	30	70	45	102.7
Chromium, Cr	27.7	28.9	97	24	45.3	26.7
Cobalt, Co	97	14.1	31	24	14.3	17.3
Copper, Cu	11.2	11	20	9.5	14.7	12.9
Fluorine, F	169.9	112.5	155	97.5	116.5	117.3
Gallium, Ga	7	7	14	4	11.5	6.2
Germanium, Ge	7.2	8.1	23	7.5	14	7
Lead, Pb	11.1	13.3	24	13	22.7	8
Lithium, Li	47.9	18.5	96	6	56.8	22.6
Manganese, Mn	58.8	49.1	58	82	80	42.6
Nickel, Ni	20.1	28.3	33	17.5	18.7	23.4
Strontium, Sr	440.7	452.8	822	69.5	491.2	399.7
Vanadium, V	26.6	29	42	50.5	33.3	32.4
Zinc, Zn	12.5	20.3	17	43.5	17.2	16.8

Table A1.6. Average concentration (ppm) of trace elements in Tshikondeni coal and Refcoal.

Element	Original coal	Refcoal	Washed with HOAc	Washed with HCl	Washed with HF + HCl
Antimony, Sb	0.7	0.1	0.5	0.1	0.1
Arsenic, As	1.1	0.1	0.1	0.1	0.1
Boron, B	17	2	3	2	ND
Cadmium, Cd	0.0	0.7	0.2	0.3	0.1
Calcium, Ca	4582	112	103	46	114
Cesium, Cs	0.6	0.0	0.0	0.0	0.0
Chromium, Cr	15.9	6.1	7.6	6.3	5.6
Cobalt, Co	4.8	2.8	3.8	2.3	2.4
Copper, Cu	9.1	6.3	6.9	6.1	7.6
Europium, Eu	0.4	0.1	0.1	0.1	0.1
Galium, Ga	6.2	1.1	1.7	1.4	1.3
Hafnium, Hf	3.8	2.5	2.8	2.4	2.0
Iron, Fe	6662	162	239	110	107
Lanthanum, La	11.0	1.4	2.1	1.5	2.0
Lithium, Li	8.8	0.5	0.7	0.7	0.2
Magnesium, Mg	817	22	22	17	14
Manganese, Mn	68.1	1.3	1.1	0.3	0.2
Mercury, Hg	0.1	0.2	0.4	0.4	0.6
Molybdenum, Mo	4.2	0.7	1.1	1.0	0.9
Nickel, Ni	14	8	10	9	8
Phosphorus, P	2152	143	171	108	30
Rubidium, Rb	4.4	0.2	0.2	0.2	0.0
Scandium, Sc	4.4	1.6	1.9	1.3	1.8
Silicon, Si	28419	1344	1727	1530	1565
Sulfur, S	10433	2678	4162	3240	2780
Strontium, Sr	140	23	26	19	18
Tantalum, Ta	0.6	0.5	0.7	0.6	0.7
Tin, Sn	2.4	1.1	1.3	1.1	1
Titanium, Ti	1029	475	626	528	418
Vanadium, V	12.9	4.9	5.7	4.9	5.1
Ytterbium, Yb	1.7	0.5	0.7	0.6	0.7
Yttrium, Y	10.8	4.9	5.9	4.3	6.2
Zirconium, Zr	129	100	127	107	75

ND = Not determined due to contamination

Table A1.7. Sensitivities of different methods for coal analysis

	NAA ^a (g)	SSMS (ng)	CIMS	ICPAES (µg/ml)	NFAAS	XRFS (µg)	ASV	ICPMS ^b µg/g	LAICPMS ^b µg/g
Ag	10 ⁻¹⁰ - 10 ⁻⁹	0.2	-	0.004	0.001ng/ml	1.2	0.25ppb	0.0019	0.001
Al	10 ⁻¹⁰ - 10 ⁻⁹	0.02	-	0.002	1x10 ⁻¹² g	5.0	-	0.66	1.80
As	10 ⁻¹⁰ - 10 ⁻⁹	0.06	-	-	-	0.11	-	0.022	0.008
Au	10 ⁻¹² - 10 ⁻¹¹	0.2	-	0.04	1x10 ⁻¹² g	0.001 /cm ²	1.0ppb	0.0005	0.001
B	-	-	-	-	-	-	-	0.15	8
Ba	10 ⁻¹⁰ - 10 ⁻⁹	0.2	-	0.01	6x10 ⁻¹² g	0.12	-	0.017	0.028
Be	-	0.008	-	0.005	3x10 ⁻¹⁴ g	-	-	0.0015	0.024
Bi	10 ⁻⁸ - 10 ⁻⁷	0.2	-	0.05	4x10 ⁻¹² g	0.61	0.01ng/ml	0.0001	0.001
Br	-	-	-	-	-	-	-	8.4	17
Ca	10 ⁻⁸ - 10 ⁻⁷	0.03	-	0.00007	4x10 ⁻¹³ g	0.1	-	3.9	9.00
Cd	10 ⁻⁹ - 10 ⁻⁸	0.3	-	0.002	0.03ng/ml	0.40	0.005ng/ml	0.0007	0.011
Ce	10 ⁻⁹ - 10 ⁻⁸	0.1	-	0.007	-	0.17	-	0.004	0.003
Co	10 ⁻¹⁰ - 10 ⁻⁹	0.05	1x10 ⁻¹¹	0.003	2x10 ⁻¹² g	0.05	-	0.012	0.022
Cr	10 ⁻⁸ - 10 ⁻⁷	0.05	1x10 ⁻¹¹	0.001	1.2x10 ⁻¹² g	0.00006	-	0.017	0.001
Cs	10 ⁻⁹ - 10 ⁻⁸	0.1	-	-	-	0.15	-	0.0001	0.0004
Cu	10 ⁻¹⁰ - 10 ⁻⁹	0.08	1x10 ⁻¹¹	0.001	6x10 ⁻¹³ g	0.00002	0.005ng/ml	0.041	0.140
Dy	10 ⁻¹³ - 10 ⁻¹²	0.5	5x10 ⁻¹¹	0.004	2.2x10 ⁻¹⁰ g	-	-	0.0002	0.003
Er	10 ⁻¹⁰ - 10 ⁻⁹	0.5	5x10 ⁻¹¹	0.001	3.7x10 ⁻¹¹ g	-	-	0.0007	0.002
Eu	10 ⁻¹³ - 10 ⁻¹²	0.2	5x10 ⁻¹¹	0.001	3x10 ⁻¹¹ g	0.66	-	0.0001	0.003
Fe	10 ⁻⁶ - 10 ⁻⁵	0.05	1x10 ⁻¹¹	0.005	2x10 ⁻¹³ g	0.0085	-	0.36	0.50
Ga	10 ⁻¹⁰ - 10 ⁻⁹	0.09	-	0.014	1x10 ⁻¹² g	0.01	0.4ng/ml	0.003	0.008
Gd	10 ⁻⁹ - 10 ⁻⁸	0.5	5x10 ⁻¹¹	0.007	-	-	-	0.0002	0.014
Hf	10 ⁻¹¹ - 10 ⁻¹⁰	-	-	0.01	-	-	-	0.0062	0.003
Hg	10 ⁻¹⁰ - 10 ⁻⁹	0.6	-	0.2	8x10 ⁻¹¹ g	0.24	4x10 ⁻⁹ M	0.008	0.060
Ho	10 ⁻¹¹ - 10 ⁻¹⁰	0.1	5x10 ⁻¹¹	0.01	3.3x10 ⁻¹⁰ g	-	-	0.00002	0.0005
I	-	-	-	-	-	-	-	0.41	0.37
In	10 ⁻¹² - 10 ⁻¹¹	0.1	-	0.03	4x10 ⁻¹³ g	1.1	0.1ng/ml	-	-
Ir	10 ⁻¹¹ - 10 ⁻¹⁰	0.3	-	-	-	-	-	0.00004	-
K	-	0.03	-	-	-	0.52	1x10 ⁻⁵ M	4.6	60
La	10 ⁻¹¹ - 10 ⁻¹⁰	0.1	5x10 ⁻¹¹	0.003	0.1ng/ml	0.12	-	0.001	0.006
Li	-	0.0006	-	-	-	-	-	0.028	12
Lu	10 ⁻¹⁰ - 10 ⁻⁹	0.1	5x10 ⁻¹¹	0.008	-	-	-	0.00006	0.002
Mg	10 ⁻⁸ - 10 ⁻⁷	0.03	-	0.0007	4x10 ⁻¹⁴ g	-	-	2.7	17
Mn	10 ⁻¹² - 10 ⁻¹¹	0.05	1x10 ⁻¹¹	0.007	2x10 ⁻¹³ g	0.00015	-	0.03	1.20
Mo	10 ⁻⁹ - 10 ⁻⁸	0.3	-	0.005	3x10 ⁻¹² g	0.072	-	0.024	0.018
Na	10 ⁻¹⁰ - 10 ⁻⁹	0.02	-	0.0002	1x10 ⁻¹² g	-	-	6.9	11.0
Nb	-	0.08	-	0.01	12.0µg/ml	-	-	-	0.0012
Nd	-	0.4	5x10 ⁻¹¹	0.05	-	0.30	-	0.002	0.005
Ni	10 ⁻⁸ - 10 ⁻⁷	-	1x10 ⁻¹¹	0.006	4x10 ⁻¹² g	0.06	0.1g/ml	0.074	0.620
Os	10 ⁻⁹ - 10 ⁻⁸	0.4	-	-	-	-	-	-	-
P	-	-	-	-	-	0.01	-	0.37	1.500
Pb	10 ⁻⁷ - 10 ⁻⁶	0.3	-	0.008	0.002ng/ml	0.0003	0.01ng/ml	0.009	0.002
Pd	10 ⁻¹⁰ - 10 ⁻⁹	0.3	1x10 ⁻¹¹	0.007	4x10 ⁻¹² g	-	-	0.0033	0.003
Pr	10 ⁻¹⁰ - 10 ⁻⁹	0.1	5x10 ⁻¹¹	0.07	-	-	-	0.0002	0.002
Pt	10 ⁻⁹ - 10 ⁻⁸	0.5	1x10 ⁻¹¹	0.08	1x10 ⁻¹¹ g	-	1x10 ⁻⁹ m	0.0004	0.002
Rb	-	-	-	-	-	0.0075	-	0.007	0.010
Re	10 ⁻¹¹ - 10 ⁻¹⁰	0.2	-	-	-	-	-	0.00002	0.001
Rh	10 ⁻¹¹ - 10 ⁻¹⁰	0.09	1x10 ⁻¹¹	0.003	8x10 ⁻¹² g	103µg/ml	0.1ng/ml	0.00009	-
Ru	10 ⁻⁹ - 10 ⁻⁸	0.03	1x10 ⁻¹¹	-	-	-	-	0.0003	0.004
S	-	-	-	-	-	-	-	25	26
Sb	10 ⁻¹⁰ - 10 ⁻⁹	-	-	-	-	-	-	0.0013	0.007
Sc	10 ⁻¹⁰ - 10 ⁻⁹	0.04	-	0.003	-	0.38	-	0.0005	0.003
Se	-	-	-	-	-	-	-	0.19	0.111
Si	-	-	-	-	-	-	-	5.4	14000
Sm	10 ⁻¹¹ - 10 ⁻¹⁰	0.5	5x10 ⁻¹¹	0.02	-	4.1µg/ml	-	0.0003	0.003
Sn	-	0.3	-	0.3	2x10 ⁻¹² g	3.9ppm	2.0ng/l	0.034	0.019
Sr	10 ⁻⁹ - 10 ⁻⁸	0.09	-	0.00002	1x10 ⁻¹² g	0.00007	-	0.013	0.045
Ta	10 ⁻⁹ - 10 ⁻⁸	0.2	-	0.07	7.0µg/ml	-	-	0.0008	0.003
Tb	10 ⁻⁹ - 10 ⁻⁸	0.1	5x10 ⁻¹¹ g	0.2	-	159µg/ml	-	0.0001	0.001
Te	10 ⁻⁹ - 10 ⁻⁷	-	-	-	-	0.12	-	0.0047	0.018
Th	10 ⁻⁹ - 10 ⁻⁸	0.2	-	0.003	-	6.5µg/ml	-	0.0017	0.001
Ti	10 ⁻⁹ - 10 ⁻⁷	0.05	-	0.003	1x10 ⁻¹² g	0.001	-	0.47	0.05

NOTE: Continued on next page

Table A1.7.(continued). Sensitivities of different methods for coal analysis

	NAA ^a (ng)	SSMS (g)	CIMS	ICPAES (µg/ml)	NFAAS	XRFS (µg)	ASV	ICPMS ^b µg/g	LAICPMS ^b µg/g
Tl	10 ⁻⁸ - 10 ⁻⁷	0.2	-	0.2	1x10 ⁻¹² g	-	0.1ng/ml	0.0006	0.004
Tm	10 ⁻⁹ - 10 ⁻⁸	0.1	5x10 ⁻¹² g	0.007	-	-	-	0.00003	0.000
U	10 ⁻¹⁰ - 10 ⁻⁹	-	-	0.03	-	0.00002	-	0.0005	0.000
V	10 ⁻¹¹ - 10 ⁻¹⁰	0.04	1x10 ⁻¹¹ g	0.006	5x10 ⁻¹¹ g	-	-	0.016	0.005
W	10 ⁻¹⁰ - 10 ⁻⁹	0.5	-	0.002	1.0µg/ml	-	-	0.0054	0.001
Y	-	-	-	0.002	10µg/ml	0.22	-	0.0012	0.006
Yb	10 ⁻¹⁰ - 10 ⁻⁹	0.5	5x10 ⁻¹¹ g	0.00009	-	6.8µg/ml	-	0.0001	0.006
Zn	10 ⁻⁸ - 10 ⁻⁷	0.1	1x10 ⁻¹¹ g	0.002	2x10 ⁻¹⁴ g	0.00004	0.04µg/ml	-	0.15
Zr	10 ⁻⁸ - 10 ⁻⁷	0.1	-	0.005	5.0µg/ml	0.00002	-	0.018	0.016

NOTE: ^a : From Dulka and Risby [81] ^b : From Roduskin et al [58]

NAA = neutron activation analysis; SSMS = spark source mass spectrometry; CIMS = chemical ionization mass spectrometry; ICPAES = inductively coupled plasma atomic emission spectrometry; NFAAS = none-flame atomic absorption spectrometry; XRFS = X-ray fluorescence spectrometry; ASV = anodic stripping voltametry; ICPMS = inductively coupled plasma mass spectrometry; LAICPMS = laser ablation inductively coupled plasma mass spectrometry

Table A1.8. Concentration (µg/g) of trace elements in SRC as determined by AA [30].

Element	Pittsburg No.8 feed coal	Amax feed coal	Monterey feed coal	Illinois feed coal	Western Kentucky feed coal
Al	147	171	77.8	32	107
Ca	105	23.7	93.5	5486	1297
Cd	<0.07	2.8	0.5	0.3	0.3
Co	<2	19.2	12	5	4.8
Cr	5.9	5.7	11.2	11.9	3.7
Cu	12.4	3.2	3.6	0.8	1.4
Fe	423	11797	714	738	3300
K	113	22.3	27.2	40.9	33.5
Mg	24.3	58.9	29	8.3	8
Mn	21.6	4.4	39.6	8.7	3.6
Ni	12	16.4	13.8	7.7	3.3
Pb	<0.5	12.8	23.7	4.9	2.1

Table A1.9 Concentration ($\mu\text{g/g}$) of trace elements in SRC as determined by INAA [103].

Element	Coal	SRC
AS	13.6	1.39
Ba	62.6	2.48
Br	3.51	3.95
Ce	17	0.553
Co	3.7	0.31
Cr	14	2.68
Cs	0.89	0.023
Eu	0.292	0.013
Fe, %	1.73	0.068
Hg	0.436	0.025
K	1500	315
Lu	0.125	0.004
Na	148	9.55
Ni	20	2.7
Rb	22.4	0.57
Sb	0.5	0.074
Sc	2.8	0.13
Se	1.53	0.148
Sm	1.37	0.04
Sr	152	4.4
Tb	0.437	0.014
Th	1.66	0.055

Table A1.9. Trace elements in NMP coal extract. Concentration in ppm

	Water precipitated	Vacuum-evaporation
Ash%	0.06	0.08
Al	11	24
Ca	7.8	46
Cr	6.7	7.4
Cu	5.9	17
Fe	170	225
K	1.8	3.3
Mg	2.4	13
Mn	0.2	1.2
Na	3.3	34
Ni	7.6	11
P	7.7	8.8
Si	31	68
Ti	52	82
V	2.7	3.9
Zn	5.9	22
As Oxides %	0.06	0.09

Table A1.10. Analysis and extent of extraction in NMP of various coals

Coal	Proximate analysis			Ultimate analysis				%C Extraction
	%Moisture	% Ash	%C	%C	%H	%N	%S	
Hlobane Gus	1.2	10.9	77	87	4.9	2.2	0.6	41.3
Hlobane Dundus	1.1	13.4	74	87	5.2	2.2	0.7	54.9
Vryheid Coronation, Vrede	2	14.4	71	85	5.2	2.1	0.7	36.5
Vryheid Coronation, Leeuwnek	1.2	14.5	74	87	5.1	2.3	0.9	67
Moatize	0.9	19	71	88	5	2.1	0.9	80.3
Tshikondeni Floatation Product	0.9	7.8	81	89	5.2	2.1	0.8	90.3
Upper Freeport	1.13	13.03	73	86	4.7	1.6		85.8
Wyodak	28.09	6.31	49	75	5.4	1.1		6
Illinois # 6	7.97	14.25	60	78	5	1.4		14.4
Pittsburgh # 8	1.65	9.1	74	83	5.3	1.6		25.3
Pocahantas # 3	0.65	4.74	86	91	4.4	1.3		76.9
Blind Canyons	4.63	4.49	73	81	5.8	1.6		16.2
Stockton	2.42	19.36	65	83	5.3	1.6		17.5
Beulah Zap	32.24	6.59	45	73	4.8	1.2		6.4
Polish coal	1.6	0.65	80	87	5.4	1.8	0.7	41.2

Table A1.11. Properties of Nuclear Grade Graphite [5]

Property	Anisotropic graphite	Isotropic graphite
Density, g/cm ³	1.71	1.86
Resistance, $\mu\Omega \cdot \text{Cm}$	735	1000
Tensile strength, kPa	9930	46172
Coefficient of thermal expansion (CTE), $10^{-6}/^{\circ}\text{C}$		
with grain	2.2	5.3
against grain	3.8	5.3
Anisotropy ratio (CTE ratio)	1.73	1
Total ash, ppm	740	400
Boron content, ppm	0.4	0.3

APPENDIX 2

Table A2.1. The progress of extraction with NaOH only

Time, min		0	5	10	15	30	45	60	90	120	180	240	300
RUN 1	Mass, g	0.109	0.108	0.109	0.102	0.111	0.105	0.103	0.102	0.101	0.103	0.109	0.101
	Absorbance	0.000	0.000	0.000	0.006	0.112	0.230	0.357	0.608	0.813	0.945	1.046	1.008
	Corrected Absorbance	0.000	0.000	0.000	0.006	0.101	0.218	0.348	0.597	0.802	0.917	0.961	0.998
RUN 2	Mass, g	0.106	0.104	0.103	0.101	0.100	0.104	0.104	0.112	0.110	0.101	0.103	0.106
	Absorbance	0.000	0.000	0.005	0.021	0.202	0.355	0.527	0.793	0.940	0.933	0.991	1.044
	Corrected Absorbance	0.000	0.000	0.005	0.021	0.201	0.341	0.509	0.709	0.856	0.927	0.965	0.984
RUN 3	Mass, g	0.104	0.140	0.120	0.122	0.107	0.117	0.117	0.112	0.101	0.101	0.108	0.124
	Absorbance	0.000	0.000	0.000	0.013	0.100	0.252	0.387	0.670	0.765	0.863	0.987	1.188
	Corrected Absorbance	0.000	0.000	0.000	0.011	0.093	0.215	0.330	0.600	0.757	0.854	0.912	0.955
RUN 4	Mass, g	0.115	0.108	0.103	0.114	0.102	0.117	0.102	0.143	0.113	0.111	0.113	0.116
	Absorbance	0.000	0.002	0.006	0.047	0.170	0.308	0.415	0.874	0.897	0.986	1.043	1.069
	Corrected Absorbance	0.000	0.002	0.006	0.041	0.167	0.264	0.408	0.611	0.796	0.892	0.921	0.925
RUN 5	Mass, g	0.100	0.127	0.111	0.111	0.110	0.106	0.107	0.120	0.100	0.108	0.106	0.119
	Absorbance	0.000	0.005	0.008	0.024	0.166	0.288	0.482	0.836	0.822	1.005	1.042	1.172
	Corrected Absorbance	0.000	0.004	0.007	0.022	0.150	0.272	0.451	0.695	0.826	0.934	0.985	0.987
Average Corrected Absorbance		0.000	0.003	0.006	0.020	0.142	0.262	0.409	0.642	0.807	0.905	0.949	0.970

Table A2.2. The progress of extraction with Na₂S only

Time, min		0	5	10	15	30	45	60	90	120	180	240	300
6.34g Na ₂ S	Mass, g	0.114	0.116	0.106	0.108	0.106	0.106	0.118	0.119	0.120	0.105	0.118	0.103
	Absorbance	0.016	0.044	0.058	0.097	0.148	0.174	0.181	0.192	0.176	0.164	0.194	0.172
	Corrected Absorbance	0.014	0.038	0.055	0.090	0.140	0.150	0.154	0.162	0.171	0.156	0.164	0.167
12.61g Na ₂ S	Mass, g	0.107	0.103	0.121	0.111	0.111	0.108	0.104	0.113	0.104	0.103	0.110	0.111
	Absorbance	0.014	0.017	0.040	0.054	0.169	0.220	0.265	0.312	0.305	0.293	0.306	0.295
	Corrected Absorbance	0.013	0.016	0.033	0.048	0.153	0.204	0.254	0.275	0.294	0.283	0.278	0.266
25.17g Na ₂ S	Mass, g	0.101	0.114	0.103	0.104	0.107	0.108	0.102	0.109	0.113	0.107	0.120	0.102
	Absorbance	0.009	0.057	0.175	0.227	0.432	0.526	0.478	0.460	0.387	0.250	0.253	0.215
	Corrected Absorbance	0.009	0.050	0.170	0.219	0.402	0.488	0.470	0.424	0.341	0.234	0.211	0.211
25.17g Na ₂ S	Mass, g	0.110	0.104	0.107	0.116	0.106	0.104	0.104	0.105	0.108	0.108	0.104	0.106
	Absorbance	0.012	0.021	0.067	0.179	0.346	0.415	0.455	0.415	0.371	0.290	0.244	0.245
	Corrected Absorbance	0.011	0.020	0.065	0.154	0.328	0.398	0.436	0.396	0.344	0.269	0.234	0.231
Average Corrected Absorbance		0.010	0.035	0.118	0.187	0.365	0.443	0.453	0.410	0.343	0.252	0.223	0.221

Table A2.3. The progress of extraction with NaOH and Na₂S

Time,min		0	5	10	15	30	45	60	90	120	180	240	300
10:1 NaOH :Na ₂ S mole ratio	Mass, g	0.106	0.104	0.105	0.103	0.109	0.112	0.105	0.101	0.107	0.105	0.105	0.127
	Absorbance	0.023	0.053	0.086	0.239	0.339	0.385	0.506	0.506	0.618	0.618	0.723	0.769
	Corrected Absorbance	0.011	0.022	0.051	0.084	0.022	0.303	0.367	0.503	0.579	0.690	0.732	0.729
8:1 NaOH :Na ₂ S mole ratio	Mass, g	0.106	0.107	0.110	0.118	0.121	0.102	0.111	0.113	0.110	0.104	0.117	0.116
	Absorbance	0.006	0.046	0.108	0.158	0.325	0.510	0.534	0.820	0.928	0.894	1.035	1.027
	Corrected Absorbance	0.006	0.043	0.095	0.143	0.276	0.423	0.525	0.742	0.824	0.861	0.882	0.884
4:1 NaOH :Na ₂ S mole ratio	Mass, g	0.104	0.106	0.104	0.101	0.113	0.100	0.109	0.104	0.106	0.111	0.108	0.108
	Absorbance	0.013	0.015	0.047	0.075	0.205	0.226	0.343	0.458	0.566	0.754	0.765	0.793
	Corrected Absorbance	0.012	0.014	0.045	0.074	0.182	0.225	0.314	0.440	0.536	0.679	0.699	0.736
2:1 NaOH :Na ₂ S mole ratio	Mass, g	0.110	0.100	0.109	0.106	0.107	0.101	0.104	0.102	0.104	0.112	0.145	0.107
	Absorbance	0.126	0.180	0.251	0.291	0.401	0.406	0.464	0.502	0.558	0.623	0.900	0.727
	Corrected Absorbance	0.114	0.180	0.231	0.274	0.373	0.400	0.446	0.494	0.536	0.594	0.675	0.681
1:1 NaOH :Na ₂ S mole ratio Run 1	Mass, g	0.108	0.110	0.105	0.101	0.112	0.108	0.111	0.105	0.111	0.112	0.103	0.103
	Absorbance	0.048	0.265	0.306	0.350	0.475	0.515	0.584	0.575	0.556	0.387	0.249	0.234
	Corrected Absorbance	0.044	0.242	0.282	0.347	0.423	0.475	0.525	0.547	0.499	0.347	0.241	0.227
1:1 NaOH :Na ₂ S mole ratio Run 2	Mass, g	0.113	0.108	0.106	0.101	0.116	0.119	0.121	0.124	0.112	0.110	0.108	0.111
	Absorbance	0.124	0.265	0.289	0.386	0.546	0.642	0.677	0.657	0.474	0.331	0.277	0.261
	Corrected Absorbance	0.110	0.245	0.272	0.384	0.472	0.540	0.560	0.531	0.423	0.301	0.257	0.235
1:1 NaOH :Na ₂ S mole ratio Run 3	Mass, g	0.116	0.116	0.116	0.095	0.108	0.099	0.112	0.112	0.102	0.125	0.121	0.115
	Absorbance	0.005	0.283	0.430	0.381	0.504	0.505	0.581	0.558	0.455	0.408	0.304	0.272
	Corrected Absorbance	0.005	0.244	0.371	0.401	0.467	0.511	0.520	0.496	0.445	0.327	0.251	0.236
Average Corrected Absorbance		0.053	0.244	0.308	0.377	0.454	0.509	0.535	0.525	0.456	0.325	0.250	0.233

APPENDIX 3

Table A3.1. Concentrations of trace elements in Coal and Refcoal precipitated from water (ppm).

		Sample	La	Br	Sm	U	Hf	Tb	Th	Sc	Cs	Eu	Co	Cr	Ta	Fe
Coal		C1	11.6	7.20	2.70	2.52	3.04	0.56	4.87	3.32	0.90		5.45	8.45	0.55	3400
		C2	20.6	0.98	2.7	1.44	2.26		3.21	5.31	0.99	0.46	8.29	5.88	0.72	
		C3					3.01		5.81	7.38	1.22	0.6	10.57	14.59	0.68	
		C4					2.84		5.81	6.92	1.24	0.61	10.41	14.87	0.62	
		Average	15.8	4.1	2.7	2	2.8	0.6	4.9	5.7	1.1	0.6	8.7	11	0.6	3400
Refcoal	No	RCW16	2.16	nd	0.83	1.30	2.40	0.08	3.20	3.15	0.13	0.18	7.58		0.68	200
		RCW18	1.80	0.20	0.76	0.96	1.21	0.38	5.44	1.37	0.80		7.04	4.28	0.68	800
	Na ₂ S	RCW19	2.17	0.45	1.10	0.72	2.18	0.24	2.73	4.46	nd		6.51	9.61	0.23	300
		RCW22	1.79	0.65	0.26	1.18	0.44		0.87	0.85	0.13	0.06	4.19	6.64	0.14	
		RCW24	nd	2.42	nd	nd	2.09		0.78	3.82	0.22	nd	9.37	8.18	0.47	
		Average	1.6	0.7	0.6	0.8	1.7	0.2	2.6	2.7	0.3	0.08	6.9	7.2	0.4	433
	With	RCW17a	44.8	nd	4.75	1.46	3.45	nd	15.3	1.73	0.2		4.08	6.00	0.44	7800
		RCW17b					nd		1.88	2.06	0.11	0.13	5.5	7.27	0.43	
	Na ₂ S	RCW20a	5.82	0.32	1.38	0.79	1.86	1.32	2.55	3.94	nd		6.47	9.05	0.45	400
		RCW21	3.84	2.30	0.85	1.53	0.40		0.80	0.78	0.14	0.06	3.80	6.13	0.13	
		Average	4.8	0.9	2.3	1.3	1.9	0.7	1.7	2.2	0.1	0.1	4.8	7.1	0.3	4100

NOTE: nd = Not Detected

Table A3.2. Concentrations of trace elements in Refcoal derived from Refcoal gel treated with acid (ppm).

Acid		Sample	La	Br	Sm	U	Hf	Tb	Th	Sc	Cs	Eu	Co	Cr	Ta	Fe
HCl	No Na ₂ S	RCA44	2.2	0.73	0.43	0.89	nd	nd	2.59	0.18	nd		6.89	7.29	0.53	200
		RCA48	nd	4.48	0.06	4.35	0.4	nd	0.08	0.19	nd	nd	2.58	3.54	0.39	100
		RCA44b	nd	4.82	nd	0.87	1.85		1.43	0.87	0.1	nd	7.43	6.11	0.64	
		RCA73	nd	0.37	0.04	nd	0.91		0.98	0.36	nd	nd	4.98	3	0.63	
		Average	0.6	2.6	0.1	1.5	0.8	nd	1.3	0.4	0.03	nd	5.5	5	0.5	150
	With Na ₂ S	RCA46	0.18	1.81	0.06	nd	0.40	nd	nd	0.6	nd		2.79	3.07	0.42	100
		RCA60	0.32	2.67	0.06	0.37	0.72		0.17	0.30	0.06	0.01	4.71	4.98	0.59	
		Average	0.7	2.2	0.06	0.2	0.6	nd	0.09	0.5	0.3	0.01	2.4	4	0.5	100
HF	No Na ₂ S	RCA41	1.60	0.53	0.33	1.54	2.31	nd	2.21	0.10	nd		6.89	5.16	0.41	nd
		RCA45b	nd	4.67	0.07	0.54	0.33		3.61	0.13	nd	nd	7.75	9.32	0.66	
		RCA49	0.30	4.25	0.11	2.1	0.2	nd	0.15	0.11	nd		2.97	4.41	0.50	40
		Average	0.6	3.2	0.1	1.4	0.9	nd	2	0.1	nd	nd	5.9	6.3	0.51	40
	With Na ₂ S	RCA43	1.30	0.92	0.30	1.25	1.64	1.75	nd	0.54	nd		4.12	5.34	0.50	nd
		RCA47	0.23	1.29	0.07	nd	0.10	nd	0.08	0.07	nd		2.61	2.68	0.48	nd
		RCA62	0.30	2.77	0.05	1.11	3.09		0.88	1.13	0.20	0.07	7.81	8.89	0.80	
		RCA74	nd	3.22	nd	nd	0.21		0.69	0.06	0.08	nd	5.91	4.63	0.69	
		Average	0.5	2.1	0.1	0.6	1.3	0.9	0.4	0.5	0.08	0.05	5.1	5.4	0.6	nd

NOTE: nd = Not Detected

Table A3.3. Concentrations of trace elements in Refcoal derived from Refcoal solution treated with chelating resins (ppm).

	Resin	Sample	La	Br	Sm	U	Hf	Tb	Th	Sc	Cs	Eu	Co	Cr	Ta	Fe
No Na ₂ S	TP260	RCR17a	3.50	11.30	0.92	1.73	1.99	0.22	3.07	2.93	0.18	0.18	6.36		0.65	200
		RCR31	1.30	1.27	0.64	1.05	0.99	nd	1.51	1.81	nd		3.38	6.07	0.08	200
		Average	2.4	6.3	0.8	1.4	1.5	0.1	2.3	2.4	0.09	0.2	4.9	6.1	0.4	200
	TP208	RCR19a	0.01	0.02	0.01	0.02	0.83	0.10	1.46	1.36	0.11	0.08	3.18		0.32	100
		RCR19b	2.30	0.72	0.86	1.71	3.23	nd	3.22	1.22	nd		3.80	4.01	0.21	nd
		RCR29	2.20	0.58	0.74	1.48	2.58	0.37	2.65	2.56	nd		9.87	9.57	nd	200
		RCR51	5.02	3.77	0.31	1.12	1.82	ND	6.75	3.29	0.15	0.04	7.71	5.89	0.57	
		Average	0.7	0.4	0.5	1.1	2.2	0.2	2.4	1.7	0.07	0.04	5.6	6.8	0.2	100
	TP214	RCR16	3.26	11.53	1.64	0.99	1.90	0.22	2.93	2.76	0.23	0.17	6.12		0.64	200
		RCR32	0.04	2.34	0.88	1.34	1.19	nd	1.82	2.58	nd		4.23	9.04	0.36	100
		Average	1.7	6.9	1.3	1.2	1.5	0.1	2.4	2.7	0.1	0.2	5.2	9.0	0.5	200
	With Na ₂ S	TP260	RCR6	2.40	10.87	0.71	1.11	1.08	0.23	2.93	2.95	0.09	0.15	7.25		0.60
RCR23			2.60	0.30	0.73	1.35	2.27	nd	2.55	1.96	nd		7.57	8.54	0.40	200
Average			2.5	5.6	0.7	1.2	1.7	0.1	2.7	2.5	0.04	0.2	7.4	8.5	0.50	200
TP208		RCR18	1.00	4.86	0.31	nd	nd	0.27	1.88	1.68	nd		4.02	8.21	0.34	300
		RCR24	2.20	1.49	0.76	1.45	2.95	nd	2.59	2.32	nd		8.75	9.45	0.48	300
		RCR8	3.07	10.34	0.77	1.38	1.74	0.18	2.64	2.40	0.12	0.15	5.47		0.58	100
		Average	1.6	3.2	0.5	0.7	1.5	0.1	2.2	2.0	0.040	0.2	6.2	8.8	0.4	300
TP214		RCR14	3.51	12.53	0.83	1.09	2.01	0.18	2.62	2.68	0.15		6.40		0.51	200
		RCR25	1.80	2.27	0.27	2.00	6.25	0.09	2.50	0.02	0.10		6.07	6.35	0.38	nd
		RCR9	3.35	10.62	0.81	1.59	1.67	0.17	2.54	2.34	0.18	0.16	5.35		0.51	200
	Average	2.7	7.4	0.6	1.5	4.1	0.1	2.6	1.4	0.1	0.2	6.2	6.4	0.5	100	

NOTE: nd = Not Detected

Table A3.4. Concentrations of trace elements in Refcoal derived from Refcoal gel treated with chelating resins (ppm).

	Resin	Sample	La	Br	Sm	U	Hf	Tb	Th	Sc	Cs	Eu	Co	Cr	Ta	Fe
No Na ₂ S	TP260	RCR22	0.02	1.08	0.02	nd	0.04	nd	0.03	0.10	nd	nd	5.51		0.56	40
		RCR35	1.28	1.96	0.18	nd	0.21	nd	0.15	0.10	nd		3.41	3.24	0.12	nd
		RCR43	nd	0.05	nd	nd	0.06		2.13	0.12	0.07	nd	4.73	5.19	0.57	nd
		RCR58	nd	0.74	nd	nd	0.20		0.21	0.05	nd	nd	5.50	5.53	0.70	
		Average	0.3	1.0	0.05	nd	0.1	nd	0.6	0.09	0.02	nd	4.8	4.7	0.5	10
	TP208	RCR21	0.23	1.25	0.03	nd	0.06	nd	0.08	0.10	nd	nd	5.52		0.57	40
		RCR36	0.50	1.60	0.11	nd	0.11	nd	2.02	0.10	nd	nd	3.99	4.90	0.53	100
		RCR42	1.73	0.60	0.85	1.520	0.08	nd	0.30	0.11	0.06		3.00	4.16	0.45	nd
		RCR48	0.36	3.89	0.05	nd	0.03		0.01	0.03	0.04	nd	3.84	3.37	0.67	
		RCR52		3.42	0.78	nd	0.29		1.11	0.04	0.09	nd	5.20	4.22	0.58	
		Average	0.7	2.2	0.4	0.3	0.1	nd	0.7	0.08	0.04	nd	4.3	4.2	0.6	50
	TP214	RCR20	0.75	1.69	0.03	nd	0.04	nd	0.03	0.10	0.03	nd	5.52		0.61	40
		RCR34	1.61	2.06	0.31	nd	0.08	nd	1.84	0.10	0.10	nd	4.16	4.15	0.51	nd
		RCR44	0.04	0.24	0.09	0.11	0.16	nd	nd	0.07	nd		2.27	3.79	nd	100
		RCR50	3.01	1.85	0.76	0.64	0.04		0.88	0.03	0.09	nd	4.72	2.43	nd	

NOTE: nd = Not Detected

Table A3.4(Continued). Concentrations of trace elements in Refcoal derived from Refcoal gel treated with chelating resins (ppm).

Resin	Sample	La	Br	Sm	U	Hf	Tb	Th	Sc	Cs	Eu	Co	Cr	Ta	Fe
	RCR54	3.670	0.760	0.540	0.430	0.070		3.440	0.050	nd	0.03	5.760	4.340	0.640	
	Average	1.8	1.3	0.3	0.2	0.08	nd	1.240	0.08	0.04	0.008	4.490	3.680	0.30	50
	RCR39	0.04	3.570	0.04	nd	0.09	nd	nd	0.07	nd	nd	2.800	3.850	0.470	200
	RCR46	0.02	5.100	0.01	0.210	0.03		0.14	0.03	0.05	0.01	4.050	3.120	0.500	
	Average	0.03	4.30	0.03	0.110	0.12	nd	0.07	0.05	0.03	0.005	3.420	3.480	0.480	200
	RCR40	0.09	1.85	0.03	nd	0.08	nd	0.10	0.400	nd	nd	0.400	4.000	0.490	nd
	RCR45	0.19	3.88	0.03	1.250	0.32	nd	0.03	0.03	0.060	nd	4.300	4.780	0.630	
	Average	0.7	2.9	0.03	0.650	0.200	nd	0.07	0.210	0.03	nd	2.4	4.4	0.6	nd
	RCR38	nd	3.180	0.04	nd	nd	nd	0.100	0.07	nd	nd	3.290	3.720	nd	100
	RCR47	0.07	4.040	0.05	0.800	0.09		0.18	0.03	0.05	nd	4.540	4.300	0.630	
	Average	0.04	3.610	0.04	0.400	0.04	nd	0.140	0.05	0.03	nd	3.910	4.0	0.310	100

NOTE: nd = Not Detected

APPENDIX 4

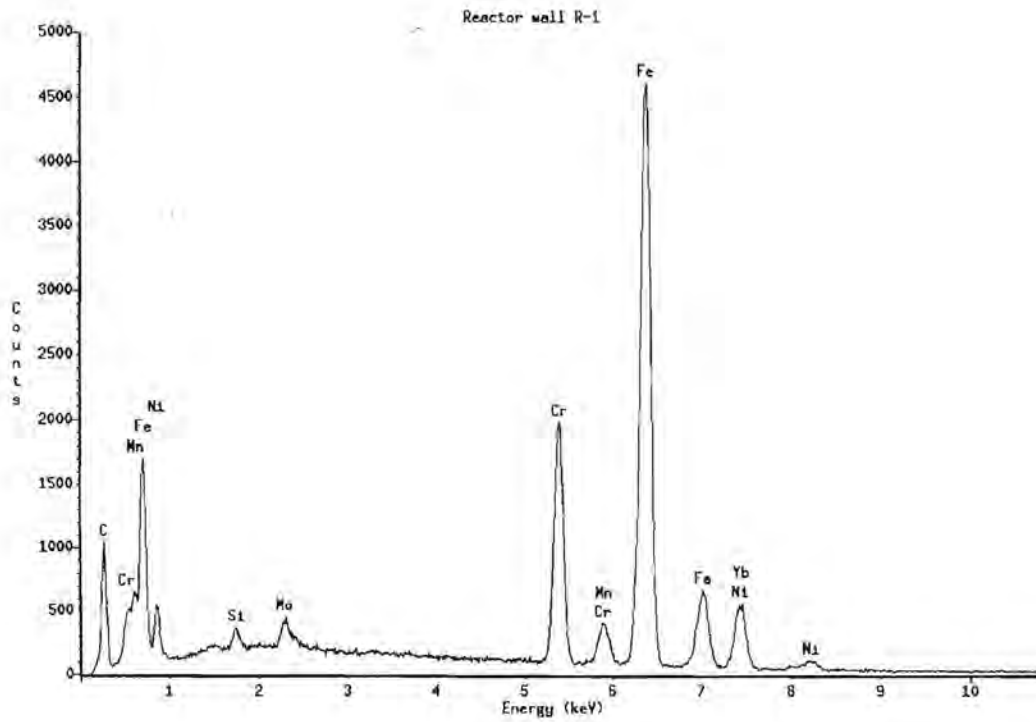


Figure A4.1. TEM spectrum of reactor wall sample

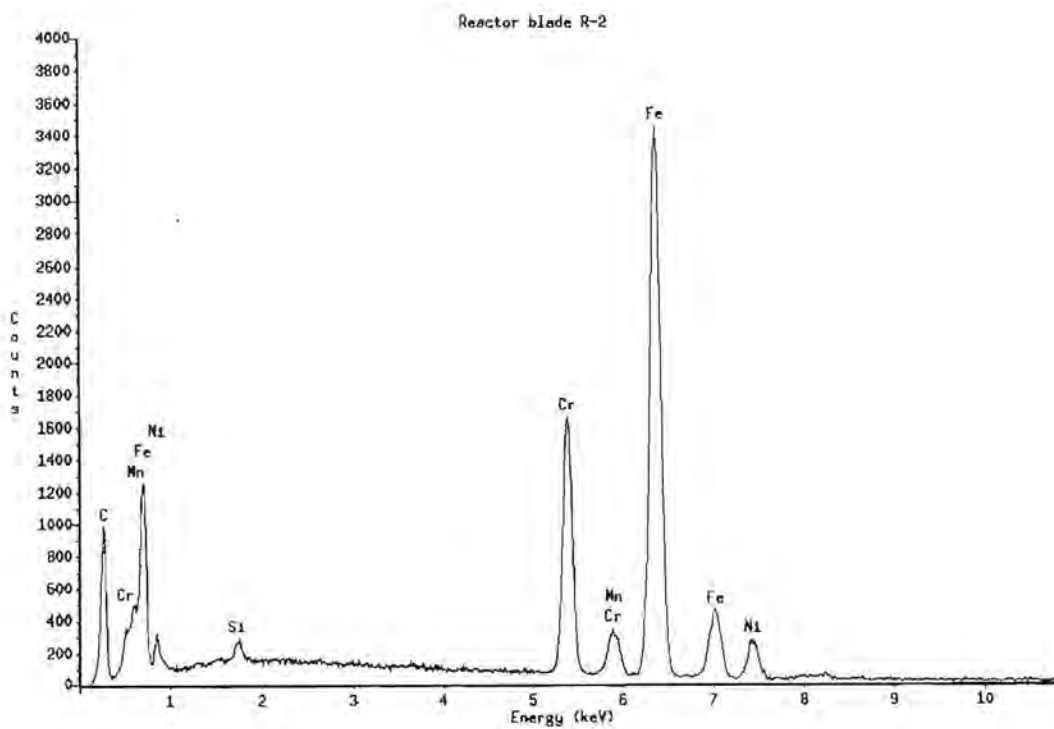


Figure A4.2. TEM spectrum of reactor blade sample

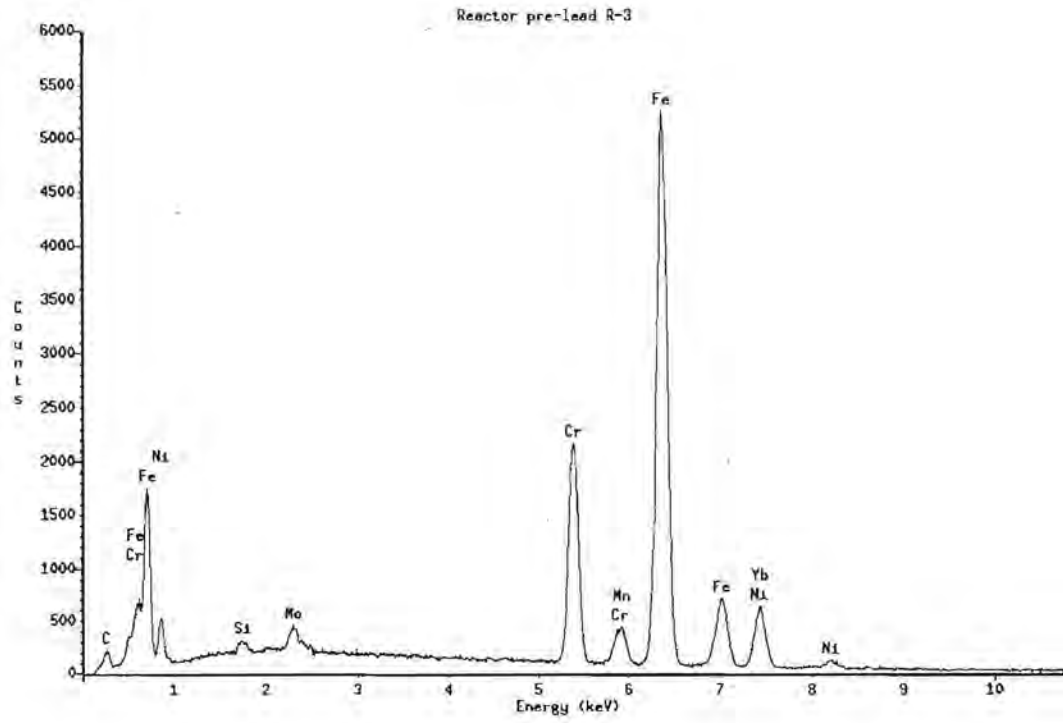


Figure A4.3. TEM spectrum of reactor pre-lid

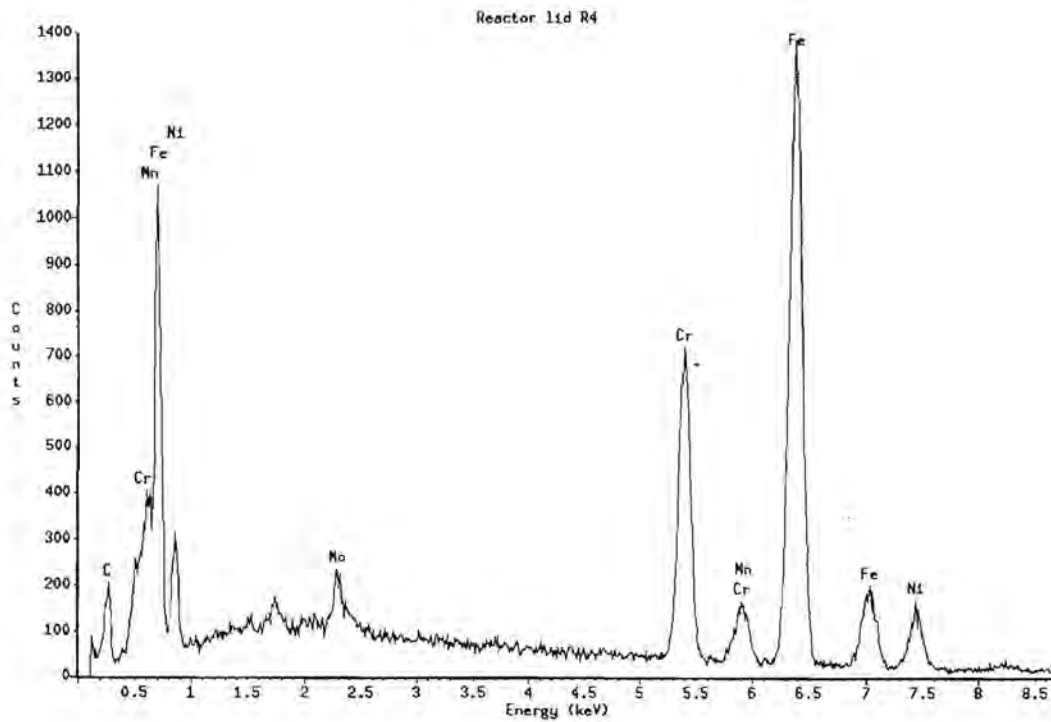


Figure A4.4. TEM spectrum of reactor lid

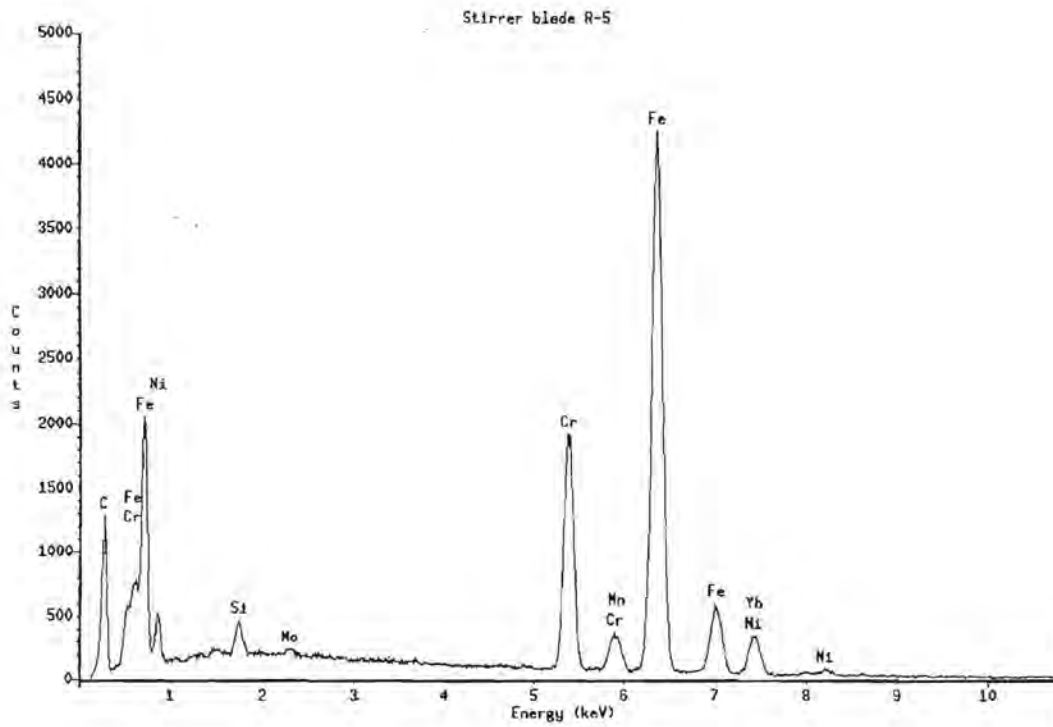


Figure A4.5. TEM spectrum of stirrer blade

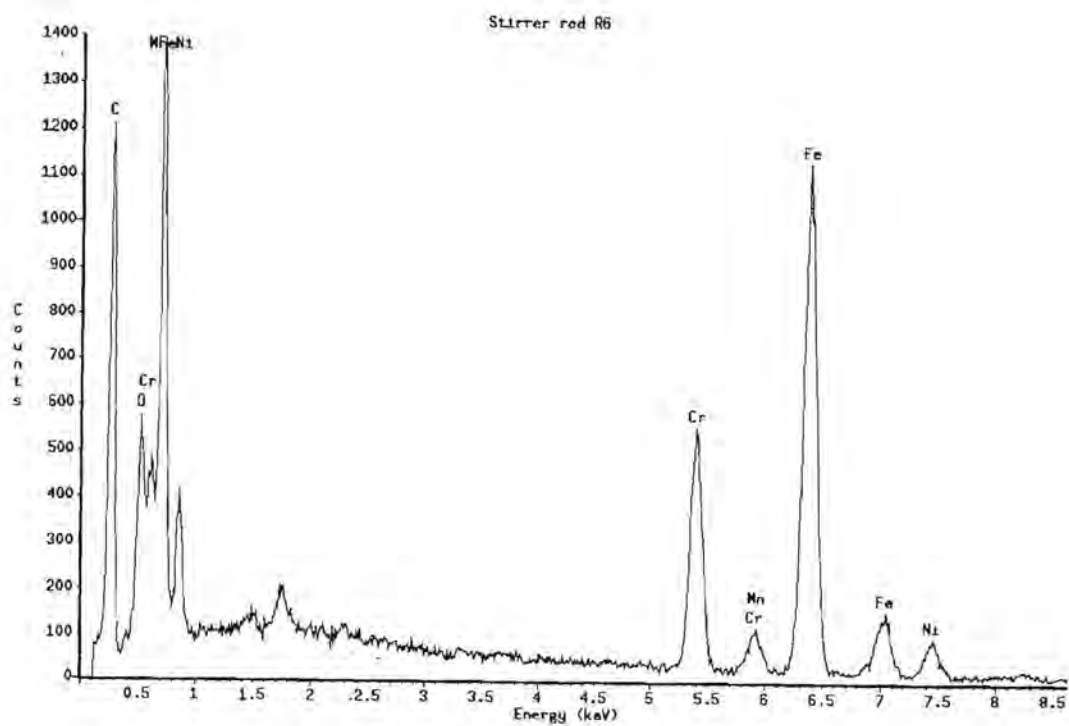


Figure A4.6. TEM spectrum of stirrer rod

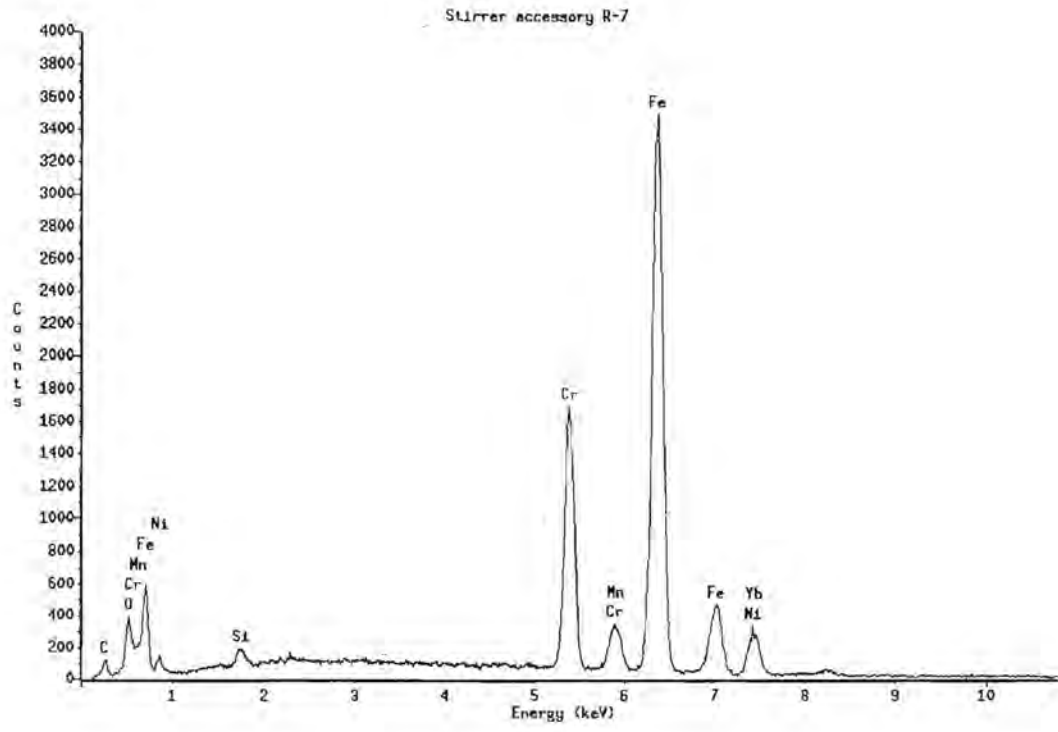


Figure A4.7. TEM spectrum of stirrer accessory

APPENDIX 5

Symbols used in the last column of the table are:

β^- Negative β -particle (negatron) emission

β^+ Positive β -particle (positron) emission

EC Orbital electron capture

α Alpha-particle emission

IT Isomeric transition (decay from an excited metastable state to a lower state)

Table A5.1. Isotopes and their neutron activated reactions

Isotope	Natural Abundance, %	Thermal Neutron Cross-section, barns	Neutron activated reaction type and product	Half-life	Equivalent Boron, $\times 10^3$ ppm	Radioactive Decay
${}^6_3\text{Li}$	7.5	71	$(n,\alpha) {}^3_1\text{H}$	12.26 yrs	1455.09	β^-
${}^7_3\text{Li}$	92.5					
${}^9_4\text{Be}$	100	8 mb	$(n,\alpha) {}^6_2\text{He}$	0.797 s	0.13	
${}^9_4\text{Be}$			$(n,p) {}^9_3\text{Li}$	0.176 s		
${}^9_4\text{Be}$			$(n,\gamma) {}^{10}_4\text{Be}$	2.5×10^6 yrs		
${}^{10}_5\text{B}$	19.9	7.6×10^{-2}	$(n,\alpha) {}^7_3\text{Li}$		10000	α
${}^{11}_5\text{B}$	80.1		$(n,p) {}^{11}_4\text{Be}$	13.6 s		β^-
${}^{12}_6\text{C}$	98.89	3.6 mb			0.04	
${}^{13}_6\text{C}$	1.11					
${}^{14}_7\text{N}$	99.624	1.9	$(n,p) {}^{14}_6\text{C}$	5730 yrs	19.3	β^-
${}^{15}_7\text{N}$	0.366		$(n,\gamma) {}^{16}_7\text{N}$	7.22 s		β
${}^{23}_{11}\text{Na}$	100	0.525	$(n,p) {}^{23}_{10}\text{Ne}$	40.2 s	3.25	β^-
${}^{23}_{11}\text{Na}$			$(n,\gamma) {}^{24}_{11}\text{Na}$	15.1 hrs		β^-
${}^{24}_{12}\text{Mg}$	78.99	63 mb			0.37	
${}^{25}_{12}\text{Mg}$	10		$(n,p) {}^{25}_{11}\text{Na}$	60 s		β
${}^{26}_{12}\text{Mg}$	11.01		$(n,p) {}^{26}_{11}\text{Na}$	1.04 s		β^-
${}^{26}_{12}\text{Mg}$			$(n,\gamma) {}^{27}_{12}\text{Mg}$	9.46 min.		β^-

Table A5.1 (continued).Isotopes and their neutron activated reactions

Isotope	Natural Abundance, %	Thermal Neutron Cross-section, barns	Neutron activated reaction type and product	Half-life	Equivalent Boron, x 10 ³ ppm	Radioactive Decay
²⁷ ₁₃ Al	100	0.23	(n,γ) ²⁸ ₁₃ Al	2.31 min.	1.21	β ⁻
²⁸ ₁₄ Si	92.33	0.166			0.84	
²⁹ ₁₄ Si	4.67					
³⁰ ₁₄ Si	3.1		(n,p) ³⁰ ₁₃ Al	3 s		β ⁻
³⁰ ₁₄ Si			(n,γ) ³¹ ₁₄ Si	2.62 hrs		β ⁻
³¹ ₁₅ P	100	0.16	(n,γ) ³² ₁₅ P	14.3 d	0.73	β ⁻
³² ₁₆ S	95.02	0.54	(n,p) ³² ₁₅ P	14.28 d	2.4	β ⁻
³³ ₁₆ S	0.75		(n,p) ³³ ₁₅ P	24.8 d		β ⁻
³⁴ ₁₆ S	4.21		(n,p) ³⁴ ₁₅ P	12.7 s		β ⁻
³⁴ ₁₆ S			(n,γ) ³⁵ ₁₆ S	87.9 d		β ⁻
³⁶ ₁₆ S	0.02		(n,γ) ³⁷ ₁₆ S	5.04 min		β ⁻
³⁹ ₁₉ K	93.2851	2.1			7.64	
⁴⁰ ₁₉ K	0.0117			1.2 x 10 ⁹ yrs		β ⁻ (89%)
⁴¹ ₁₉ K	6.7302		(n,γ) ⁴¹ ₁₉ K	12.4 hrs		β ⁻
⁴² ₂₀ Ca	96.941	0.43	(n,γ) ⁴³ ₂₀ Ca	4 x 10 ⁴ yrs	1.53	EC
⁴² ₂₀ Ca	0.647					
⁴³ ₂₀ Ca	0.135					
⁴⁴ ₂₀ Ca	2.086		(n,γ) ⁴⁵ ₂₀ Ca	165 d		β ⁻
⁴⁴ ₂₀ Ca			(n,p) ⁴⁴ ₁₉ K	22.0 min		β ⁻
⁴⁶ ₂₀ Ca	0.004		(n,γ) ⁴⁷ ₂₀ Ca	4.53 d		β ⁻
⁴⁸ ₂₀ Ca	0.187		(n,γ) ⁴⁹ ₂₀ Ca	8.8 min.		β ⁻
⁴⁵ ₂₁ Sc	100	27.2	(n,γ) ⁴⁶ ₂₁ Sc	84.2 d	86.07	β ⁻
⁴⁶ ₂₂ Ti	8.25	6.1			18.12	
⁴⁷ ₂₂ Ti	7.44					
⁴⁸ ₂₂ Ti	73.72					
⁴⁹ ₂₂ Ti	5.41					
⁵⁰ ₂₂ Ti	5.18		(n,p) ⁴⁹ ₂₁ Sc	1.7 min		β ⁻

Table A5.1 (continued).Isotopes and their neutron activated reactions

Isotope	Natural Abundance, %	Thermal Neutron Cross-section, barns	Neutron activated reaction type and product	Half-life	Equivalent Boron, x 10 ³ ppm	Radioactive Decay
⁴⁸ ₂₂ Ti			(n,γ) ⁴⁸ ₂₂ Ti	5.8 min.		β ⁻
⁵⁰ ₂₃ V	0.25	5			13.96	
⁵¹ ₂₃ V	99.75		(n,γ) ⁵² ₂₃ V	3.75 min.		β ⁻
⁵² ₂₄ Cr	83.79					
⁵³ ₂₄ Cr	9.5		(n,p) ⁵³ ₂₃ V	2.0 min		β ⁻
⁵⁴ ₂₄ Cr	2.365		(n,p) ⁵⁴ ₂₃ V	55 s		β ⁻
⁵⁴ ₂₄ Cr			(n,γ) ⁵⁵ ₂₄ Cr	3.52 min		β ⁻
⁵⁵ ₂₅ Mn	100	13.3	(n,γ) ⁵⁶ ₂₅ Mn	2.58 hrs	34.44	β ⁻
⁵⁴ ₂₆ Fe	5.85	2.6	(n,γ) ⁵⁵ ₂₆ Fe	2.6 yrs	6.62	EC
⁵⁶ ₂₆ Fe	91.75					
⁵⁷ ₂₆ Fe	2.12		(n,p) ⁵⁷ ₂₅ Mn	1.7 min.		β ⁻
⁵⁸ ₂₆ Fe	0.28		(n,p) ⁵⁸ ₂₅ Mn	1.1 min.		β ⁻
⁵⁹ ₂₆ Fe			(n,γ) ⁶⁰ ₂₆ Fe	45.6 d.		β ⁻
⁵⁹ ₂₇ Co	100	37.19	(n,γ) ⁶⁰ ₂₇ Co	2.56 yrs	89.77	β ⁻
⁵⁸ ₂₈ Ni	68.077	4.5	(n,γ) ⁵⁹ ₂₈ Ni	8 x 10 ⁴ yrs	10.91	EC
⁶⁰ ₂₈ Ni	26.223					
⁶¹ ₂₈ Ni	1.14		(n,p) ⁶¹ ₂₇ Co	99.0 min.		β ⁻
⁶² ₂₈ Ni	3.634		(n,p) ⁶² ₂₇ Co	13.9 min		β ⁻
⁶⁴ ₂₈ Ni	0.926		(n,γ) ⁶⁵ ₂₈ Ni	2.56 hrs		β ⁻
⁶¹ ₂₈ Ni			(n,α) ⁶¹ ₂₆ Fe	6.0 min.		β ⁻
⁶³ ₂₉ Cu	69.17	3.8	(n,γ) ⁶⁴ ₂₉ Cu	12.8 hrs	8.51	EC(43%),β ⁻
⁶⁵ ₂₉ Cu	30.83		(n,γ) ⁶⁶ ₂₉ Cu	5.10 min.		β ⁻
⁶⁴ ₃₀ Zn	48.6	1.1	(n,γ) ⁶⁵ ₃₀ Zn	245 d	2.39	EC(98.3%),β ⁻ (1.7%)
⁶⁶ ₃₀ Zn	27.9					
⁶⁷ ₃₀ Zn	4.1		(n,p) ⁶⁷ ₂₉ Cu	58.5 hrs		β ⁻

Table A5.1 (continued).Isotopes and their neutron activated reactions

Isotope	Natural Abundance, %	Thermal Neutron Cross-section, barns	Neutron activated reaction type and product	Half-life	Equivalent Boron, x 10 ³ ppm	Radioactive Decay
⁶⁴ ₃₀ Zn	18.8		(n,p) ⁶⁴ ₂₉ Cu	30 s		β ⁻
⁶⁶ ₃₀ Zn			(n,γ) ⁶⁶ ₃₀ Zn	57 min.		β ⁻
⁶⁸ ₃₀ Zn	0.6		(n,α) ⁶⁴ ₂₈ Ni	50 s		β ⁻
⁷⁰ ₃₀ Zn			(n,γ) ⁷⁰ ₃₀ Zn	2.4 min.		β ⁻
⁶⁹ ₃₁ Ga	60.108	2.9	(n,γ) ⁶⁹ ₃₁ Ga	20 min	5.92	β ⁻
⁷¹ ₃₁ Ga	39.892		(n,γ) ⁷¹ ₃₁ Ga	14.3 hrs		β ⁻
⁷¹ ₃₁ Ga			(n,α) ⁶⁸ ₂₉ Cu	58.5 hrs		β ⁻
⁷⁰ ₃₂ Ge	21.23	2.9	(n,γ) ⁷⁰ ₃₂ Ge	11.4 d	5.68	EC
⁷² ₃₂ Ge	27.66					
⁷³ ₃₂ Ge	7.73		(n,p) ⁷³ ₃₁ Ga	5.0 hrs		β ⁻
⁷⁴ ₃₂ Ge	35.94		(n,p) ⁷⁴ ₃₁ Ga	8.0 min.		β ⁻
⁷⁶ ₃₂ Ge			(n,γ) ⁷⁶ ₃₂ Ge	82 min.		β ⁻
⁷⁶ ₃₂ Ge	7.44		(n,p) ⁷⁶ ₃₁ Ga	32 s		β ⁻
⁷⁶ ₃₂ Ge			(n,γ) ⁷⁶ ₃₂ Ge	11.3 hrs		β ⁻
⁷⁵ ₃₃ As	100	4	(n,p) ⁷⁵ ₃₂ Ge	79 min.	7.59	β ⁻
⁷⁵ ₃₃ As			(n,γ) ⁷⁵ ₃₃ As	26.2 hrs		β ⁻
⁷⁴ ₃₄ Se	0.89	12	(n,γ) ⁷⁴ ₃₄ Se	127 d	21.62	EC
⁷⁶ ₃₄ Se	9.36		(n,γ) ⁷⁶ ₃₄ Se	17.5 s		IT
⁷⁷ ₃₄ Se	7.63					
⁷⁸ ₃₄ Se	23.78		(n,p) ⁷⁸ ₃₃ As	91 min		β ⁻
⁷⁸ ₃₄ Se			(n,γ) ⁷⁸ ₃₄ Se	3.91 min		IT
⁸⁰ ₃₄ Se	49.61		(n,γ) ⁸⁰ ₃₄ Se	18.6 min		β ⁻
⁸² ₃₄ Se	8.73		(n,α) ⁷⁹ ₃₃ As	9.0 min		β ⁻
⁸² ₃₄ Se			(n,γ) ⁸² ₃₄ Se	26 min		β ⁻
⁸⁵ ₃₇ Rb	72.17	0.39	(n,α) ⁸¹ ₃₅ Br	31.7 min	0.65	β ⁻
⁸⁵ ₃₇ Rb			(n,γ) ⁸⁵ ₃₇ Rb	18.66 d		β ⁻
⁸⁷ ₃₇ Rb	27.83		(n,γ) ⁸⁷ ₃₇ Rb	18 min		β ⁻ (β ⁻)

Table 5.1 (continued).Isotopes and their neutron activated reactions

Isotope	Natural Abundance, %	Thermal Neutron Cross-section, barns	Neutron activated reaction type and product	Half-life	Equivalent Boron, x 10 ³ ppm	Radioactive Decay
⁸⁴ ₃₈ Sr	0.56		(n,γ) ⁸⁵ ₃₈ Sr	63.9 d	1.95	EC
⁸⁶ ₃₈ Sr	9.86		(n,γ) ⁸⁷ ₃₈ Sr	2.88 hrs		IT(99.4%),
⁸⁷ ₃₈ Sr	7					
⁸⁸ ₃₈ Sr	82.58		(n,γ) ⁸⁹ ₃₈ Sr	50.5 d		β ⁻
⁹² ₄₂ Mo	14.84	2.5	(n,γ) ⁹³ ₄₂ Mo	6.95 hrs	3.71	EC
⁹⁴ ₄₂ Mo	9.25					
⁹⁶ ₄₂ Mo	15.92					
⁹⁷ ₄₂ Mo	16.68					
⁹⁸ ₄₂ Mo	9.55					
⁹⁹ ₄₂ Mo	24.13		(n,γ) ¹⁰⁰ ₄₂ Mo	66.7 hrs		β ⁻
¹⁰⁰ ₄₂ Mo			(n,p) ¹⁰⁰ ₄₁ Nb	51 min.		β ⁻
¹⁰¹ ₄₂ Mo	9.63		(n,γ) ¹⁰² ₄₂ Mo	14.6 min		β ⁻
¹⁰² ₄₂ Mo			(n,p) ¹⁰² ₄₁ Nb	11 min.		β ⁻
¹⁰⁶ ₄₆ Ag	51.839	62	(n,γ) ¹⁰⁷ ₄₆ Ag	2.42 min.	81.76	β ⁻
¹⁰⁸ ₄₆ Ag	48.161		(n,γ) ¹⁰⁹ ₄₆ Ag	24.4 s		β ⁻
¹¹³ ₄₈ Cd	1.25	2.5 x 10 ³	(n,γ) ¹¹⁴ ₄₈ Cd	6.49 hrs	3188.92	EC
¹¹⁴ ₄₈ Cd	0.89		(n,γ) ¹¹⁵ ₄₈ Cd	453 d		EC
¹¹⁶ ₄₈ Cd	12.49		(n,γ) ¹¹⁷ ₄₈ Cd	48.6 min.		IT
¹¹⁷ ₄₈ Cd	12.8					
¹¹⁸ ₄₈ Cd	24.13		(n,γ) ¹¹⁹ ₄₈ Cd	13.6 yrs		β ⁻
¹¹⁹ ₄₈ Cd	12.22					
¹²⁰ ₄₈ Cd	28.73		(n,γ) ¹²¹ ₄₈ Cd	53.5 hrs		β ⁻
¹²² ₄₈ Cd	7.49		(n,γ) ¹²³ ₄₈ Cd	2.4 hrs		β ⁻
¹²⁴ ₅₀ Sn	0.97	0.61	(n,γ) ¹²⁵ ₅₀ Sn	118 d	0.73	EC
¹²⁶ ₅₀ Sn	0.65					
¹²⁸ ₅₀ Sn	0.34					
¹³⁰ ₅₀ Sn	14.53		(n,γ) ¹³¹ ₅₀ Sn	140 d		IT

Table A5.1 (continued).Isotopes and their neutron activated reactions

Isotope	Natural Abundance, %	Thermal Neutron Cross-section, barns	Neutron activated reaction type and product	Half-life	Equivalent Boron, x 10 ³ ppm	Radioactive Decay
¹¹³ ₅₀ Sn	7.68					
¹¹⁴ ₅₀ Sn	24.23		(n,γ) ¹¹⁴ ₅₀ Sn	≈ 250 d		IT
¹¹⁵ ₅₀ Sn			(n,p) ¹¹⁵ ₄₉ In	5.0 s		β ⁻
¹¹⁶ ₅₀ Sn	8.59					
¹¹⁷ ₅₀ Sn	32.59		(n,γ) ¹¹⁷ ₅₀ Sn	27.5 hrs		β ⁻
¹¹⁸ ₅₀ Sn			(n,p) ¹¹⁸ ₄₉ In	3.2 s		β ⁻
¹¹⁹ ₅₀ Sn	4.63		(n,γ) ¹¹⁹ ₅₀ Sn	125 d		β ⁻
¹²⁰ ₅₀ Sn			(n,p) ¹²⁰ ₄₉ In	8 s		β ⁻
¹²¹ ₅₀ Sn	5.79		(n,p) ¹²¹ ₄₉ In	≈ 3.6 s		β ⁻
¹²² ₅₁ Sb	57.21	5.3	(n,γ) ¹²² ₅₁ Sb	2.80 d	6.19	β ⁻ (97%), EC
¹²³ ₅₁ Sb			(n,α) ¹²³ ₄₉ In	3 s		β ⁻
¹²⁴ ₅₁ Sb	42.79		(n,γ) ¹²⁴ ₅₁ Sb	60.4 d		β ⁻
¹²⁵ ₅₁ Sb			(n,p) ¹²⁵ ₅₀ Sb	21 min		IT
¹³² ₅₅ Cs	100	30.4	(n,α) ¹³² ₅₃ I	12.3 hrs	32.54	β ⁻
¹³⁴ ₅₅ Cs			(n,γ) ¹³⁴ ₅₅ Cs	2.046 yrs		β ⁻
¹³⁵ ₅₆ Ba	0.106	1.3	(n,γ) ¹³⁵ ₅₆ Ba	12.0 d	1.35	EC
¹³⁶ ₅₆ Ba	0.101		(n,γ) ¹³⁶ ₅₆ Ba	7.2 yrs		EC
¹³⁷ ₅₆ Ba	2.417					
¹³⁸ ₅₆ Ba	6.592		(n,p) ¹³⁸ ₅₅ Cs	53 min		IT
¹³⁹ ₅₆ Ba	7.854					
¹⁴⁰ ₅₆ Ba	11.23					
¹⁴¹ ₅₆ Ba	71.7		(n,γ) ¹⁴¹ ₅₆ Ba	82.9 min		β ⁻
¹⁴² ₅₆ Ba			(n,p) ¹⁴² ₅₅ Cs	32.1		β ⁻
¹⁴³ ₅₆ Ba			(n,α) ¹⁴³ ₅₄ Xe	9.2 hrs		β ⁻
¹³⁸ ₅₇ La	0.0902	9.2		1.12 x 10 ¹¹ yrs	9.42	β ⁻
¹³⁹ ₅₇ La	99.9098		(n,γ) ¹⁴⁰ ₅₇ La	40.22 hrs		β ⁻
¹³⁶ ₅₈ Ce	0.19	0.64	(n,γ) ¹³⁷ ₅₈ Ce	9.0 hrs	0.65	EC

Table A5.1 (continued).Isotopes and their neutron activated reactions

Isotope	Natural Abundance, %	Thermal Neutron Cross-section, barns	Neutron activated reaction type and product	Half-life	Equivalent Boron, x 10 ³ ppm	Radioactive Decay
¹³⁷ ₅₈ Ce	0.25		(n,γ) ¹³⁷ ₅₈ Ce	140 d		EC
¹³⁸ ₅₈ Ce	88.43		(n,γ) ¹³⁸ ₅₈ Ce	33.1 d		β ⁻
¹³⁹ ₅₈ Ce	11.13		(n,p) ¹³⁹ ₅₇ La	77 min		β ⁻
¹⁴⁰ ₅₈ Ce			(n,γ) ¹⁴⁰ ₅₈ Ce	33 hrs		β ⁻
¹⁴¹ ₅₉ Pr	100	11.5	(n,γ) ¹⁴¹ ₅₉ Pr	19.2 hrs	11.61	β ⁻
¹⁴² ₅₉ Pr			(n,p) ¹⁴² ₅₈ Ce	33.1 d		β ⁻
¹⁴³ ₆₀ Nd	27.13	51			50.3	
¹⁴⁴ ₆₀ Nd	12.18					
¹⁴⁵ ₆₀ Nd	23.8					
¹⁴⁶ ₆₀ Nd	8.3					
¹⁴⁷ ₆₀ Nd	17.19		(n,p) ¹⁴⁷ ₅₉ Pr	240 min		β ⁻
¹⁴⁸ ₆₀ Nd			(n,γ) ¹⁴⁸ ₆₀ Nd	11.1 d		β ⁻
¹⁴⁹ ₆₀ Nd	5.76		(n,p) ¹⁴⁹ ₅₉ Pr	2.0 min		β ⁻
¹⁵⁰ ₆₀ Nd			(n,γ) ¹⁵⁰ ₆₀ Nd	2.0 hrs		β ⁻
¹⁵¹ ₆₀ Nd	5.64		(n,γ) ¹⁵¹ ₆₀ Nd	12 min		β ⁻
¹⁵² ₆₂ Sm	3.1	5.6 x 10 ³	(n,γ) ¹⁵² ₆₂ Sm	340 d	5297.95	EC
¹⁵³ ₆₂ Sm	15		(n,2n) ¹⁵³ ₆₂ Sm	7 x 10 ⁴ yrs		α
¹⁵⁴ ₆₂ Sm	11.3					
¹⁵⁵ ₆₂ Sm	13.8					
¹⁵⁶ ₆₂ Sm	7.4		(n,γ) ¹⁵⁶ ₆₂ Sm	120 yrs		β ⁻
¹⁵⁷ ₆₂ Sm	26.7		(n,γ) ¹⁵⁷ ₆₂ Sm	46.8 hrs		β ⁻
¹⁵⁸ ₆₂ Sm			(n,p) ¹⁵⁸ ₆₁ Pm	6.5 min.		β ⁻
¹⁵⁹ ₆₂ Sm	22.7		(n,γ) ¹⁵⁹ ₆₂ Sm	21.9 min.		β ⁻
¹⁶⁰ ₆₃ Eu	47.8	4570	(n,γ) ¹⁶⁰ ₆₃ Eu	12.7 yrs	4277.84	β ⁻ (28%),EC(72)
¹⁶¹ ₆₃ Eu	52.2		(n,γ) ¹⁶¹ ₆₃ Eu	16 yrs		β ⁻
¹⁶² ₆₄ Gd	0.2	48.8 x 10 ³	(n,γ) ¹⁶² ₆₄ Gd	242 d	44144.99	EC
¹⁶³ ₆₄ Gd	2.18					

Table A5.1 (continued).Isotopes and their neutron activated reactions

Isotope	Natural Abundance, %	Thermal Neutron Cross-section, barns	Neutron activated reaction type and product	Half-life	Equivalent Boron, x 10 ³ ppm	Radioactive Decay
¹⁵² Gd	14.8					
¹⁵⁴ Gd	20.17					
¹⁵⁷ Gd	15.65					
¹⁵⁸ Gd	24.84		(n,γ) ¹⁵⁹ ₆₄ Gd	18.0 hrs		β ⁻
¹⁶⁰ Gd	21.86		(n,α) ¹⁵⁷ ₆₂ Sm	0.5 min.		β ⁻
¹⁶⁰ Gd			(n,p) ¹⁶⁰ ₆₃ Eu	≈ 2.5 min.		β ⁻
¹⁵⁹ Tb	100	23.2	(n,γ) ¹⁶⁰ ₆₅ Tb	6.9 d	20.77	β ⁻
¹⁵⁶ Dy	0.06	9.5 x 10 ²			831.62	
¹⁵¹ Dy	0.1		(n,γ) ¹⁵² ₆₆ Dy	144 d		EC
¹⁵² Dy	2.34					
¹⁵⁴ Dy	18.9					
¹⁵⁹ Dy	25.5		(n,p) ¹⁵⁹ ₆₅ Tb	7.48 min.		β ⁻
¹⁶¹ Dy	24.9		(n,p) ¹⁶¹ ₆₅ Tb	6.5 hrs		β ⁻
¹⁶⁴ Dy	28.2		(n,γ) ¹⁶⁵ ₆₆ Dy	139.2 min.		β ⁻
¹⁶² Er	0.14	169			143.73	
¹⁶³ Er	1.61		(n,γ) ¹⁶⁴ ₆₈ Er	10.4 hrs		EC
¹⁶⁴ Er	33.6		(n,γ) ¹⁶⁵ ₆₈ Er	2.3 s		IT
¹⁶⁷ Er	22.95					
¹⁶⁸ Er	26.8		(n,γ) ¹⁶⁹ ₆₈ Er	9.4 d		β ⁻
¹⁶⁹ Er	14.9		(n,α) ¹⁶⁶ ₆₆ Dy	4.4 min		β ⁻
¹⁷⁰ Er			(n,p) ¹⁷⁰ ₆₇ Er	45 s		β ⁻
¹⁷¹ Er			(n,γ) ¹⁷² ₆₈ Er	7.52 hrs		β ⁻
¹⁷⁸ Hf	0.162	106	(n,γ) ¹⁷⁹ ₇₂ Hf	23.6 hrs	84.48	EC
¹⁷⁹ Hf	5.206					
¹⁸⁰ Hf	18.606					
¹⁸¹ Hf	27.297		(n,γ) ¹⁸² ₇₂ Hf	18.6 s		IT
¹⁸² Hf	13.629					

Table A5.1 (continued).Isotopes and their neutron activated reactions

Isotope	Natural Abundance, %	Thermal Neutron Cross-section, barns	Neutron activated reaction type and product	Half-life	Equivalent Boron, x 10 ³ ppm	Radioactive Decay
¹⁷⁷ Hf	35.1		(n,γ) ¹⁷⁷ Hf	42.5 d		β ⁻
¹⁸⁰ W	0.12	18	(n,γ) ¹⁸⁰ W	140 d	13.93	EC
¹⁷⁵ W	26.5		(n,γ) ¹⁷⁵ W	5.5 s		IT
¹⁸¹ W	14.31					
¹⁸² W	30.43		(n,p) ¹⁸² Ta	8.7 hrs		β ⁻
¹⁸³ W			(n,γ) ¹⁸³ W	75 d		β ⁻
¹⁸⁴ W	28.43		(n,γ) ¹⁸⁴ W	23.9 hrs		β ⁻
¹⁸⁶ W			(n,α) ¹⁸³ Hf	65 min		β ⁻
¹⁸⁷ W			(n,p) ¹⁸⁷ Ta	10.5 min		β ⁻
¹⁹⁹ Hg	0.15	3.7 x 10 ²			262.39	
²⁰⁰ Hg	9.97					
²⁰¹ Hg	16.87					
²⁰² Hg	23.1					
²⁰³ Hg	13.18					
²⁰⁴ Hg	29.86		(n,γ) ²⁰⁴ Hg	46.9 d		β ⁻
¹⁹⁸ Hg	6.87		(n,α) ¹⁹⁵ Pt	2.3 min		β ⁻
²⁰⁰ Hg			(n,γ) ²⁰⁰ Hg	5.5 min		β ⁻
²⁰⁸ Pb	1.4	0.172	(n,γ) ²⁰⁸ Pb	3.0 x 10 ⁵ yrs	0.12	EC
²⁰⁶ Pb	24.1					
²⁰⁷ Pb	22.1					
²¹⁰ Pb	52.4		(n,γ) ²¹⁰ Pb	3.30 hrs		β ⁻
²⁰⁹ Bi	100	0.034	(n,γ) ²⁰⁹ Bi	5.0 d	0.02	β ⁻
²¹⁰ Bi			(n,γ) ²¹⁰ Bi	2.6 x 10 ⁶ yrs		β ⁻ (0.4%), α
²³² Th	100	7.4	(n,γ) ²³² Th	22.5 min	4.54	β ⁻