

**The Chemistry of the alkali-induced
Solubilisation of Coal**

by

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Abstract

This thesis outlines a study carried out to understand the effects of coal dissolution variables. Several parameters that are thought to have a direct influence on the degree of coal dissolution in organic solvents were investigated by means of a series of experiments. The work done constitutes part of the research being carried out for the PBMR Company, whose aim is to synthesise nuclear-grade graphite from coal-based materials. To enhance the efficiency of the process, it was necessary to gain a clear-cut understanding of the parameters that affect the process.

The work carried in this project was divided into two sections. The first section involved the solubilisation of coal in polar aprotic organic solvents with the addition of a small amount of alkali. In this section as well, many parameters that influence the process were investigated. The second section involved the use of various analytical techniques to obtain information on the composition of coal extracts.

The conclusions reached were as follows:

- An alkali is required for the solubilisation of coal to occur in polar organic solvents. This also gives an overall high extraction percentage of ~ 92%.
- In pure dimethylformamide (DMF), the sodium hydroxide (NaOH) does not go into solution but on the addition of coal, the NaOH goes into solution.

- The characteristic smell of the Refcoal solution confirms the presence of dimethylamine, although the titration results show otherwise.
- The texture of the alkali used in the extraction affects the rate and degree of extraction. Finely ground alkali gives a faster dissolution rate, as well as a high extraction percentage.
- There is no hydrolysis of solvent during the extraction of coal.
- The concentration of the alkali used in the extraction process affects the degree to which coal can be extracted.
- The use of a strong alkali increases the rate at which coal can be dissolved in the solvent.
- Temperature does not affect the degree of extraction, as shown by the closeness of the extractions done at different temperatures. Also, external factors, such as oxidation and weathering of coal, have little effect on the extent of extraction.
- Coal characterization techniques provide information about the composition of coal extracts. The coals used in this process consisted of aliphatic and aromatic compounds.

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LIST OF ABBREVIATIONS

AA	atomic absorption spectroscopy
CSIR	Council for Scientific and Industrial Research
daf	dry ash free
DMAA	dimethylacetamide
DMF	dimethylformamide
ESR	electron spin resonance spectroscopy
FC	fixed carbon content
GS	gas chromatography
HPC	Hypercoal process
HTGR	high-temperature gas reactor
MN	methylnaphthalene
MS	mass spectroscopy
NaOH	sodium hydroxide
NMP	N-methyl-pyrrolidinone
NMR	nuclear magnetic resonance spectroscopy
NRF	National Research Foundation
PBMR	Pebble Bed Modular Reactor
ppm	parts per million
TGA	thermo gravimetric analysis
VM	volatile matter content

Chapter 1: Introduction

South African power utility Eskom is playing a central and important role in investigations into the possibility of generating electricity using the Pebble Bed Modular Reactor (PBMR) technology. The PBMR is classified as a High-Temperature Gas Reactor (HTGR) and this means that its core will be gas cooled [29]. Prototype pebble bed nuclear reactors were first developed in Germany in the late 1950s. The collapse of the USSR, budget constraints and a public outcry for Germany to start closing nuclear plants after the Chernobyl disaster resulted in the pebble bed modular reactor being scrapped. The project, which was developed by Rolf Schulten, operated for 21 years. However, in South Africa, Eskom bought millions of rands worth of technology that would otherwise have been left idle.

1.1 Why the Pebble Bed Modular Reactor?

At present, the safety of fossil fuel power stations is being questioned due to public concerns about carbon dioxide emissions possibly leading to global warming. The United Nations conference in Kyoto, Japan, in December 1997 resulted in the Kyoto Protocol, which sets limits on countries' carbon dioxide emissions. This in turn brings pressure to bear on the development of fossil fuel power stations that may emit excessive carbon dioxide.

1.2 Economics of the Pebble Bed Modular Reactor

The cost of electricity generated from the Pebble Bed Modular Reactor is expected to be lower than the cost of local electricity or the world average generation cost of US\$0.34 per kilowatt-hour. These two scenarios are the key factors that led Eskom

to take the initiative in the development of a small modular pebble bed nuclear reactor.

Eskom has been investigating PBMR technology since 1993 as a power source within the country, as well as for export. As South Africa is expected to run out of electricity capacity in the next three to seven years at its current rate of generation, Eskom will have to provide 1 000 megawatts of additional electricity capacity each year to cope up with the growth in the demand for electricity, both local and international. It is estimated that ~71 % of the energy consumption in South Africa is provided by coal and only 3% by nuclear power from Koeberg.

Both domestically and in Africa and the rest of the world, South Africa is regarded as the regional economic powerhouse and that being the case; it is assumed to have moral obligations to engage in the economic upliftment of the region. The idea of the Pebble Bed Modular Reactor is being championed by the PBMR Company in conjunction with Eskom and other technical partners from the UK and the USA. Substantial ground has been covered in various areas of research, despite appeals by environmental activists with regard to safety considerations and spent fuel disposal. Upon successful completion, the reactor will create a lucrative market for electricity within South Africa and the rest of the African continent, as well as creating employment opportunities. Potential exports of PBMR plants are projected to be around 640 units over the next 25 years.

1.3 Safety of the Pebble Bed Modular Reactor

At present there is much concern with regard to the safety of nuclear reactors. There is anxiety about the storage and disposal of the toxic radioactive nuclear waste material discharged from the reactor and also about the possibility of a repeat of the Chernobyl explosion which took place in the USSR in 1986. However, the risk of an accident on the scale of Chernobyl will be minimal if proper waste management and disposal structures are in place.

With regard to the PBMR, stringent waste management practices have already been put in place to ensure that radioactive waste material is safely contained and therefore not harmful to people and the environment. The safety of the PBMR lies in the fact that the silicon carbide layer that surrounds the uranium oxide beads is capable of containing almost all of the fission products generated up to a temperature of 2 000°C [29]. If helium were to stop flowing, the reactor would heat up to 1 350°C, at which point the negative coefficient of criticality would bring the nuclear chain reaction to a close. Fission products emanating from the radioactive decay would continue to heat the fuel until a temperature of around 1 600°C was reached, the heat losses through the reactor would balance heat production and the core would begin to cool down. Loss of the fission products' radioactivity is not possible.

1.4 The fuel elements of the Pebble Bed Modular Reactor

The fuel components of the PBMR are cricket-ball-sized spheres of graphite, 60 mm in diameter, containing coated uranium dioxide particles that are evenly distributed. The uranium dioxide spheres are coated so as to contain the fission products. The coatings used are put on by chemical vapour deposition and consist of two layers of

carbon with differing porosity; then there is a barrier layer of silicon carbide and then a third layer of carbon. The coated beads are mixed with finely powdered graphite consisting of 75% natural graphite and 25% synthetic graphite, binder resin and they are moulded into spherical shape. The pebbles will be baked to a temperature of ~ 1 900°C, after which they will be ready to be used in the reactor. The uranium used has an enrichment of 8% and a uranium content of 9 g.

1.5 Operation of the Pebble Bed Modular Reactor

During the operation of the PBMR, ~ 440 000 fuel elements are loaded into the top of the reactor and discharged at the bottom where their degree of burn-up is measured. They are then returned to the reactor to allow the decay of short-lived fission products to take place. The heat generated by the nuclear reaction is removed by passing helium gas at 450°C through the pressure vessel. The helium used passes between the fuel pebbles, leaving the bottom of the reactor at a temperature of 900°C. The heat removed by the helium drives the turbine/generator, giving a full capacity of about 110 MW. The modular nature of the system allows close to ten reactors to be built on one site, with a possibility of sharing a single control room. The properties of helium that make it a good coolant in the PBMR are its resistance to corrosion and good heating properties. There is also no condensation, giving it the possibility of operating at any temperature. In addition, it has a negligible neutron-absorption cross-section and can be used in a direct cycle, thus driving the turbine with high efficiency.

1.6 The role of graphite

The major material in the construction of the reactor core is carbon and this contributes to the safety of the reactor due to its high sublimation point, which is more than 3 000°C in inert atmospheres as it has a slow rate of oxidation. The graphite to be used in the PBMR has specifications with regard to chemical purity, as well as to the physical structure, hence the need to purify the coal by extraction prior to coking and graphitisation. It is recommended that the reflector graphite, at the atomic scale, be highly anisotropic. Graphite was found to be a suitable moderator for nuclear fission reactors because of it being the most readily available material with a low thermal neutron-capture cross-section, thus allowing efficient use of the neutrons generated (see Table 1.1 and Figure 1.1). This is usually expressed in terms of an equivalent boron concentration by summing the concentrations of the individual impurity concentrations, weighted by their thermal neutron capture cross-section.

Table 1.1 Properties of isotropic and anisotropic graphite

Property	Anisotropic graphite	Isotropic graphite
Density (g/cm ³)	1.71	1.86
Resistance (μΩ.cm)	735	1 000
Tensile strength (kPa)	9 930	46 172
Coefficient of thermal expansion (CTE) (10 ⁶ /°C)	2.2	5.3
Anisotropy ratio (CTE)	1.73	1.0
Total ash (ppm)	740	400
Boron content (ppm)	0.4	0.3

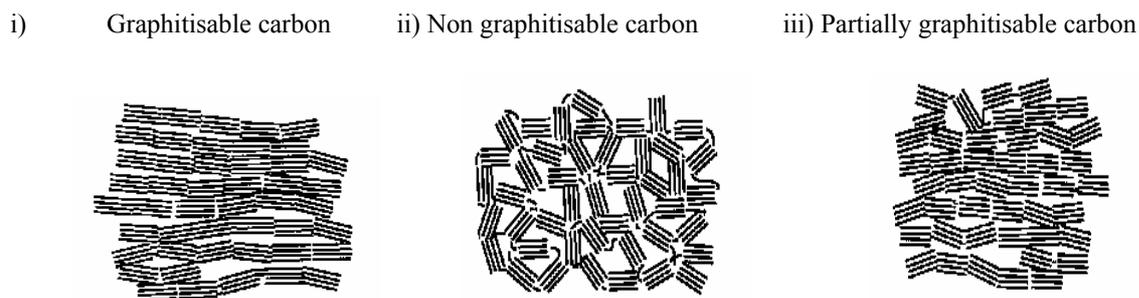


Figure 1.1 Structures of graphitisable, non-graphitisable and partially graphitisable carbons [13, 30]

1.7 Graphite from Refcoal

The manufacture of nuclear-grade graphite from coal will depend on the availability of raw materials and the ability to convert them into cokes. This process of extracting coal with polar organic solvents provides a means of pre-purifying coal prior to coking and graphitisation. The so-called Refcoal process ensures that most of the organic parts contained in coal (~ 92%) are dissolved in the solvent on addition of alkali. The undissolved inorganics (~ 8%) and other mineral matter will be separated out on centrifugation. The idea of extracting coal with organic solvents was considered to be most suitable due to the fact that one of the major raw materials (coal) is available locally. However, due to the relatively high cost of the solvent and alkali, it was important to investigate and quantify all the minor and major reactions and mechanisms that occur during the dissolution of coal.

The objectives of this project were to compare various parameters that affect the amount of coal dissolved during the Refcoal process. Also, it was important during the study to understand the chemical interactions that take place during the process of dissolving coal in organic solvents. One of the research efforts reported here was to test the possibility of using alternative solvents for coal extraction. Apart from very

good extraction yield and reasonable cost, there are other requirements that would make a solvent ideal. These include: solvent loss during extraction should be minimal; the coal-solvent ratio required for extraction should be minimal; and the solvent should be 'friendly' towards both the environment and the people using it. The possible solvents studied were two different polar aprotic organic solvents (dimethylformamide (DMF) and dimethylacetamide (DMAA)). The dissolution of coal in organic solvents using an alternative base in the form of sodium tert-butoxide was also investigated. The kinetics of the coal extraction process and the behaviour of the alkali were studied using the two above-mentioned solvents. Studying the reaction mechanism and optimising the coal extraction process will help to quantify the amount of alkali that can effectively take the coal into solution. Also of prime importance to the study was investigating the base hydrolysis of the solvent that takes place between the solvent and the alkali. To strengthen understanding of the nature of coal solutions and the coal dissolution process, several characterisation techniques for coal products were used to try to determine the functional groups, free radical concentrations and hydrogen content, as well as the aromatic ring distributions. Some of the analytical techniques that were used on the coal solutions included nuclear magnetic resonance spectroscopy (NMR), electron spin resonance spectroscopy (ESR) and atomic absorption spectroscopy (AA) These analytical techniques are outlined in detail in Chapter 3. The Refcoal solution obtained during this project was used to synthesise nuclear-grade graphite to be used in Eskom's PBMR. Table 1.2 outlines some potential uses of coal extracts.

Table 1.2 Uses of coal extracts

Products	Potential Customers
Fuel	
Low-ash slurry or solid fuel	Power generation, transportation
High-grade coke	
Electrodes	Steel industry
Anodes	Aluminium industry
Graphite	Nuclear reactors
C-C composites	Military and nuclear
Pitch	
Binder	Steel industry

Chapter 2: Literature survey

2.1 Coal

Coal can be defined as a huge three-dimensional heterogeneous macromolecular structure with many small entities filling the pores in the giant network structure [2, 16, 24]. The various organic entities that make up the coal structure are held together by various forces, including van der Waal's forces, hydrogen bonds and charge transfer and pi-pi (π - π) interactions [42].

The coal macromolecular structure was formed from the microbial decomposition and compaction of various plants remains, which accumulated in waterlogged areas [17, 20]. Differences in the kinds of plant materials, the degree of metamorphism (rank) and the range of impurity (grade) are some of the parameters that can be used for the classification of coal. Coal deposits are the most abundant fossil fuel resource, with deposits scattered all over the world [6].

Table 2.1 shows how coal deposits are distributed globally [12].

Table 2.1 Distribution of coal reserves in the world

Country	Estimated Resources	Proven Resources
Australia	600	32.8
Canada	323	4.2
Germany	247	34.4
India	81	12.4
China	1 438	98.9
Poland	139	59.6
South Africa	72	43
United Kingdom	190	45
USA	2 570	167
USSR	4 860	110

Coal is usually regarded as fossilised plant matter. The conversion of plant materials to coal is a three-step process. The steps involved in the process are:

1. *Accumulation*: This is the gradual gathering of coal-forming plant materials.
2. *Diagenesis*: This is the first step that involves the biological decomposition of coal forming plant material.
3. *Metamorphosis*: Chemical reactions take place within and on fossil plants, such that eventually the fossilised plant material is converted into coal.

As mentioned earlier on, coal is thought to have originated from several decomposed plant types and plant parts [17]. The process of decomposition and conversion of plant matter to coal took place under certain conditions of temperature, pressure and time [12]. Plant material decomposition depends on the environment in which the fossilised plant materials are situated. Efficient plant matter decomposition requires the presence of moisture, which stimulates several bacterial processes that lead to the formation of peat, which then goes through various coalification stages until coal is obtained. The aerobic bacteria ensure that all the organic matter is disintegrated, with little remaining. Aerobic organisms decompose the plant parts which were composed largely of cellulose, as well as protein and porphyrin materials (diagenesis).

2.1.2 Coalification

This is the process in which decomposed plant material is converted from peat, through several stages, into anthracites [40]. There are nine different rank stages as shown in Table 2.2 [25].

Table 2.2 Rank stages involved during coal formation

Rank Stage	% C	% Volatile Matter	Specific Energy (MJ/kg)	% In situ Moisture
1. Wood	50	>65	-	-
2. Peat	60	>60	14.7	75
3. Brown coal	71	52	23	30
4. Sub-bituminous	80	40	33.5	5
5. High-volatile bituminous	86	31	35.6	3
6. Medium-volatile bituminous	90	22	36	<1
7. Low-volatile bituminous	91	14	36.4	1
8. Semi-anthracite	92	8	36	1
9. Anthracite	95	2	35.2	2

The stages involved in the transformation of plant matter to coal are as shown below [12].

Peat \Rightarrow lignite \Rightarrow sub-bituminous \Rightarrow bituminous \Rightarrow anthracite.

2.1.2 Peat

Peat is formed from the deposition of organic matter under anaerobic conditions (limited oxygen supply). Peat formation is controlled by four factors, namely vegetation, water, time and sedimentary environment[19].

2.1.3 Lignites

These are high-oxygen, low heating value and young coals. The reaction shown below in

Figure 2.1 is a proposed route for the coalification of lignin [20].

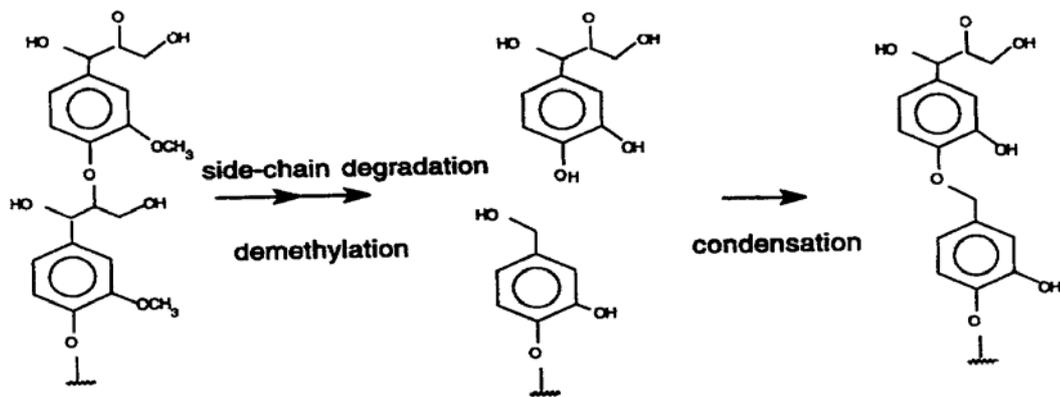


Figure 2.1 Coalification of lignin [39]

2.1.4 Bituminous

These are classified as middle-rank coals (Figure 2.3) and their volatile matter content ranges between 10 and 30%. Bituminous coals dissolve quite reasonably in most organic solvents.

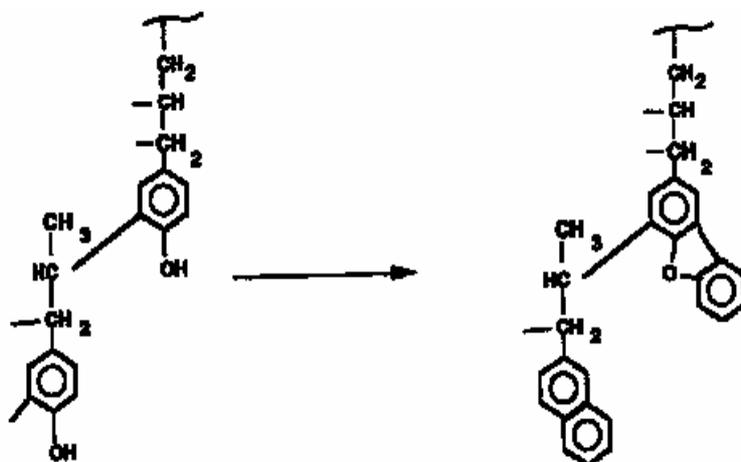


Figure 2.2 Transformation of lignite structures to bituminous coal [39]

2.1.5 Anthracites

These are high-rank coals characterised by high carbon content. The high carbon content makes it difficult to dissolve anthracites in organic solvents. The plant and mineral matter lying buried beneath the surface are highly diversified and the conditions to which it was subjected make it clear that the coal is made up of different materials, which have different chemical and physical compositions. These variations in coal are basically due to differing conditions of temperature and pressure at which coalification occurred and they can be observed on the macroscopic and microscopic levels. The diversification of the plant matter found in coal has a direct impact on the characterisation of coal and coal solutions.

These transformations are shown from the elemental analyses given in Table 2.3 below [25].

Table 2.3 Transformation of plant material to coal

Coal	Carbon	Hydrogen	Oxygen
Wood	49.3	6.7	44.4
Peat	60.5	5.6	33.8
Lignite	69.8	4.7	25.5
Sub-bituminous	73.3	5.1	18.4
Bituminous	82.9	5.7	9.9
Anthracite	93.7	2.0	2.2

2.2 Coal analysis

2.2.1 Proximate analysis

The proximate analysis in coal refers to its empirical characterisation. This method of analysis was developed as a means of classifying coal by analysing the product distribution in coal during heating under standard conditions. Proximate analysis is expressed in terms of the following four constituents.

(1) *Moisture content*

The moisture content is the difference between the weight of the coal sample as obtained and its weight after drying in an inert environment at a temperature of 110°C [22]. Knowing the moisture content of a coal is essential because it affects the heating value of the coal.

(2) Volatile matter content (VM)

This refers to the gases and vapours that are driven off during pyrolysis (heating of coal to ~ 900°C in an inert environment). Volatile matter is made up of gases such as carbon dioxide, carbon monoxide, methane, water and tar from the organic materials in coal, as well as carbon dioxide, water, sulphur dioxide and hydrogen sulphide from certain minerals. Volatile matter depends on coal rank and ranges from < 5% for anthracites to > 50% for sub-bituminous coals and lignites [41].

(3) Ash

Inorganic materials (mineral matter) in coals are easily oxidizable upon combustion once all combustible substances have been burnt off. The most commonly found minerals in coal are clays, quartz, sulphides and carbonates [31]. The presence of mineral matter in coal reduces the heating value.

(4) Fixed carbon content (FC)

This is the carbon remaining as the non-volatile fraction of the pyrolysed coal defined by

$$FC = 100 - (\% H_2O + \% VM + \% Ash)$$

The moisture content in coal ranges from 0–70%, with the volatile matter ranging from 5–60%, ash from 1–35% and fixed carbon from 20–85%. The fixed carbon content of a coal can also be determined from thermo gravimetric analysis (TGA).

2.2.2 Ultimate analysis

This is the analysis done on a coal sample to determine its elemental composition in terms of weight percentages of carbon, hydrogen, nitrogen, (organic) sulphur and oxygen, which make up the coal substance.

2.3 Coal petrography

This is a standard method of characterising the organic (maceral) and inorganic (mineral) constituents of coal [37]. It is from these data that the rank and composition of coal can be determined. Coal macerals are optically homogenous, discrete microscopic constituents of the organic fraction of coals, and they constitute the building blocks of coal [8,31]. They are identified and classified on the basis of their morphology, source material, colour/level of reflectivity and nature of formation [12]. Macerals differ because they represent different parts of the original plant material and microorganisms. From petrographic studies, coal is shown to comprise three maceral groups – these are the vitrinites, exinites and inertinites [14].

2.3.1 Vitrinites

Most vitrinite macerals are derived from the cell-wall material (woody tissue) of plants, which are chemically composed of the polymer cellulose and lignin [8, 26, 31]. In the process of vitrinitisation, it is generally believed that during diagenesis in coal-forming swamps, the cellulose and lignin in the plant cell-walls are chemically altered and broken down into colloidal particles, which are later deposited and desiccated. This process of gelification

commonly homogenises the components so that the resulting macerals are structureless. The variation in vitrinite macerals is usually thought to be due to differences in the original plant material or to different conditions of alteration at the peat stage or during coalification. The vitrinite maceral group has three maceral groups, namely telinite, collinite and vitrodetrinite [19]. The telinite maceral came from various tree branches, trunks, stems, leaves and roots, while the collinites came from humic particles that were degraded in the early stages of coalification. The collinites were formed from gel precipitated in humic solutions. The last maceral group is vitrodetrinite, which was formed from plant and or humic particles that were degraded at very early stages. Vitrinites have densities ranging from 1.3–1.8 g/cm³ and the density is found to vary as the coal rank increases. The hydrogen and carbon contents of vitrinites lie between those of inertinites and liptinites. The hydrogen content varies between 4.5 and 5.5%, the oxygen content from 5–20% and the carbon content from 75–96%.

2.3.2 Inertinites

The inertinite macerals are derived from plant material, usually woody tissue that has been strongly altered either before or shortly after deposition. In the same coal seam, they are richer in oxygen than the accompanying vitrinite. Inertinites are characterised by a high reflectance, as well as a distinct cell texture. The submacerals are fusinites, semifusinites, inertodetrinite and scleronite. Fusinites originate from the oxidation of cellular woody tissues and they occur in varying quantities in peat, brown coal and bituminous coal. Like fusinites, semifusinites also occur in varying ranges in peat, brown coal and bituminous coal. Semifusinites are characterised by very high reflectance. Their hydrogen content is also low, ranging between 2.75 and 4.25%, while the carbon ranges from 73 to 85% and the oxygen between 13 and 25%.

Inertodetrinites originate from oxidised cell-wall fragments and they have reflectance that varies within broad limits, their reflectance being slightly higher than that of vitrinites.

2.3.3 Exinites

These are derived from the resinous and waxy material of plants, including resins, cuticles, spores, pollen exines and algal remains. Exinite is richer in hydrogen than the accompanying vitrinite. Exinites are characterised by high reactivity and volatility, and are more aliphatic. This maceral group has submacerals, namely resinites, alganites, cutinites and liptodetrinites. These also seem to have resisted changes during coalification. The cutinites found in this maceral group came from the cuticles normally found in leaves and thin plant stems. The resinites came from the resins, which were products of the metabolism of plants. Originally, the term exinite was used to describe the chemically resistant exines of spores in coal. Their resistance to metamorphism characterises exinites during the early stages of coalification. Exinites are also the lightest maceral group, with their density ranging from 1.18 g/cm³ to 1.25 g/cm³. In low-rank coals, the exinites are characterised by higher hydrogen content and upon carbonisation, they yield tar and gas. Also, they have a higher carbon content than most coals. The hydrogen content of bituminous coals ranges from 7 to 10%, the carbon content from 75 to 85%, and the oxygen content ranges from 5 to 18%.

2.4 Structure of coal

2.4.1 Nature of attractive forces in coal

Various structures within the coal structure are held together by different intermolecular forces, such as hydrogen bonds, covalent bonds, London and van der Waal's forces, and pi-pi (π - π) and charge transfer interactions [5, 42].

The whole of the coal's organic matter is most likely held together by all of the attractive forces experienced by the organic compounds. Electrodynamical interactions occur when there are instantaneous variations in the distribution of electric charge on the species. The variations generate net attractive forces, such as van der Waal's forces and π - π interactions. The presence in coal of various oxygen groups that may form hydrogen bonds, which in general have rather high energy, supports the view that the hydrogen bonds may be the major attractive forces in coal organic matter [38]. On the other hand, aromatic rings are the most abundant structures in bituminous coals and their π - π interactions may commonly occur. The diagram below (Figure 2.3) shows various forces holding together a coal [6]

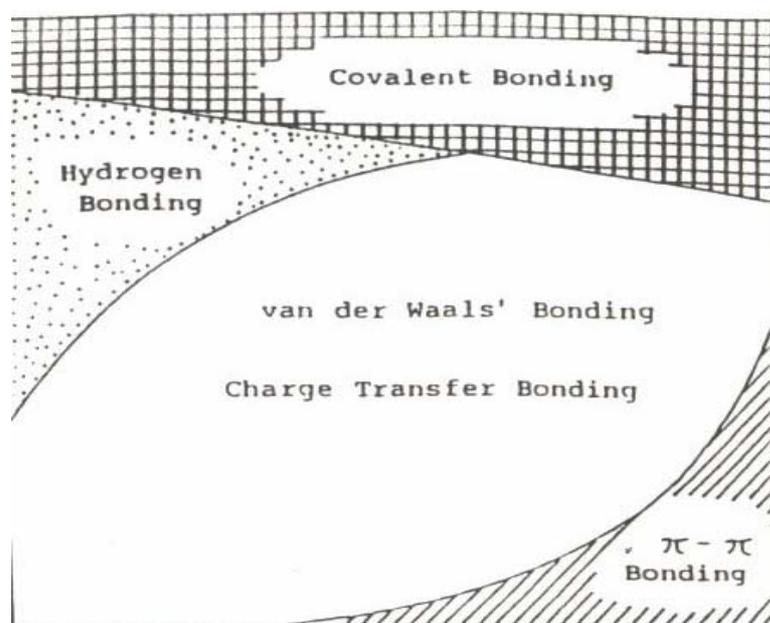


Figure 2.3 Bonds holding molecules together in the coal structure [6]

The structure of coal can be divided into three sections, which are organic, physical and inorganic.

2.4.3 Organic structure

The organic structure of coal is considered to be a two-phase model made up of a huge three-dimensional cross-linked portion (macromolecular phase) and a mobile (molecular) phase.

The macromolecular phase is insoluble in organic solvents, but the addition of additives may help improve the dissolution [15, 24]. The pure organic substance in coal consists of an organic structure in which carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and organic sulphur (S) are the major components [6]. The relative proportions of C, H and O determine to a large extent the characteristics of coal and are related to the petrographic composition (type), which is the relative proportion of the macerals vitrinite, inertinite and exinite in the coal [37].

Oxygen

This is the major component of the coal-forming materials and the oxygen content of the coal depends largely on the rank of the coal. The oxygen content is thought to decrease as the coal rank increases. The major oxygen contribution in the lignites comes from the carboxylate ($-\text{COO}^-$) group, but this is not so in several bituminous coals.

Sulphur (Figure 2.4)

When coal is burnt, the sulphur that it contains is released in form of sulphur dioxide and sulphur trioxide, both of which are detrimental to the environment. Apparently, many methods of removing sulphur from coals are on trial at laboratory scale [20]. Sulphur in coals is thought to originate from the sulphate ion derived from seawater [6]. During coal formation stages, there is much bacterial activity and these bacteria are thought to reduce the sulphate to the sulphide. Since there is some iron in the coal structure, the sulphide formed will react with iron to form pyrite, which is the principal inorganic form of sulphur in coal, and this is incorporated into the coal part of the coal. In coal, there is a mixture of organic and inorganic sulphur, with the inorganic part being mainly the pyrite.

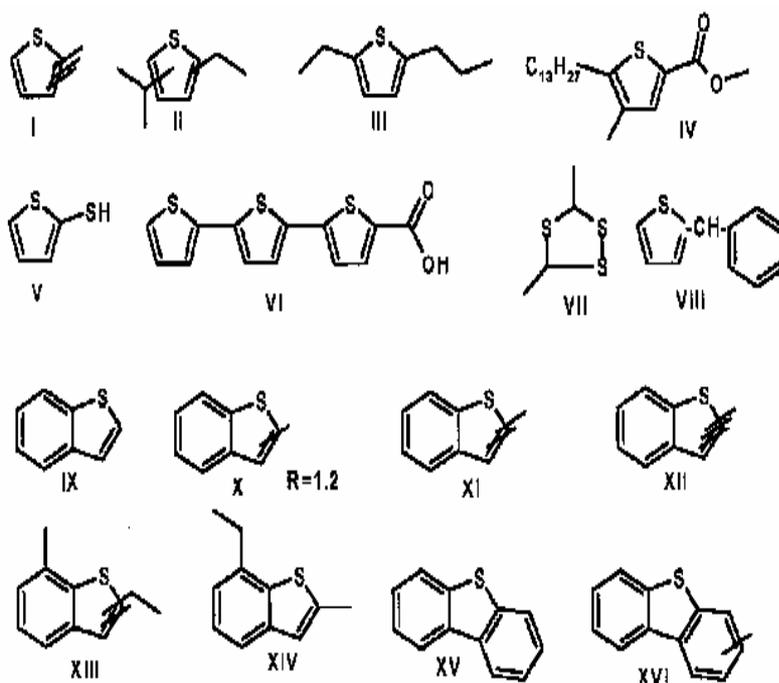


Figure 2.4 Sulphur-containing structures in coal [20]

Nitrogen (Figure 2.5)

There is not much nitrogen in the majority of the coals and its quantity is estimated to be less than 2% by weight. Nitrogen in coal is not of any principal importance. However, on a negative note, upon coal combustion, oxides of nitrogen are liberated and they tend to cause air pollution. Nitrogen originates from the amino acids and porphyrins in the plant material from which coals are derived.

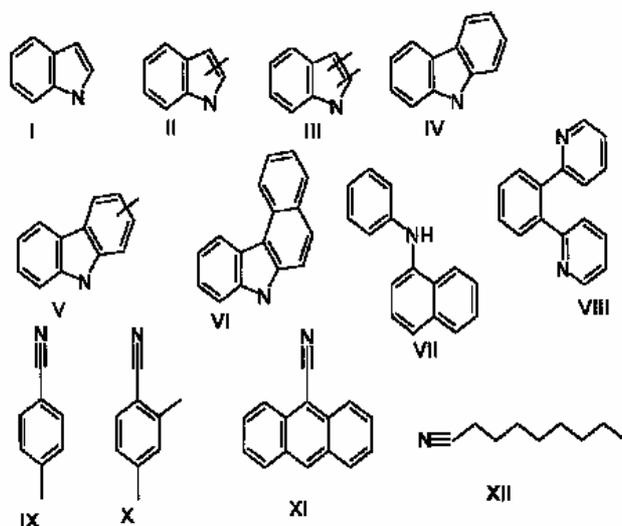


Figure 2.5 Nitrogen-containing structures in coal [20]

From analysis of coal extracts, a decrease in the amount of nitrogen as coal rank increases has been observed. This phenomenon is due to the conversion of basic amino ($-NH_2$) groups to nitrogen incorporated into the ring structures (heterocyclic nitrogen). However, there is little information with regard to the presence of nitrogen in the coals.

Carbon

There are basically two kinds of carbon in coal: aliphatic and aromatic carbons. Aliphatic carbons are found mostly in petroleum products and fuels, while aromatic

carbons are found mostly in a number of graphite structures. The carbon in coals is largely aromatic and occurs in ring structures. In many low-rank coals, there is a significant amount of long-chain aliphatic material, but it is not known whether this material is bound to the coal macromolecule or whether it is simply entangled with it.

2.4.3 Inorganic structure

All coals contain differing amounts of mineral matter but most are in the range between 9 and 10 wt %. Mineral matter is the inorganic material found in coal. Mineral matter is not necessarily inert during conversion processes and has been reported to act beneficially in some cases as a catalyst for coal liquefaction. The ways in which the inorganic matter is bound to the organic matter are not well understood. Mineral matter in coal is comprised of several inorganic components, with many minerals in them.

2.4.4 Physical structure

The physical structure of coal helps scientists to understand both the physical and chemical behaviour of coal. The physical structure of coal has been described as a porous macromolecular gel. In natural aqueous environments, coals behave like porous rocks. However, in the presence of organic solvents, coals behave like macromolecular gels. From the macromolecular network point of view, it is well known that coals imbibe solvents and swell appreciably and, in some ways, swollen coal networks take on elastomeric properties.

Scientists have come to the conclusion that coal networks are held together by a number of covalent bonds, with a very low amount of ionic bonding, occurring largely

in low-rank coals. As mentioned earlier, other than covalent bonds in coal, there are also some associative forces that hold the coal molecules together.

Figure 2.6 below shows a proposed layout of the coal structure [12, 19].

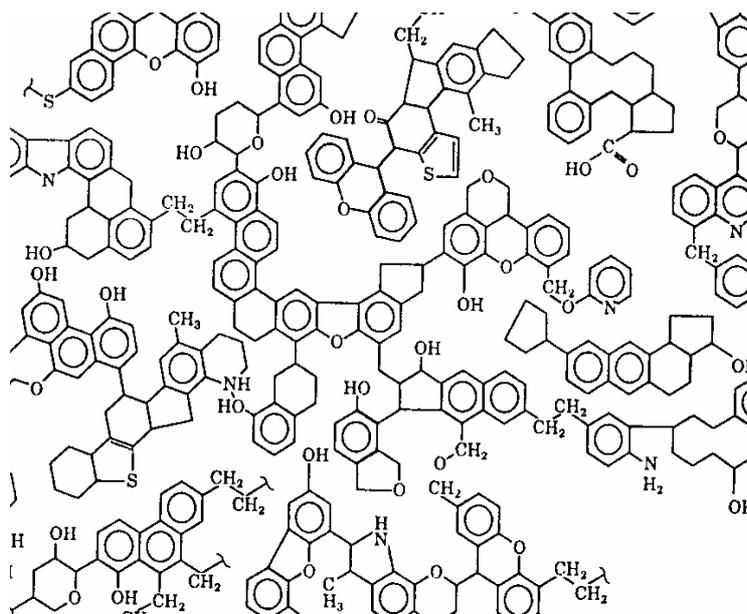


Figure 2.6 Proposed structure of coal [12, 18,19]

The structure of coal is important for the utilisation of coal in various coal conversion processes, such as liquefaction, pyrolysis and gasification. Coal is depicted as a polymeric material of very high molecular weight, but the actual structure is still unknown because of the extremely heterogeneous nature of coal.

The concept of a network structure of coal was discussed by Iino [9] and his conclusion was that there are two network models of coal – these are the covalent network model (Figure 2.7) and the non-covalent network model (Figure 2.8) of coal.

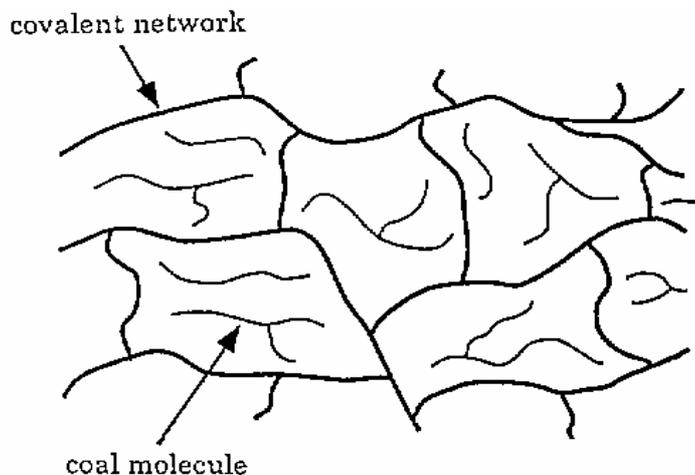


Figure 2.7 Covalent network model of coal [9]

The covalent network model of coal is based on the principle that coal is a huge macromolecule of covalently bound networks, which do not dissolve in the solvents, and there are soluble compounds of low molecular weight entrapped within the network [3, 9].

The non-covalent network model postulated that coal is comprised of huge associates and, furthermore, a mixture of coal extracts was gel-like, showing closeness to the non-covalent network model shown below (Figure 2.8).

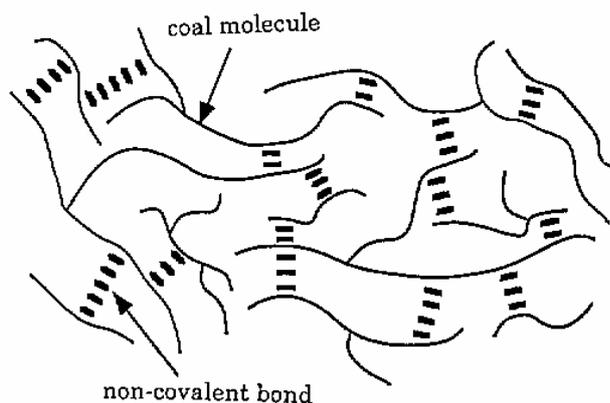


Figure 2.8 *Non-covalent network model of coal [9]*

2.5 Solvent extraction of coal

Solvent extraction of coal is a technique that was developed for the purpose of dissolving the organic part of coal with the aim of separating it from the mineral matter that might be entrapped in the coal. Coal-solvent extraction gives an insight into the molecular constituents of coal, which in turn are a source of very vital information [23]. Coal has a cross-linked, three-dimensional network structure with the coal molecules closely packed [15]. Between the molecules, there are different physical intermolecular forces, such as hydrogen bonds, London and van der Waal's forces, pi-pi (π - π) and charge transfer interactions, etc., holding the coal molecules together [5]. For efficient coal dissolution, the solvent molecules must break apart these intermolecular forces holding together the coal molecules and penetrate the solid coal. As the solvent makes its way into the coal, it swells and this swelling increases. The swelling of coal in organic solvents is said to be directly proportional to the temperature [5, 13]. The mechanism by which coals dissolve in various polar aprotic organic solvents is not yet known but is thought to involve the disruption of the bonds holding together the coal molecules [3, 41]. It is during swelling that the solvent breaks the intermolecular forces between coal molecules, such as the H-bondings, van der Waal's and London forces, and other charge

transfer and π - π interactions, and makes its own bonds with the coal molecules and extracts the coal [43]. Thus the solvent must diffuse inside the solid coal molecule and then diffuse out with the soluble coal molecules. According to Marzec *et al.*, extraction processes are largely influenced by the electron-donor-acceptor properties of solvents [2, 7, 24]. Efficient coal extraction techniques help to give information related to the functional groups that are in the coal [7]. The solvent exchange capacity and extraction capability depend on the electron-donor-acceptor properties of the solvent and the functional groups in coals [24]. The guest components are easily extractable by most solvents but stronger electron-donor solvents would be needed to extract other portions.

Good results on the dissolution of coal are obtained with polar aprotic organic solvents. These solvents have a unique electron structure, as well as the ability to mix with many organic entities embedded in the coal structure, thereby dissolving it [41].

Dryden pointed out that the potency of effective coal solvents could be associated with the existence of an unshared electron pair on a nitrogen or oxygen atom in the molecule (which makes the solvent behave as a polar fluid) [13]. An organic solvent interferes with the internal interactions in the coal network by replacing coal-coal bonds or hydrogen bonds with stronger coal-solvent hydrogen bonds [10].

Experiments that were conducted on low-rank coals by applying high hydrogen pressures and elevated temperatures resulted in the disintegration of the coal macromolecules, bringing them into solution mostly in colloidal form [1, 4, 10]. These techniques are efficient on low-rank coals but use a great deal of energy, thus making them more expensive. Furthermore, these highly aggressive conditions bring about undesirable changes and dislocations in the

structure of coal. Utilisation and conversion would become easier, more convenient and more efficient if coal could be solubilised in common and commercial organic solvents.

2.5.1 Factors affecting coal extraction

The dissolution of coal in organic solvents shows a decreasing trend as the carbon content of the coal increases. Very high carbon contents of about 90% result in little or no dissolution with a varying range of solvents. Previous work shows that various solvents give different dissolution percentages [36, 41]. The solubility of coal in organic solvents depends on a number of process parameters. The parameters that have the greatest effect on the solubility of coal are the temperature at which extraction is carried out and the time taken to do the extraction. In addition, coal particle size, moisture content and oxygen content also have some effect on coal dissolution [44].

2.5.1.1 Temperature

According to Mishra and Sharma the degree to which coal dissolves in different classes of solvents, such as amines, alcohols, alkanes, aromatics and alkenes, was found to increase with an increase in the boiling point[10]. High temperatures result in thermal disintegration of coal the molecules. This increases the diffusion of the solvent vapours inside the intermolecular space in coal particles. Intermolecular physical bonding can be weakened under the diffusion pressure in liquid and vapour form . If the chemical nature of the solvents is the same, then the higher the temperature, the greater will be the dissociation of coal molecules caused by the breaking of the intermolecular forces by heat energy, in addition to the dissociation of the coal molecules caused by attraction and interaction with organic solvents.

2.5.1.2 Solvent basicity

The dissolution of coal into various organic compounds and other amines involves the disruption of hydrogen bonds between the solvent and the functional groups in the coal. It has been proposed that a solvent will disrupt only those coal-hydrogen bonds whose bond strengths are lower than those of coal-solvent hydrogen bonds. It has also been suggested that solvents that are strongly basic are capable of breaking nearly all the hydrogen bonds in coal. The increase in extraction yields with the use of a strongly basic solvent is due to the complete disruption of all hydrogen bonds.

2.5.1.3 Coal properties

The dissolution of coal depends largely on the carbon content of a particular coal. As the carbon content of coal increases from 85 to 89 wt % (dry ash-free (daf) basis), the dissolution becomes very low. At a carbon content of 93% by weight, dissolution becomes insignificant.

The presence of moisture and oxygen in coal and the pre-treatment of the coal also affect the extraction process of coal. Oxygen has a tendency to degrade the solvents, while water or moisture impede the power of the solvent since water alone is not a good solvent for coal. Very small amounts of water will reduce the extraction yield significantly.

2.5.1.4 Coal particle size

Recent studies on the coal dissolution process show that there is a significant increase in the extraction yield as the coal particle size decreases. However, Renganathan *et al.* [41] concluded that the effect of particle size on extraction yields was insignificant.

2.6 Efficient coal extraction processes

2.6.1 Coal extraction with N-methyl-pyrrolidinone

The Chemical Engineering Department at the University of West Virginia, USA, carried out studies involving the dissolution of coal in N-methyl-pyrrolidinone (NMP) with the purpose of producing coal extracts that had various industrial applications. As explored in Chapter 3, they obtained good results regarding the yield of coal dissolved in the solvent. In comparison with other solvents, their results for coal extraction with NMP were better than those obtained using other alternative polar aprotic organic solvents. Their yield of dissolved coal was dependent on a number of factors. Furthermore, extraction with NMP was found to be very efficient in removing most of the unwanted material in coal and, also, the solvent was found to be user friendly as compared with other solvents in dissolving coal. As with most polar aprotic organic solvents, the presence of a lone pair of electrons on the nitrogen and oxygen atoms makes a good solvent[41]. In addition, NMP has a unique ability to change its conformation depending on the surroundings and this unique character results in a shift of the lone pair of electrons, thus allowing the solvent to adapt to its surroundings. This makes it a good solvent for dissolving coal. The West Virginia University process of dissolving coal was carried out at a temperature of 200°C under reflux conditions, with the coal solvent ratio being 10:1, in an inert environment for a time period of one hour. After extraction, the mixture was cooled and precipitated under nitrogen.

2.6.2 Coal extraction with carbon disulphide-N methyl-pyrrolidinone

Very substantial amounts of work related to the extraction of coals have been carried out. This work involved the use of mixed solvents to dissolve coal and this proved to be very efficient in terms of the overall yields obtained. The mixed solvents have a greater penetrating power on the coals. The mixture of CS₂-NMP was found to give higher yields during extraction at

ambient conditions. During extraction with CS₂-NMP, several coals obtained during the five stages of coalification were subjected to room-temperature extraction using the CS₂-NMP mixture. The ratio of CS₂ to NMP was 1:1. The extraction mixture was subjected to ultrasonic irradiation for 30 minutes [36]. The resultant coal solution was centrifuged and the supernatant decanted, after which a fresh aliquot of the solvent was added to the extract, with the procedure being repeated until the supernatant became clear in colour. Lino [9] in his experiments on the extraction of coal with CS₂-NMP found out that for bituminous coals at room temperature, more than 60% of the coal dissolved. The extraction yield above was found to be higher than that obtained if CS₂ and NMP were used separately under similar extraction conditions.

2.6.3 The Hypercoal process

The Hypercoal process (HPC) is a recent coal extraction technique that has been developed to produce coal that has very low ash content. This is essential since the presence of ash and other mineral matter in the coal makes it undesirable for use in the manufacture of nuclear graphite. Recent studies on the HPC process have shown that it is a technique that is based on solid-liquid separation [36]. The HPC process is divided into four sections which ensure the efficient production of an ash-free coal. The initial stage of the HPC process involves mixing the coal with a recycle solvent consisting mainly of methylnaphthalenes (MN). This is followed by heating the slurry to ~ 350°C and extracting it. The third part of the HPC process involves solid-liquid separation and, at this stage, the coal residue is separated from the coal slurry by means of gravitational concentration, with the slurry coming out at the top and the residue at the bottom. Most of the material and mineral ash is rejected with the bottoms. For effective dissolution to be achieved, the bottoms obtained as above are mixed with the recycle solvent to ensure that most of the dissolvable materials go into solution. The two slurries

obtained will be mixed and further solids removal will be done. The last stage in the HPC process involves recovery of the solvent from both the slurry and the residue.

2.6.4 The Refcoal process

The coal purification process being developed for the manufacture of high-purity nuclear-grade graphite suitable for use as a reflector in Eskom's Pebble Bed Modular Reactor (PBMR) is based on the efficient dissolution of the organic particles of coal with polar aprotic solvents on addition of alkali.

The process of extracting coal dissolves most of the organic components in the coal. On commercialisation, this process is likely to form the backbone for obtaining nuclear-grade graphite for the PBMR. It is therefore essential to understand thoroughly the chemistry involved in the whole process for trouble-shooting, as well for as economic evaluation.

In the solvent dissolution of coal, the organic part of suitable coals can be very efficiently dissolved in polar aprotic organic solvents. The addition of an alkali (sodium hydroxide – in pearl form) vastly improves the amount of organic material dissolved in the solvents. Centrifuging the coal solution separates the bulk of the inorganic minerals and the purified organic material recovered. Most of the inorganic impurities will be left in the residue and can be discarded.

The extraction of coal with polar aprotic organic solvents is enhanced by the addition of alkali (sodium hydroxide) during the extraction process. This is a CSIR-developed process [11], which results in the production of a refined coal solution (*Refcoal*

Solution). The Refcoal process makes use of various polar aprotic organic solvents including dimethylformamide (DMF) and dimethylacetamide (DMAA). The addition of an alkali (sodium hydroxide) results in a marked improvement in the amount of coal dissolved in the organic solvent. The extent to which coal is dissolved in the organic solvents was determined by taking slurry, centrifuging and weighing ~ 0.1 g of the sample into a 50 ml volumetric flask and diluting it by volume. The absorbencies of the solutions taken over the time period of extraction were measured at a wavelength of 600 nm. The measured absorbance was corrected to exactly 0.1 g. The kinetics of extraction showed an autocatalytic form, with the dissolved coal acting as a phase-transfer catalyst.

The concept of dissolving coal in organic solvents was first developed in Germany during the Second World War, with the aim of producing low-ash electrode-grade coke. This process of dissolving coal in organic solvents with the addition of alkali is being investigated because it has the potential to form the backbone of the Refcoal process being developed for the manufacture of nuclear-grade graphite to be used in the PBMR. In South Africa, the concept of dissolving coal in organic solvents with the addition of alkali was initially developed at the CSIR at laboratory level. Having seen that the process described above has the capacity required to manufacture nuclear-grade graphite for use in the PBMR, Eskom contracted the Institute of Applied Materials at the University of Pretoria to carry out further investigations into the process before the idea could be commercialised. The idea was also to provide a platform to train people in carbon technology.

Due to its great abundance and relatively low cost, coal has been proposed as a possible substitute for petroleum. The only drawback with regard to coal is its high amount of impurities, which maybe detrimental to the environment. To be used effectively, coal needs to be purified and this purification is achieved by dissolving coal in organic solvents.

The solvent being used in the Refcoal process is N, N dimethylformamide (DMF). DMF, due to its polarity and also being aprotic in nature, was found to be extremely effective in extracting fairly large amounts of the organic materials in coal. Also, DMF was found to be the least expensive option and was much easier to recover. However, there are also other solvents that are capable of dissolving most of the organic material in coal. These include solvents like dimethylacetamide (DMAA) and N-methylpyrrolidinone (NMP).

Chapter 3: Experimental

3.1 Coal extractions

3.1.1 Small-scale solvent extraction of coal

Dimethylformamide (DMF) (70 g), coal (7 g) and NaOH (0.7 g) were mixed in ten stainless steel reactors. Nitrogen gas was purged into each reactor for three minutes and the reactors were sealed. The reactors were mounted on a rotating machine for 48 hours. Thereafter, they were removed from the machine, weighed, balanced and centrifuged for 30 minutes. To extract the dissolved coal solution, the dissolved components of each reactor were filtered on a pre-weighed sinter glass. The filtration was done three times by adding small but equal amounts of DMF and centrifuging for 20 minutes. The procedure was repeated for all the reactors. Finally, the sinter glasses were dried in an oven overnight at a temperature of 90°C. The dried mass of the sinter glass was recorded and the dissolved coal was calculated by mass difference.

3.1.2 Room-temperature solvent extraction of coal

As with high-temperature extraction, accurately weighed quantities of DMF (800 g), coal (80 g) and NaOH (8 g) were charged in a 1 litre centrifuge bottle, the mixture was purged with nitrogen gas and the bottle was sealed tightly. The bottle was then mounted on a magnetic stirrer and stirred continuously for 48 hours, after which the absorbance of the solution was measured on a Genesis ultraviolet spectrophotometer at a wavelength of 600 nm.

3.1.3 Large-scale solvent extraction of coal at 95°C

In a 1 litre steel reactor with a hot oil jacket around it, 800 g of fresh DMF, together with 80 g of Tshikondeni coal, were charged and the mixture was heated to 95°C, stirring at a speed of 700 r/min. At this temperature, 8 g of NaOH in pearl form was added.

Simultaneously, a stream of nitrogen was allowed to flow continuously into the reactor so as to maintain an inert environment in the reactor. The progress of the extraction was followed by taking ~ 2 ml samples of the slurry at intervals. The samples were each centrifuged for 3 minutes at a speed of 400 r/min using a Hettich or Clements centrifuge. About 0.1 g of the supernatant solution was weighed into a 50 ml volumetric flask and diluted up to volume with DMF, after which the absorbance of the solution was measured at a wavelength of 600 nm on the Genesis ultraviolet spectrophotometer. The absorbance obtained was corrected to exactly 0.1 g of sample. The progress of the extraction was monitored for 5 hours. After 5 hours, the hot mixture of Refcoal solution and the inorganic components, together with the undissolved organic components of the coal, were transferred into a 1 litre centrifuge bottle and centrifuged for 30 minutes at 3 000 r/min. After centrifuging, the supernatant (Refcoal) was separated from the residue by decanting the upper layer. The dried residue was then analysed for carbon content. Other solvents that can be used effectively for the dissolution of coal are dimethylacetamide and N methyl-2-pyrrolidinone. The above procedure was followed in carrying out the experiments detailed below.

3.1.3.1 Absorbance and absorbance measurements

Absorbance is the amount of radiation that is absorbed by an analyte. This amount can be mathematically related to its concentration. In the Refcoal process, the absorbance was measured to give an estimate of the degree to which extraction had occurred. The absorbance of the Refcoal solution was obtained by taking ~ 3 ml of slurry and centrifuging it for 3 minutes. From the centrifuged solution, ~ 0.1 g was weighed into a 50 ml volumetric flask and diluted to volume with DMF. The absorbance was measured at a wavelength of 600 nm on the ultraviolet spectrophotometer and the reading was corrected to 0.1 g of sample to give a corrected absorbance value. The process of extraction was assumed to be complete if the measured and corrected absorbance was ~ 1.

3.1.3.2 Extraction of coal with different solvents

Coal extraction was carried out as outlined in Section 3.1. However, in this experiment the amount of alkali added to the extraction medium was varied from 10% to 3.75%. The degree of extraction was determined by measuring the absorbance at 600 nm on a spectrophotometer. This procedure was also followed in carrying out experiments listed below.

3.1.3.3 Extraction of coal with different bases

3.1.3.4 Extraction of coal with different concentrations of NaOH

3.1.3.5 Extraction of coal at different temperatures

3.1.3.6 Extraction of coal with nitrobenzene

3.1.3.7 Extraction of coal with NaOH of different texture

3.1.3.8 Preparation of gels using organic solvents

Some organic solvents, when they come into contact with Refcoal solution, cause it to gel. These solvents, which include carbon tetrachloride, dichloromethane, chloroform and chlorobenzene, were added in quantities ranging from 0.1% to 10% of the Refcoal solution into a test glass vial. Inside the glass vial was a magnetic stirring bar. The vial was placed a magnetic stirrer and a stopwatch was started simultaneously. As soon as the Refcoal solution

started to form a thick paste, the stopwatch was stopped. This was repeated for each of the solvents mentioned above.

3.2 Analysis of coal solutions

3.2.1 Determination of sodium hydroxide purity

A 0.1 M NaOH solution was prepared by accurately weighing 0.8085 g in 200 ml of distilled water. From this solution, 25 ml were pipetted into a 250 ml volumetric flask and titrated against 0.1 M of HCl using phenolphthalein as an indicator until a pink colour was discharged. The volume was noted. To the same mixture, methyl orange indicator was added and the titration continued until the methyl orange changed colour from yellow to red. The experiment was repeated until a set of three consistent results had been obtained.

3.2.2 Determination of $[\text{OH}^-]$ in Refcoal solution

Freshly prepared Refcoal solution consisting of DMF, coal and NaOH in the ratio of 100:10:1, obtained as described in Section 3.1.1, was centrifuged for approximately 30 minutes. Thereafter, a sample of ~ 1.0 g was pipetted into a 100 ml sample holder. To this sample, 40 ml of distilled water were added; the mixture was stirred for 3 minutes on a magnetic stirrer and titrated on a Mettler Toledo D.L 50 automatic titrator against 0.1 M of hydrochloric acid standardised with 0.1 M Na_2CO_3 , which was 99.5% pure.

3.2.3 Determination of [Na] in Refcoal solution

The extraction apparatus was set up as described in Section 3.1 and fresh Refcoal solution was taken at regular time intervals during extraction. The absorbance of the solution was measured as described above. From the same solution taken at

intervals, approximately 1 g of sample was weighed into a 100 ml volumetric flask and made up to volume with distilled water. The mixture was stirred to mix well on the magnetic stirrer for 5 minutes, after which it was vacuum-filtered into a 100 ml volumetric flask. The solutions were analysed for sodium content on a Varian AA 1275 series spectrophotometer at a wavelength of 330.3 nm. The instrument's spectral band pass was 0.5, with an optimum working range of between 100 and 400 ppm. The lamp current was 5 mA, with the fuel and support being acetylene gas and air respectively. Before the samples were aspirated onto the atomic absorption (AA) spectroscope, the instrument was standardised using the standards ranging from 100 to 250 and 400 ppm.

3.3 Characterisation of coal solutions

3.3.1 Nuclear magnetic resonance (NMR) spectroscopy

A room-temperature extract was prepared as outlined in Section 3.1.3. After at least 48 hours, the sample was centrifuged and taken for NMR spectroscopy analysis.

3.3.2 Electron spin resonance (ESR) spectroscopy

Room-temperature extracts were prepared as outlined in Section 3.1.3. After at least 48 hours, the sample was centrifuged. Approximately 3 ml of the centrifuged solution was put into an NMR tube and sent for ESR analysis.

3.3.3 Gas chromatography-mass spectroscopy (GS-MS) analysis of coal products

To characterise the coal and the dried coal extracts, GS-MS analysis was carried out. Approximately 1.0 g of raw coal was weighed into a coking boat. The boat was

inserted into a silica tube with the U-shape at one end dipped into a liquid nitrogen dewer flask filled up to three-quarter level. The tube was slotted into an oven with the other end connected to a nitrogen supply. The nitrogen supply was opened slightly and the temperature of the oven gradually increased up to 500°C. The escaping volatile compounds were condensed in the U-shaped part of the tube (which was dipped in nitrogen) and washed into a glass vial with a 1% solution of 1, 2 dichlorobenzene in dichloromethane. Other extracts pyrolysed were those obtained by dissolving coal with NaOH, as well as with Na₂S. In the pyrolysis of the above products, anthracene and phenanthrene were used as standards for the GC-MS analysis.

Chapter 4: Results and discussion

4.1 Coal extractions

4.1.1 Coal extraction in dimethylformamide (DMF)

Figure 4.1 shows the extent of coal dissolution in DMF.

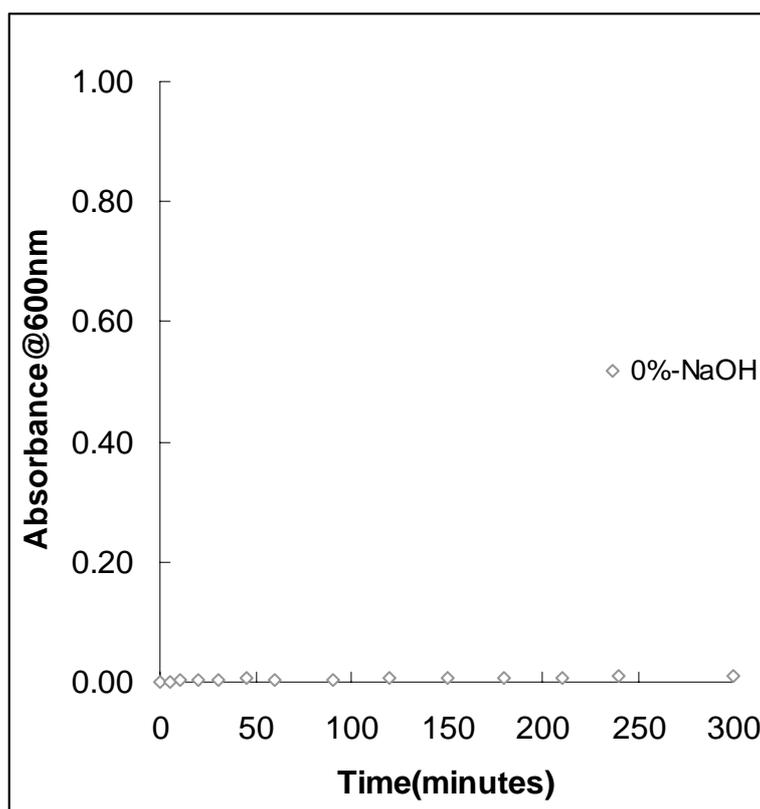


Figure 4.1 Progress of coal extraction in DMF at 95°C

DMF alone is a poor solvent for dissolving coal, as shown by the curve above. Very little coal will dissolve in this solvent alone, although the solubility of coal in DMF is increased by the addition of an alkali (e.g. NaOH). Compare this curve with that in Figure 4.2 in which coal was dissolved in DMF and NaOH.

4.1.2 Coal extraction in DMF and NaOH

Figure 4.2 shows the results of repeated experiments on the dissolution of coal in the organic solvent. The ratio of DMF: coal: NaOH was 100:10:1. These curves should be compared with the one in Figure 4.1 in which an attempt was made to dissolve coal in DMF alone.

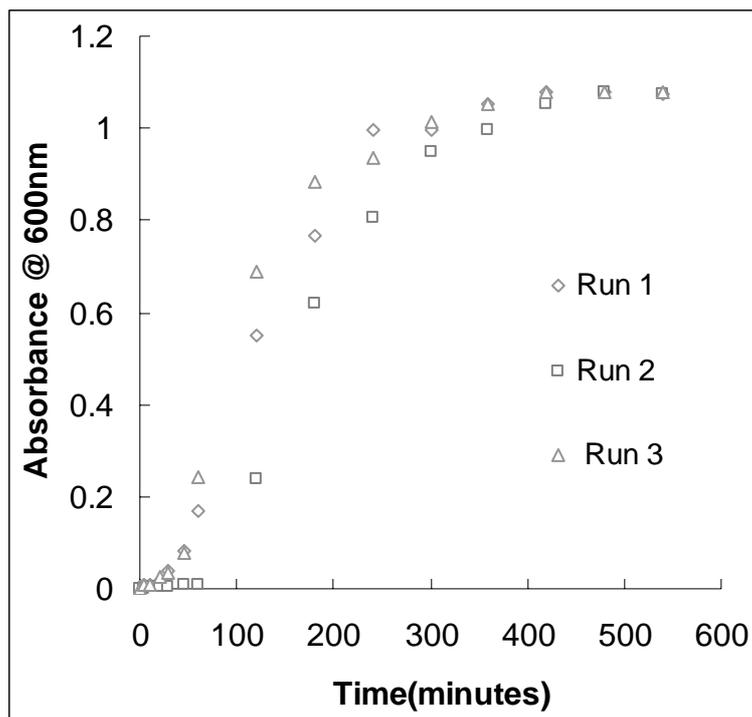


Figure 4.2 Progress of coal extraction in DMF and NaOH at 95°C

Figure 4.2 above shows how the degree of coal extraction varies with time. The higher degree of extraction obtained is a result of the addition of NaOH. A notable feature in the above curve is the induction period, which varies and is not easily reproduced, as well as the plateau at the end of the extraction, which is constant. This plateau shows the completeness of the extraction process. The Refcoal process of dissolving coal gives an extraction of 92%, which is very good compared with what other researchers in this field have found. According to Dryden [13], solvents containing either a nitrogen atom or an oxygen atom with an unshared

pair of electrons are good solvents for dissolving coal. DMF is classified as a dipolar aprotic solvent that has the ability to dissociate most of the organic material in coal

4.1.3 Comparison of coal dissolution in DMF with and without NaOH

Figure 4.3 shows a comparison of the degrees of coal extraction in DMF and also in DMF plus NaOH.

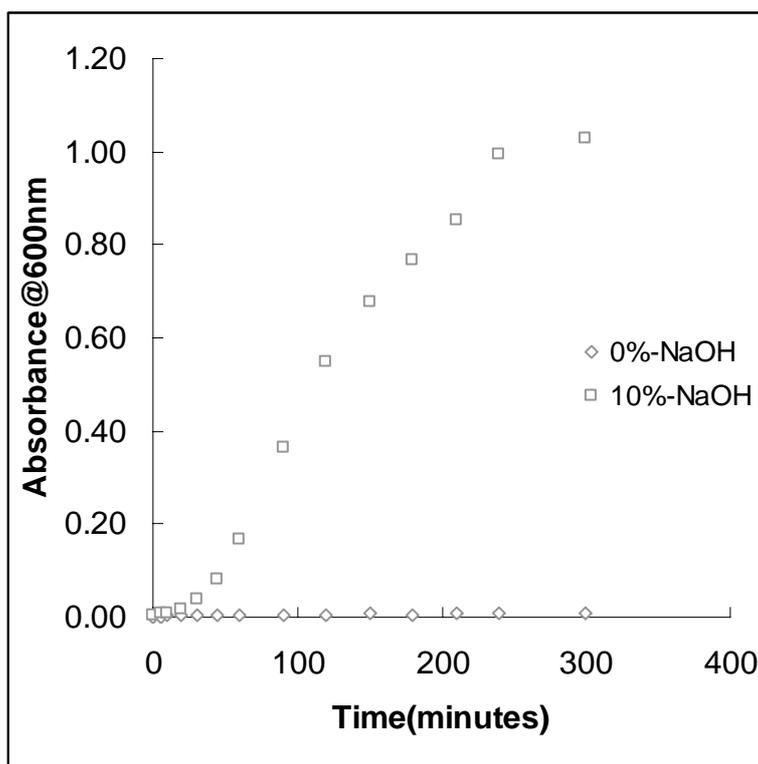


Figure 4.3 Progress of coal extraction in DMF alone and in DMF-NaOH at 95°C

The addition of NaOH gives good dissolution of coal in the organic solvent. DMF dissolves coal molecules to a very small extent, but the addition of NaOH helps to break various bonds that hold the coal molecules together, thereby causing coal to dissolve in the organic solvent in which it would not dissolve without NaOH, as shown in Figure 4.1.

4.1.4 Coal extraction with DMAA and NaOH

Figure 4.4 shows the dissolution of coal with DMAA and NaOH.

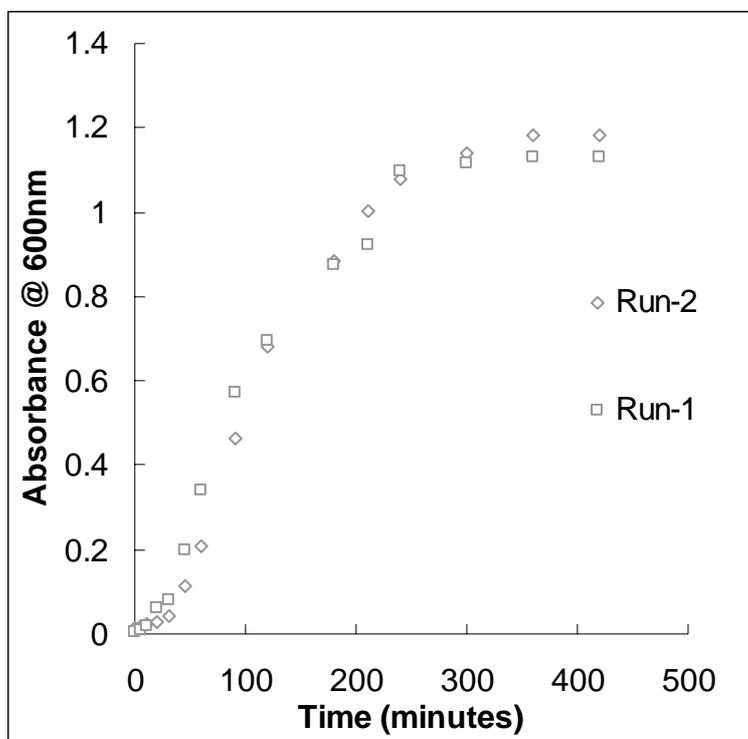


Figure 4.4 Progress of coal extraction with DMAA and NaOH at 95°C

DMAA, like DMF, is classified as a dipolar aprotic solvent and the degree to which it dissolves coal is the same as that of DMF.

4.1.5 Comparison of the degree of coal dissolution between DMF and DMAA in presence of NaOH

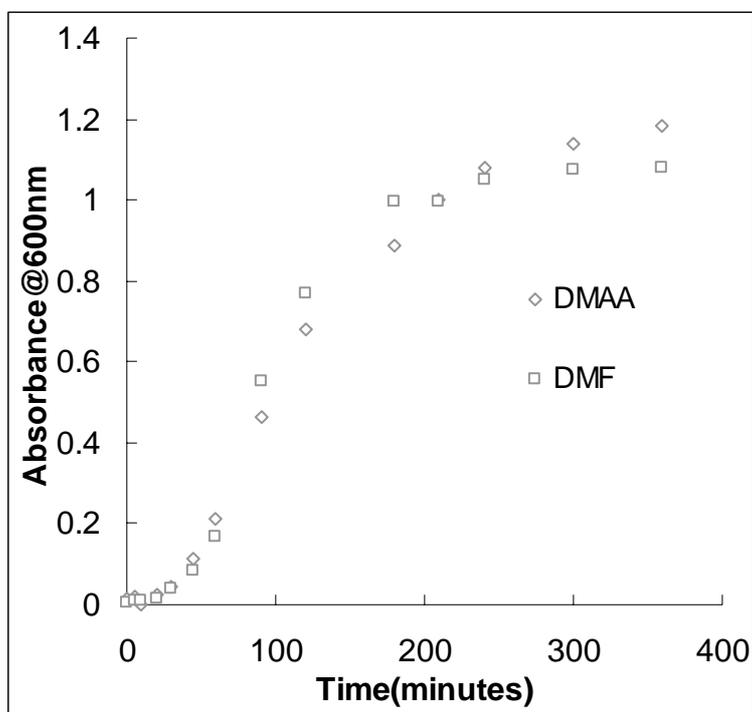


Figure 4.5 Comparison of coal extraction between DMF and DMAA at 95°C

The quantity of coal material dissolved by different solvents depends largely on the nature of the solvent and work is still being carried out to establish how the extent of dissolution depends on various physical properties of solvents. The extent of extraction between DMF and DMAA is the same as a result of the fact the two solvents have similar characteristics: the polarity index, dipole moments and boiling points of the two solvents are more or less the same, hence they gave almost similar results on extraction. The difference between the two lies in the levels of toxicity. DMF makes it easy for carcinogenic substances to be absorbed by the skin, making it harmful, unlike DMAA.

4.1.6 Effect of quantity of NaOH on extraction

Figure 4.6 shows how varying the quantity of NaOH affects the coal extraction process.

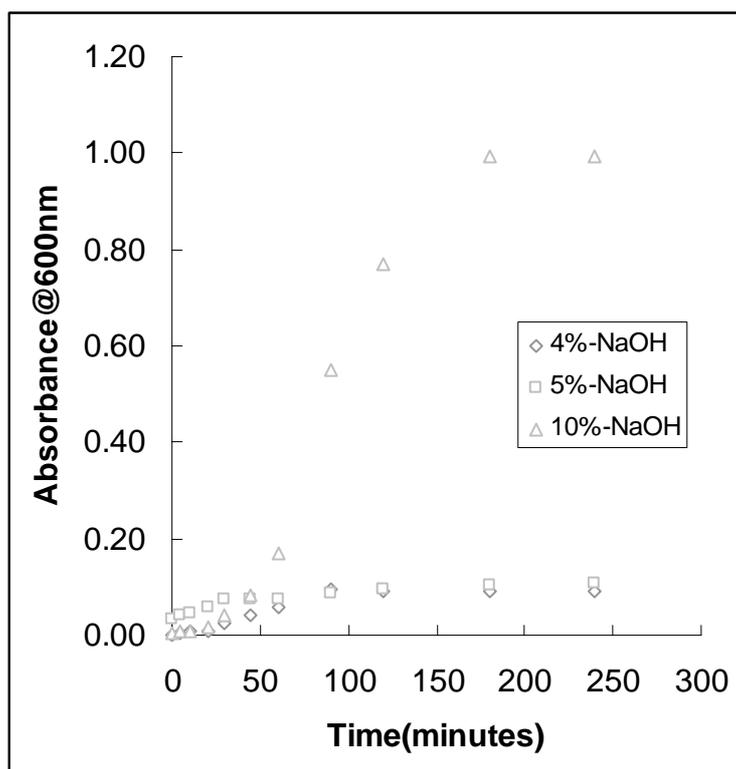


Figure 4.6 Effect of the quantity of NaOH on extraction

The process of dissolving coal in organic solvents at any temperature in the Refcoal process depends on the quantity of alkali added to the extraction recipe. Adding NaOH disrupts the interactions holding the coal molecules together, causing them to dissolve in the solvent. Specifically, the addition of NaOH during extraction breaks the pi-pi (π - π) bonds and charge transfer interactions holding together the coal molecules, causing them to dissolve in the solvent. From Figure 4.6 it can be seen that extraction with 5% of NaOH is possible [35]. The graph above shows that the extraction was possibly stopped while it was still in the induction period. Higher concentrations of NaOH give a higher yield than higher quantities of NaOH. These higher extractions with higher concentrations of NaOH show that more bonds holding together the molecules in the coal structure are broken, thus giving a high extraction yield

much faster. This can be observed by comparing the degree of extraction of 4% and 5% of NaOH against 10% of NaOH shown in Figure 4.6 above.

4.1.7 Effect of NaOH texture on extraction

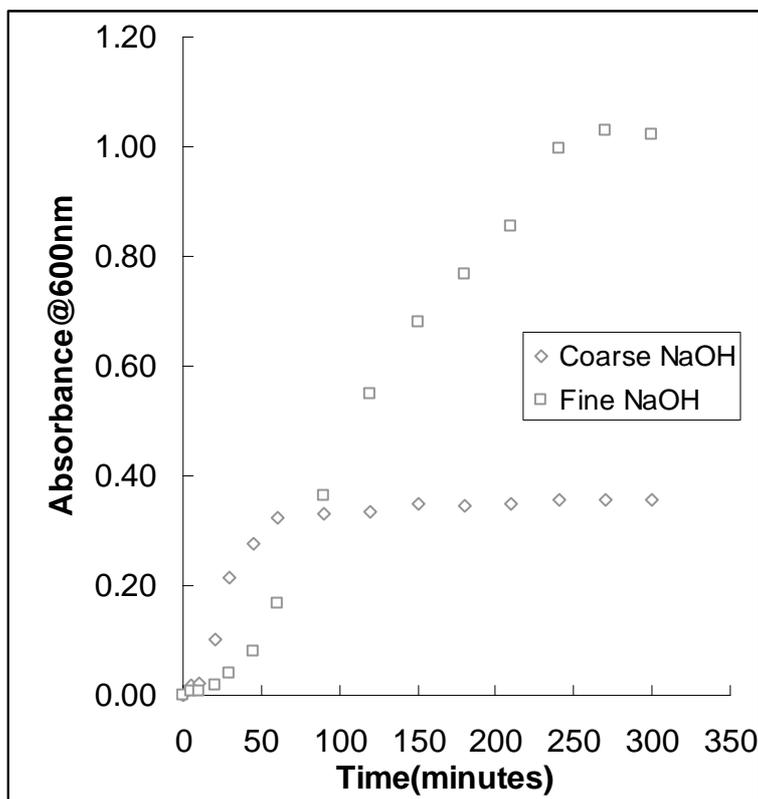


Figure 4.7 *Effect of NaOH texture on extraction*

The addition of NaOH to the extraction gives a 92% coal dissolution in the organic solvent. However, the texture of the alkali used in extraction affects the extent to which the coal dissolves. Fine NaOH gives a better degree of extraction compared with coarse NaOH. This is because fine NaOH is readily available to take part in the extraction of coal, whereas coarse NaOH is not as readily available. The shorter induction period in the extraction with coarse NaOH cannot be explained. Theoretically, it should be much longer than that for extraction with fine NaOH.

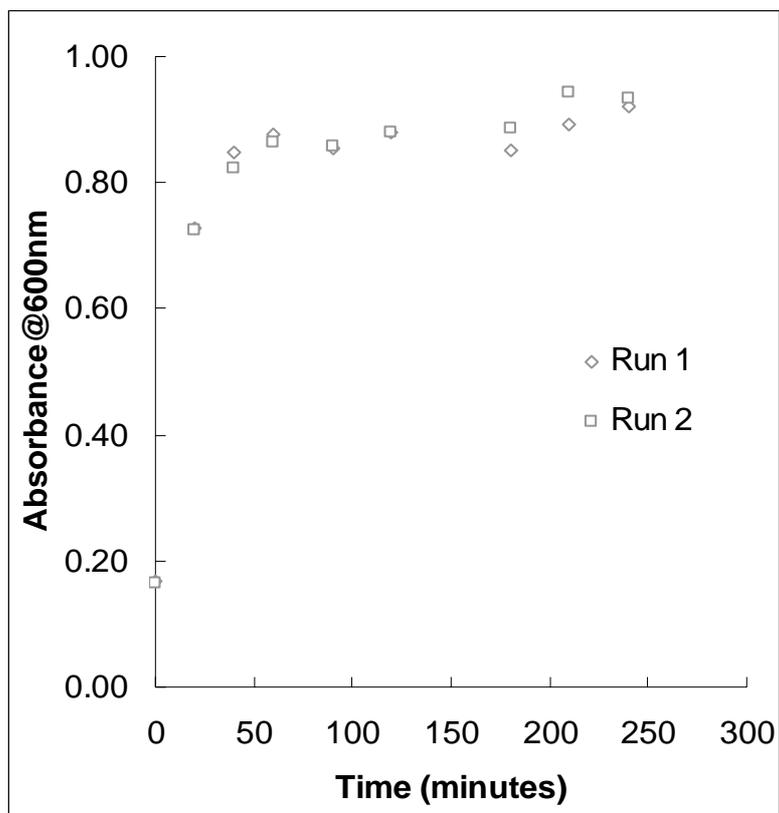
4.1.8 Coal extraction in DMF and lithium ethoxide (C₂H₅LiO)

Figure 4.8 Coal extraction with C₂H₅OLi at 95°C with the ratio of solvent:coal:C₂H₅LiO as 100:10:1 at 95°C

The dissolution of coal in C₂H₅LiO shows no induction period. This is because C₂H₅LiO is more soluble than NaOH and hence it is readily available to take part in the extraction.

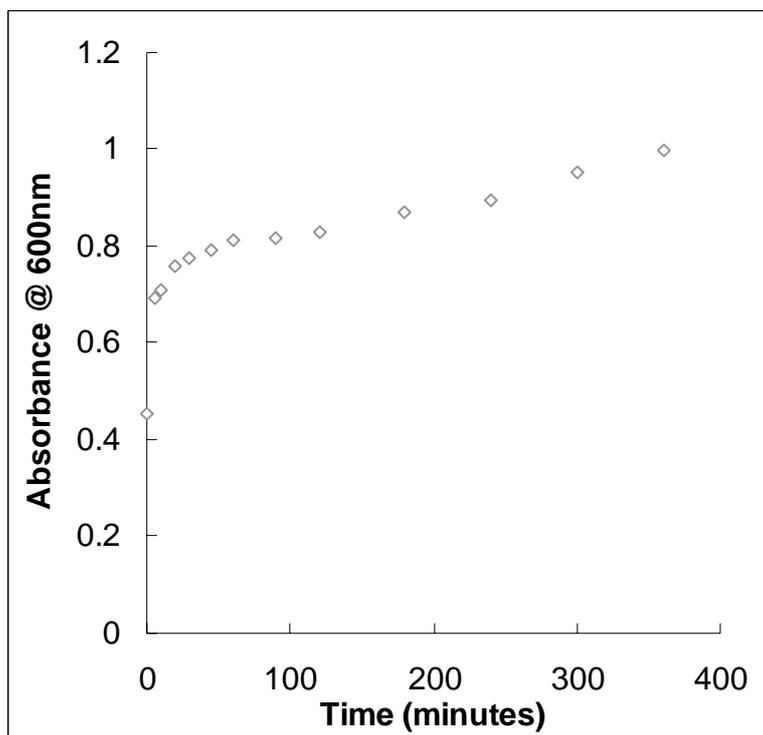
4.1.9 Coal extraction in DMF and sodium tert-butoxide (C_4H_9ONa)

Figure 4.9 Extraction with C_4H_9ONa at $95^\circ C$

The notable feature in Figure 4.9 is the absence of an induction period. Like C_2H_5LiO in Figure 4.8, C_4H_9ONa is much more soluble and readily available to take part in the extraction process.

4.1.10 Comparison of coal dissolution in DMF with the addition of different bases

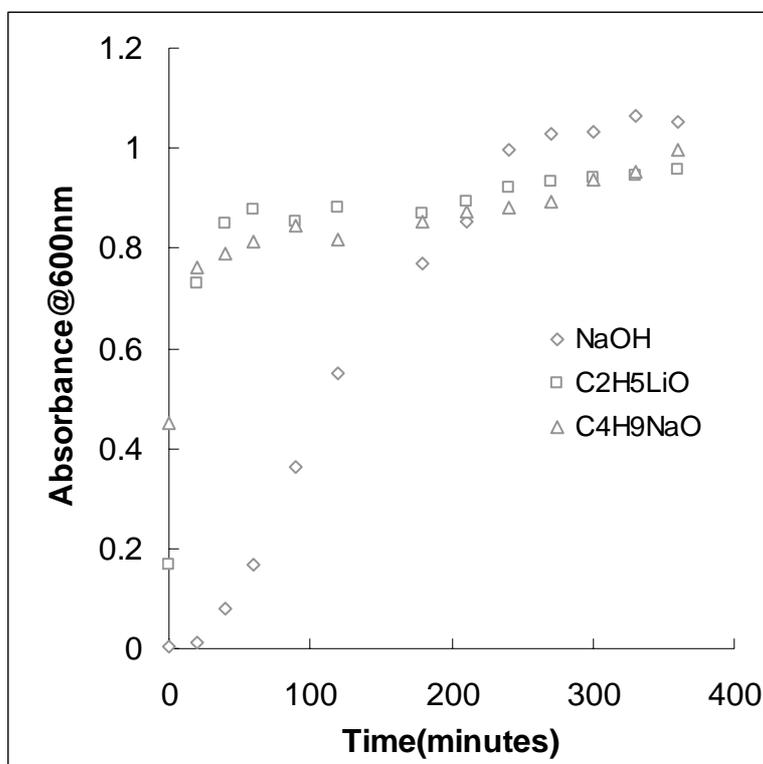


Figure 4.10 Comparison of coal extraction in DMF with different bases added

C₂H₅OLi and C₄H₉ONa are much more soluble than NaOH and they are readily available to take part in the process of dissolving coal in the organic solvent; the process is also much faster compared with NaOH. More soluble bases in extraction are characterised by a very short or no induction period during extraction.

4.1.11 Comparison of coal extraction at different temperatures

Figure 4.11 shows a comparison of the degree of extraction at different temperatures.

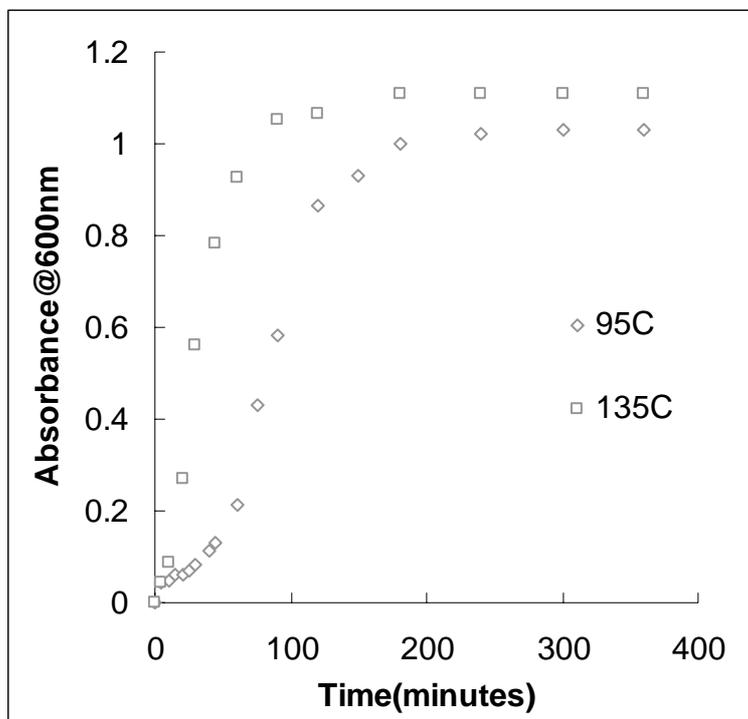


Figure 4.11 Comparison of coal dissolution at different temperatures

From Figure 4.11, it appears that the extent of coal dissolution in organic solvents in the Refcoal process does not depend on the extraction temperature. The good extraction yield (92%) of the Refcoal process does not depend to any great extent on the temperature at which it is carried out. Both room-temperature and high-temperature coal extraction processes gave good yield after extraction..

4.1.12 Comparison of dissolution of different coals

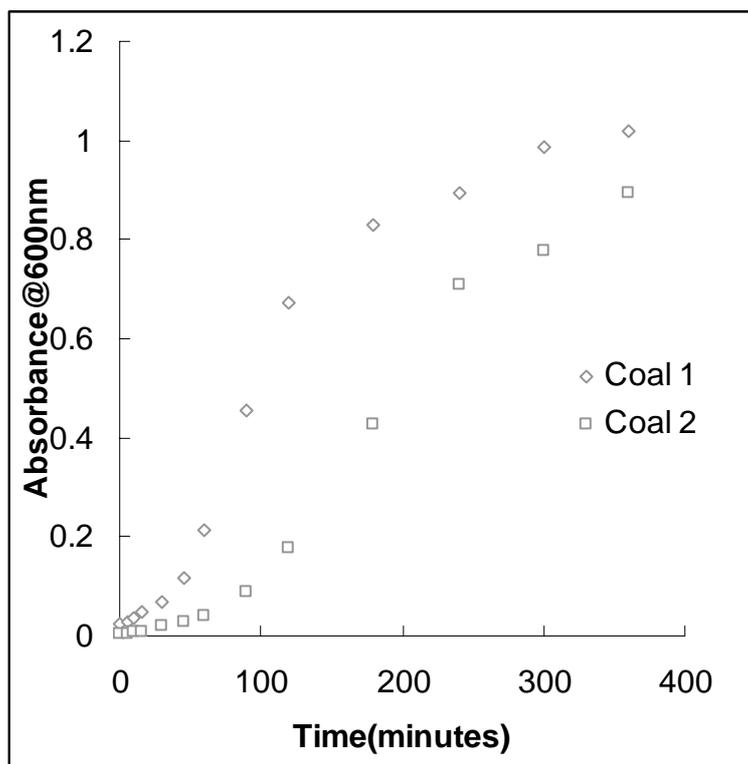


Figure 4.12 Comparison of the degree of dissolution of different coals

The exposure of coal to various external processes such as oxidation and weathering has no effect on the extractability of coal. As shown in Figure 4.12, the two coals extracted were of the same rank, with a high vitrinite content. They dissolved well in organic solvents and were extracted to the same extent, although coal 2 had a slightly longer induction period than coal

1.

4.1.13 Effect of nitrobenzene on coal dissolution

Figure 4.13 shows how the quantity of inhibitor added to the extraction affects the degree of extraction as the percentage of inhibitor is varied.

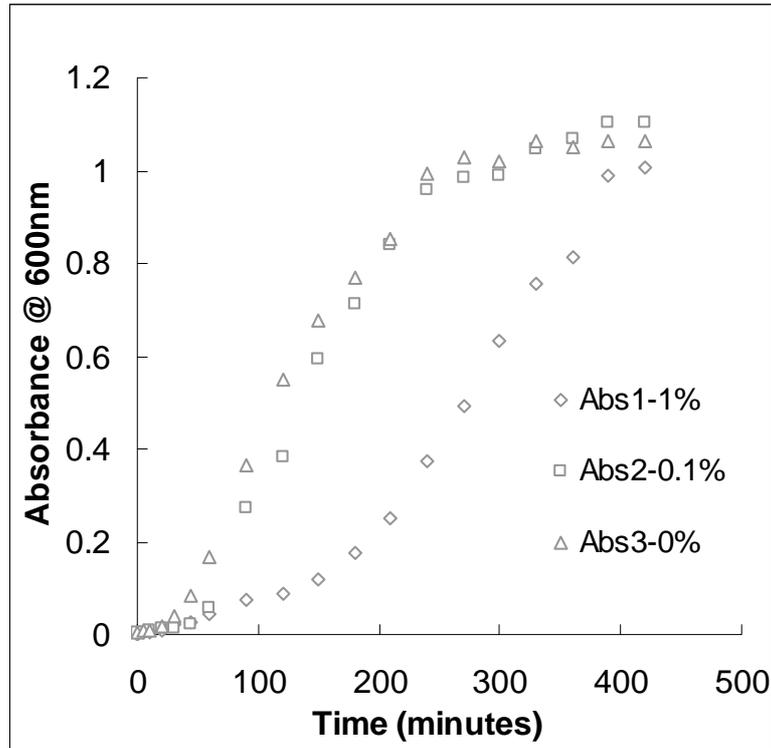


Figure 4.13 Effect of nitrobenzene on coal dissolution

The effect of inhibitors on the extraction process was studied by adding varying amounts of nitrobenzene during extraction. Nitrobenzene acts as an acid and therefore reacts with the base added, which in turn reduces the extent of extraction, as well as increasing the induction period.

4.3 Characterisation of Refcoal solutions

4.3.1 Titrations

4.3.1.1 Refcoal titration curve

Figure 4.14 shows the curve obtained from the titration of a Refcoal solution with a solvent:coal:NaOH ratio of 100:10:1

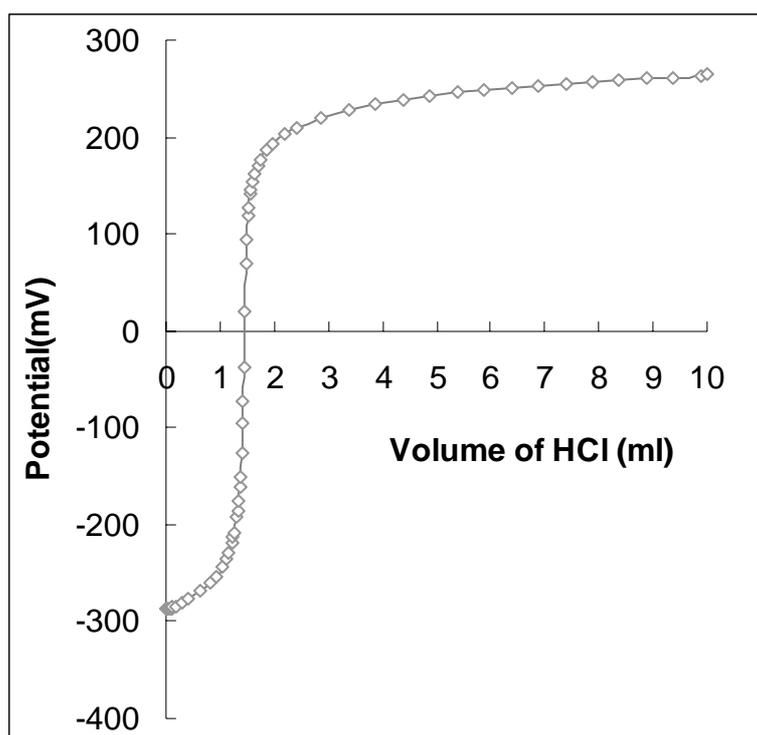


Figure 4.14 Determination of OH in Refcoal solution

The process of dissolving coal in organic solvents at any temperature depends on the concentration of alkali used in the solution. Titration of Refcoal solutions gives an estimate of the extent of the reaction between solvent and alkali.

4.3.1.2 Derivative titration curve for a coal solution with 10% NaOH

Figure 4.15 shows the derivative titration curve of Refcoal solution.

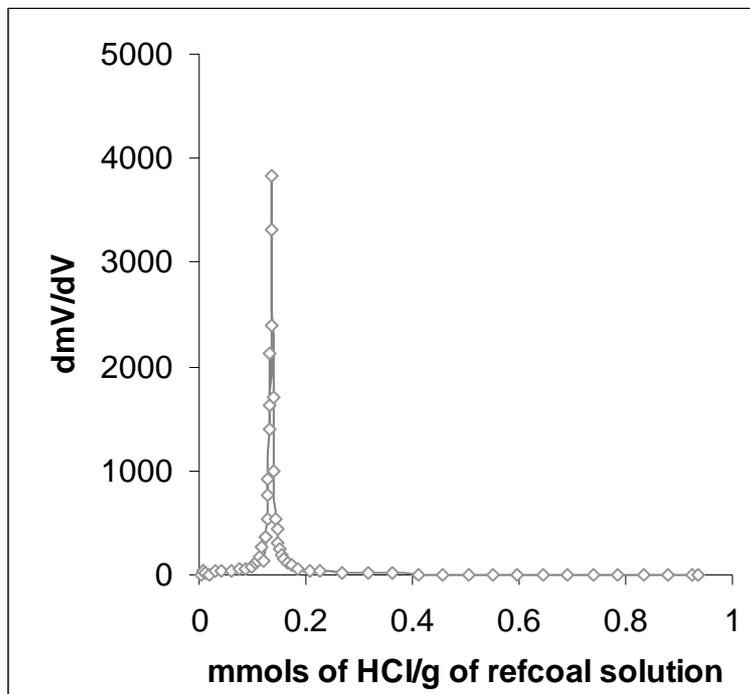


Figure 4.15 Derivative titration curve

The solvent and alkali do not react. This is confirmed by the single peak observed in the derivative titration curve.

4.3.1.3 Variation $[OH^-]$ in Refcoal solution with time during extraction

Figure 4.16 shows how the quantity of OH in solution varies with time during the course of extraction.

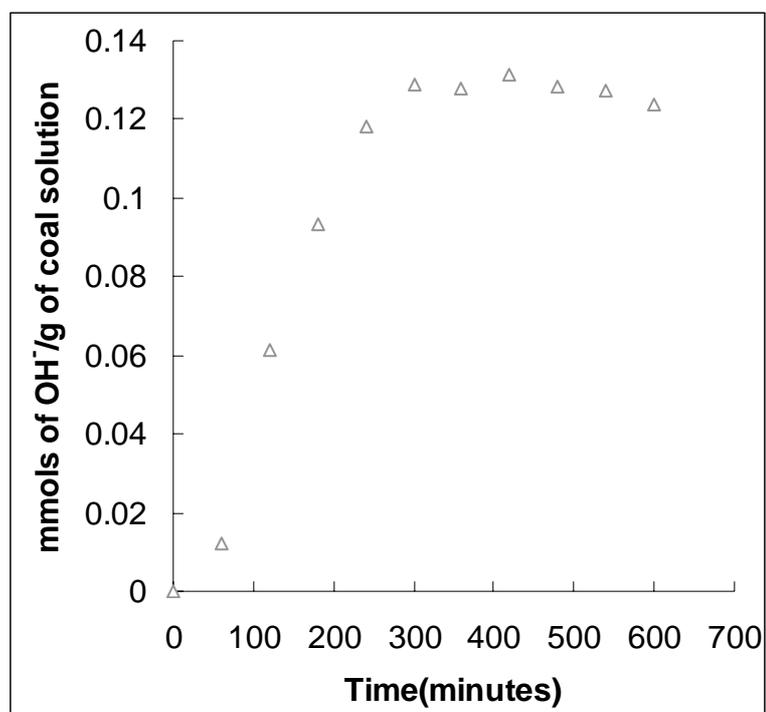


Figure 4.16 Variation of $[OH^-]$ in solution with time

The drop in the curve observed above shows that NaOH is being removed from solution. This could be the result of a reaction with some components of the mineral matter.

4.3.1.4 Variation of [Na] in Refcoal solution with time during extraction

Figure 4.17 below shows how the concentration of sodium in the solution varies with time

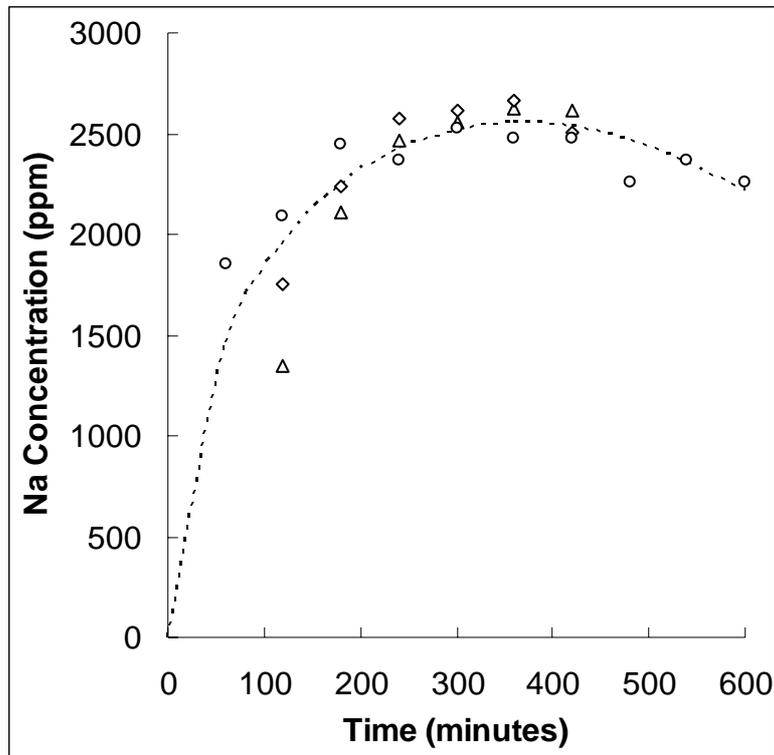


Figure 4.17 Variation of [Na] in solution with time

The results from the atomic absorption (AA) spectroscopy analysis are as shown in Table 4.1 below. These are measured concentrations of Na Refcoal solution and the extracted residue.

Table 4.1 Results of the atomic absorption spectroscopy analysis

	Experiment 1	Experiment 2	Experiment 3
Residue Na _(res)	503 mg/L	492 mg/L	507 mg/L
Solution Na _(sol)	2 190 mg/L	2 220 mg/L	2 153 mg/L

At 96% purity of Na, calculated on the basis of the [OH], the mass balance with respect to Na is accurate. With respect to [OH]⁻, the balance is out by 13%. This is due to the fact that the hydroxide reacts with some components in the coal ash to form new compounds.

4.3.1.5 Derivative titration curve for a coal solution with the 20% coal

The curve is shown below in Figure 4.18.

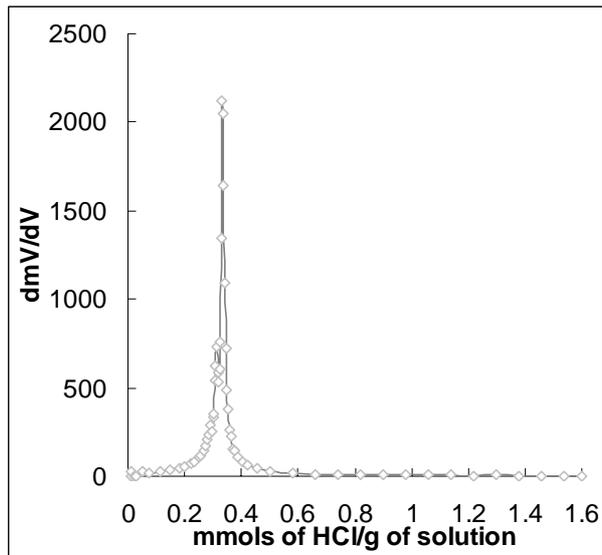


Figure 4.18 Derivative titration curve for a 100:20:1 Refcoal solution

4.3.1.6 Derivative titration curve for a coal solution with 2.5% NaOH

The curve for a solution containing 2.5% NaOH is shown in Figure 4.19.

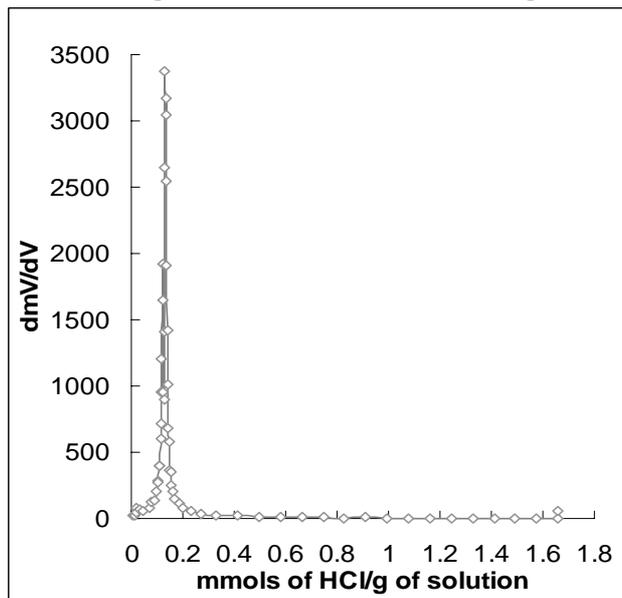
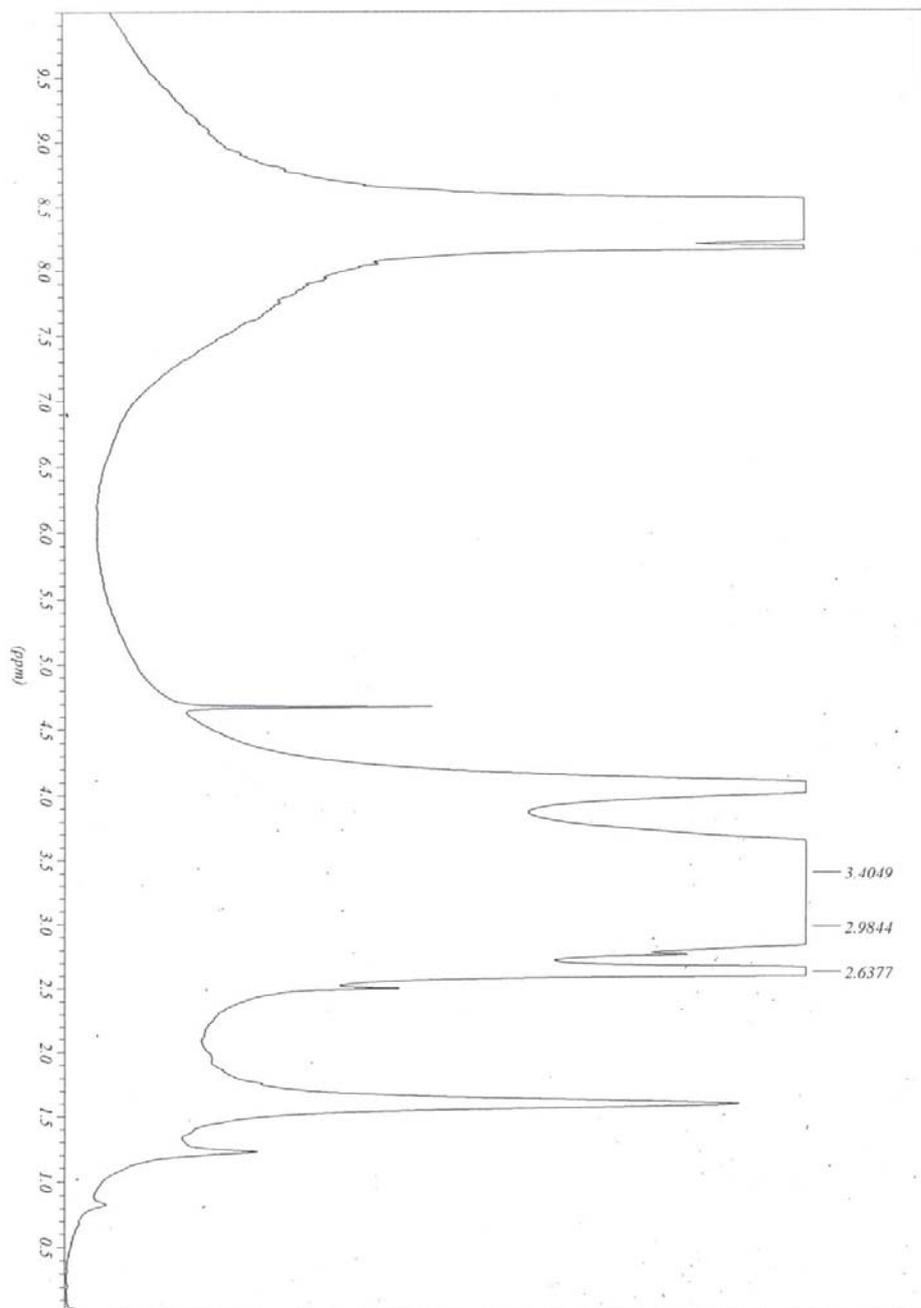


Figure 4.19 Derivative titration curve for a 100:20:0.5 Refcoal solution

4.3.2 Nuclear magnetic resonance (NMR) spectra

4.3.2.1 ^1H NMR spectra of Refcoal solution

Figure 4.20 is the proton NMR spectra of Refcoal solution.



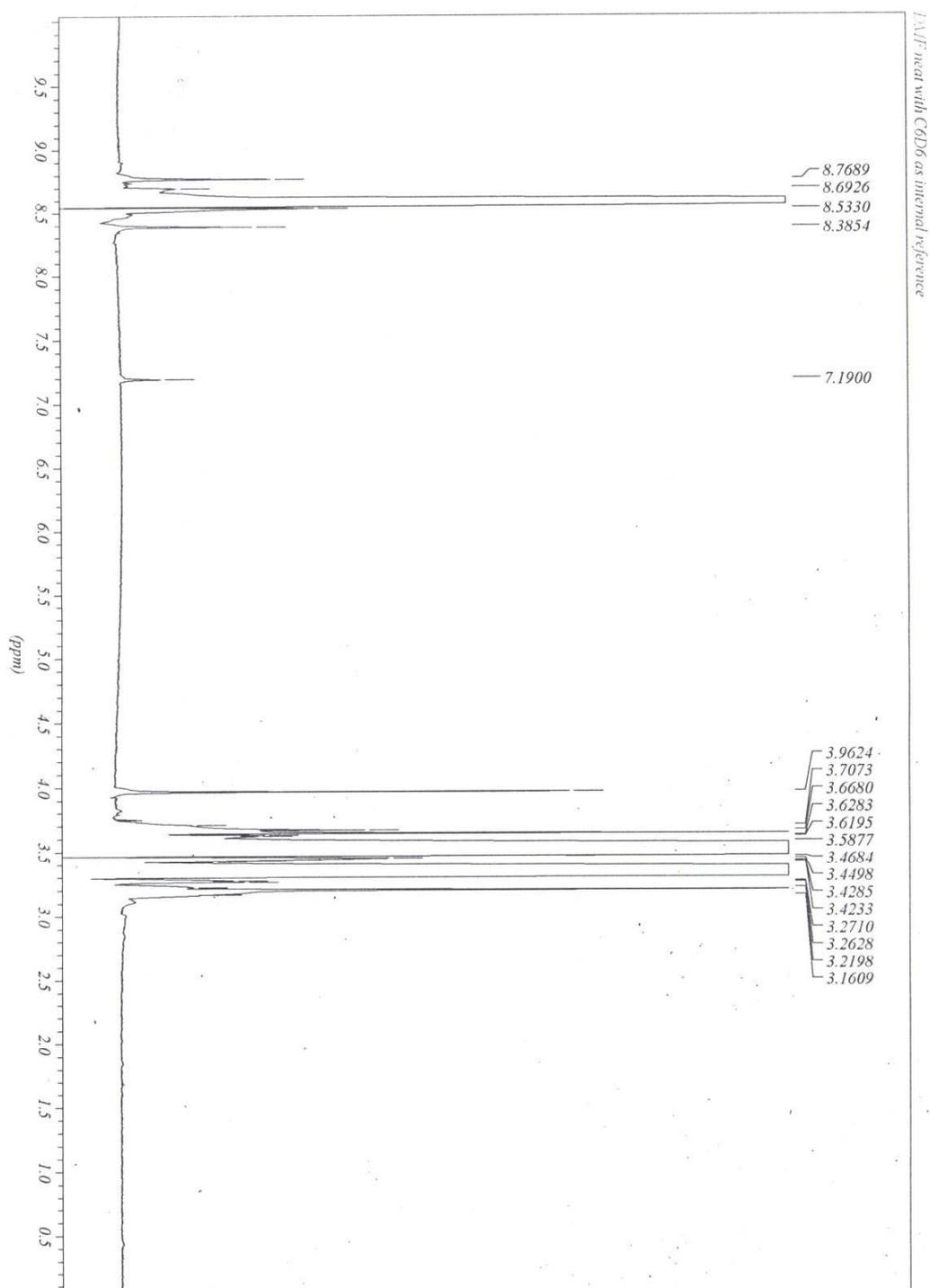


Figure 4.20 NMR spectra of room-temperature Refcoal solution

NMR studies of coal solutions give an indication of the approximate hydrogen concentrations in solution. The above data reveal that the coal solution analysed consists largely of aliphatic

and aromatic hydrogen, with concentrations ranging between 0.5 and 3.4 ppm, and 6 and 9 ppm respectively.

4.3.2.2 ^1H NMR spectra of pure NMP in $\text{D}_2\text{O}/\text{H}_2\text{O}$

Figure 4.21 shows the ^1H NMR spectra of pure NMP in $\text{D}_2\text{O}/\text{H}_2\text{O}$.

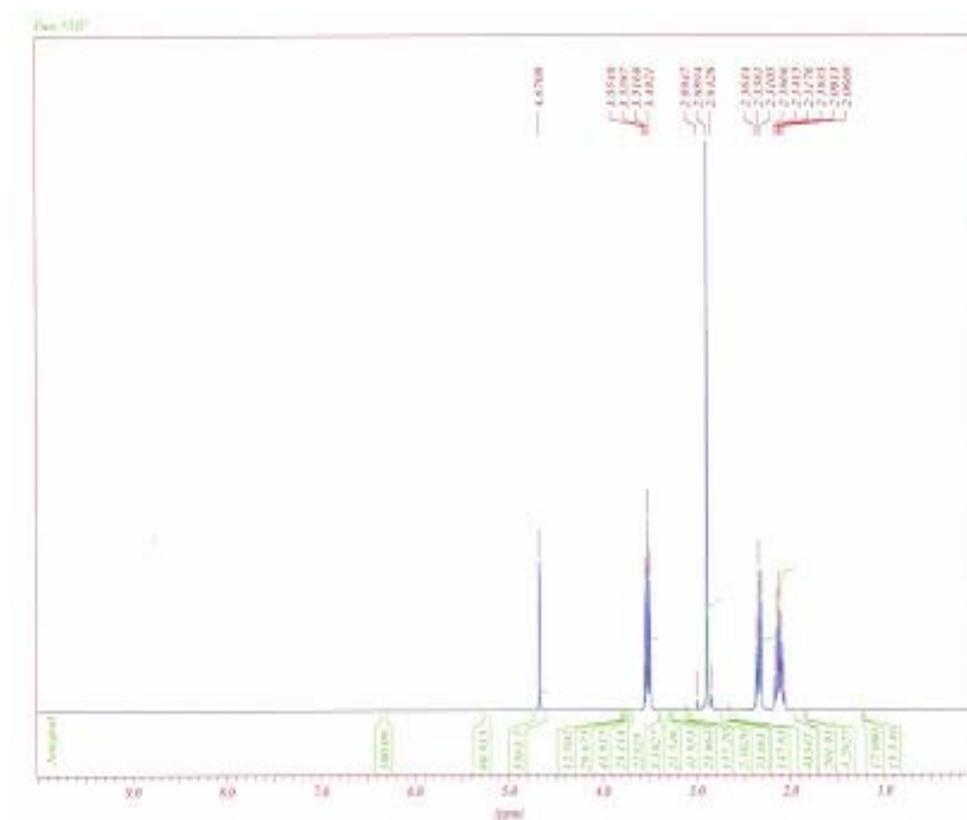


Figure 4.21 Pure NMP ^1H NMR spectra in $\text{D}_2\text{O}/\text{H}_2\text{O}$

4.3.2.3 ^1H NMR spectra of pure DMF in $\text{D}_2\text{O}/\text{H}_2\text{O}$

Figure 4.22 shows the ^1H NMR spectra of pure DMF in $\text{D}_2\text{O}/\text{H}_2\text{O}$.

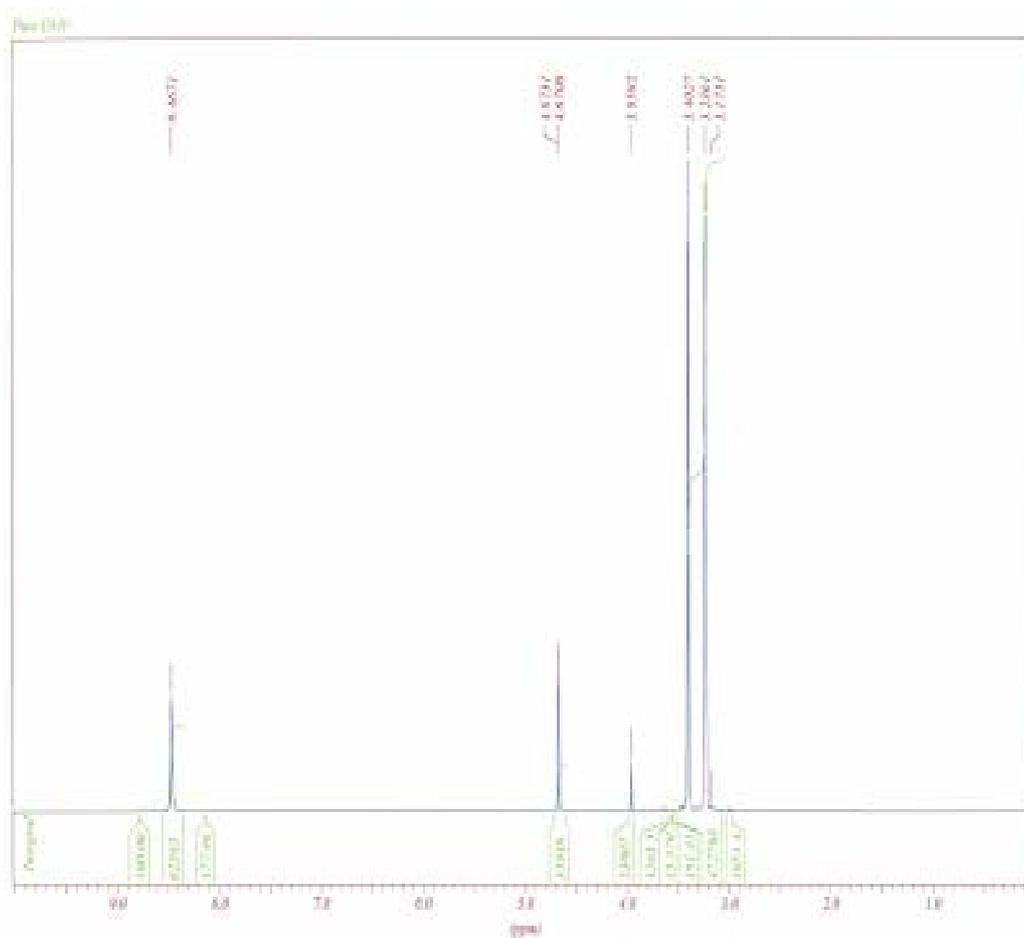


Figure 4.22 Pure DMF ^1H NMR spectra in $\text{D}_2\text{O}/\text{H}_2\text{O}$

^1H NMR spectra of coal solutions obtained using DMF and NMP give functional groups that are associated with the proton at a given chemical shift. DMF coal solutions consist of aromatic functional groups, as well as aliphatic carbons.

4.3.3 Electron spin resonance (ESR) spectra

4.3.3.1 ESR spectra of Tshikondeni room-temperature Refcoal solution

Figure 4.23 shows the ESR spectra of Tshikondeni Refcoal solution at room temperature.

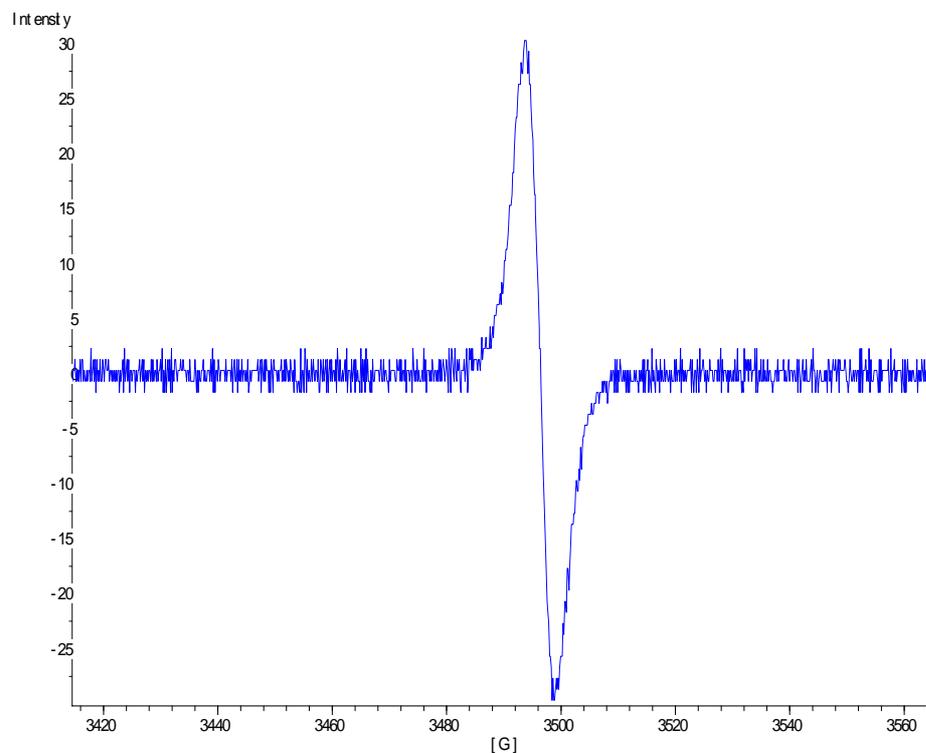


Figure 4.23 ESR spectra of Tshikondeni room-temperature Refcoal solution

4.3.3.2 ESR of Tshikondeni high temperature Refcoal solution

Figure 4.24 shows the ESR spectra of Tshikondeni Refcoal solution at high temperature.

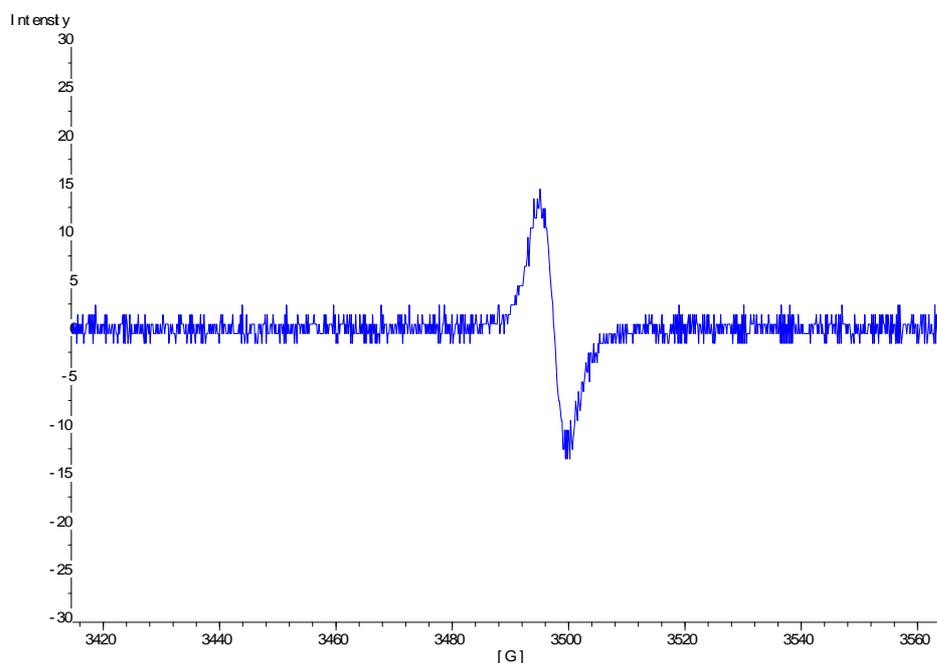


Figure 4.24 ESR of Tshikondeni high-temperature Refcoal solution

The NMR analysis conducted on Refcoal solutions highlights the presence of free radicals in coal solutions. This is in agreement with work that was carried out by John Zondlo and his colleagues at the University of West Virginia [14, 27, 41]. In their reports, they established that the free radicals found in coal have an influence on both the maceral composition and the extraction yields. A good understanding of this parameter will help to explain variations in the yields obtained when different types of coal are dissolved in organic solvents.

4.3 Gas chromatography–Mass spectroscopy

4.3.1 GC-MS *Tshikondeni coal extracted with NMP*

Figure 4.25 shows the GC-MS trace of *Tshikondeni coal* extracted with NMP.

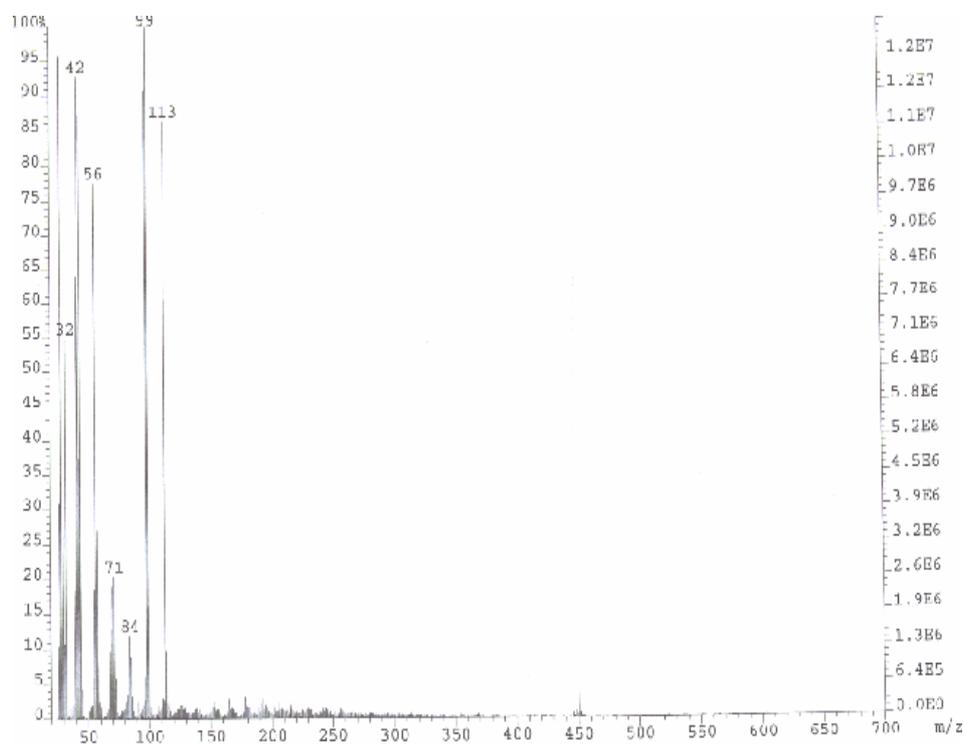


Figure 4.25 GC–MS for *Tshikondeni coal* extracted with NMP

4.4.2 GC-MS Springlake coal extracted with NMP

Figure 4.26 shows the GC-MS trace of Springlake coal extracted with NMP.

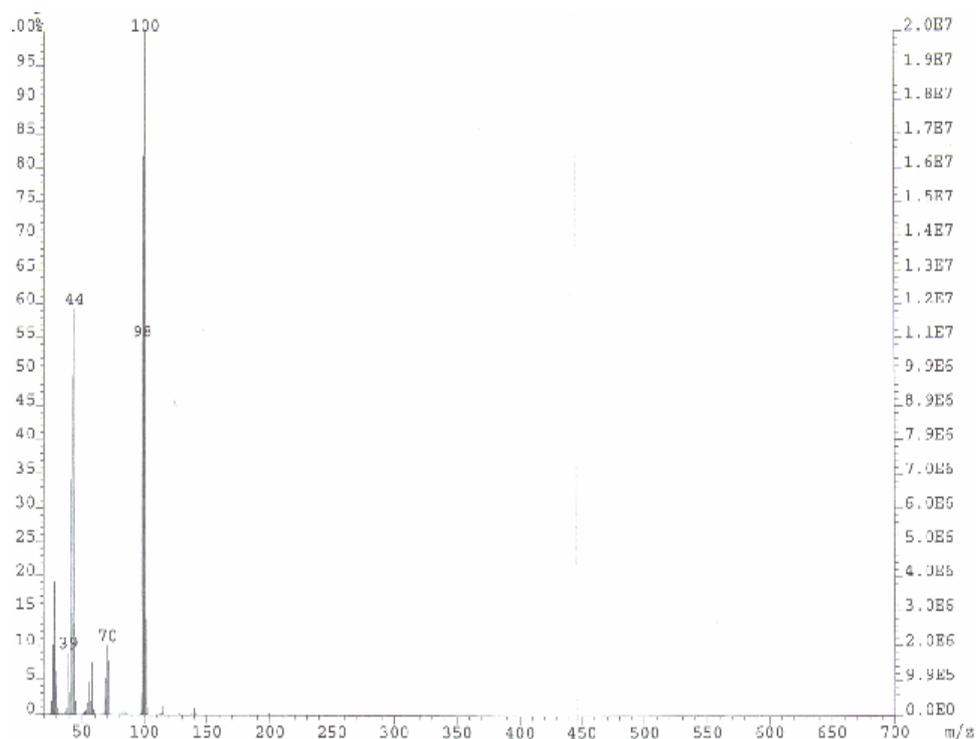


Figure 4.26 GC-MS for Springlake coal extracted with NMP

The GC-MS spectra above show the presence of mainly aliphatic/straight-chain compounds in coal solutions obtained from dissolution in NMP.

4.4 Conclusions

- An alkali is required for the solubilisation of coal to occur in polar organic solvents. This also gives an overall high extraction percentage of ~ 92%.
- In pure DMF, the NaOH does not go into solution but on the addition of coal, the NaOH goes into solution.
- The characteristic smell of the Refcoal solution confirms the presence of dimethylamine, although the titration shows otherwise.

- The texture of the alkali used in the extraction affects the rate and degree of extraction. Finely ground alkali gives a faster dissolution rate, as well as a high extraction percentage.
- There is no hydrolysis of solvent during the extraction of coal.
- The concentration of the alkali used in the extraction process affects the degree to which coal can be extracted.
- The use of a strong alkali increases the rate at which coal can be dissolved in the solvent.
- Temperature does not affect the degree of extraction, as shown by the closeness of the extractions done. Also, external factors, such as oxidation and weathering of coal, have little effect on the extent of extraction.
- Coal characterization techniques provide information about the composition of coal extracts. The coals used in this process consisted of aliphatic and aromatic compounds.

Chapter 5 Appendices

5.1 Appendix 1

Table A1.1 Proximate (air dry basis) analyses of coal used

Parameter	Coal 1 wt %	Coal 2 wt %
Moisture (air dry basis)	0.9	0.6
Ash (dry basis)	9.4	9.0
Volatile matter (dry basis)	23.3	23.3
Fixed carbon (calculation) (dry basis)	66.4	67.4
Total sulphur (dry basis)	0.81	0.85
Calorific value (MJ/kg) (air dry)		33.50
Free swelling index		9.0
Roga index		86

Table A1.2 Ultimate analysis (dry ash free basis) of coals used

Element	Coal 1	Coal 2
Carbon	84.1%	81.5%
Hydrogen	4.50%	4.38%
Nitrogen	1.95%	1.86%
Oxygen	0.46%	1.15%

Table A1.3 Petrographic characteristics of coals used

Rank(degree of maturity)	Meta-bituminous
Seam classification	Medium-rank B
Mean random reflectance	1.33
Vitrinite class distribution	V10-V16
Standard deviation	0.177
Abnormalities	Extended vitrinite class distribution
Vitrinite content %	93
Liptinite content %	<1
Total reactive macerals %	94
Total inertinite %	6
More highly reflecting material %	1
Cracks and fissures	Occasionally observed
Signs of advanced weathering/thermal effects	Very occasionally seen

Table A1.4 Ash analysis

	Coal 1	Coal 2
SiO ₂	54.4%	55.24%
Al ₂ O ₃	25.5%	24.8%
Fe ₂ O ₃	6.00%	4.47%
P ₂ O ₅	0.82%	0.52%
TiO ₂	2.24%	2.16%
CaO	5.05%	3.49%
MgO	2.52%	1.82%
K ₂ O	1.46%	1.69%
Na ₂ O	0.36%	0.84%
SO ₃	4.45%	2.31%

Table A1.5 NMR shift classifications [71]

Hydrogen Type	Symbol	Chemical shift (ppm)
Aromatic	H _A	6–9
Phenolic	H _{OH}	5–9
Ring-joining methylene	H _F	3.4–5.0
CH ₃ , CH ₂ and CH (α to aromatic ring)	H _{α}	1.9–3.4
CH ₃ , CH ₂ and CH (β or further from aromatic and paraffinic CH ₂ and CH)	H _{β}	1.0–1.9
CH ₃ (γ further from aromatic ring and paraffinic CH ₃)	H _{γ}	0.5–1.0

5.2 Appendix 2

Table A2.1 Progress of extraction with DMF

	Time (minutes)	0	5	10	20	30	45	60	120	180	240	300	360
Run 1	Mass of Refcoal	0.1116	0.1164	0.114	0.1174	0.1224	0.1028	0.105	0.1068	0.166	0.1016	0.1035	0.1057
	Absorbance @ 600 nm	0.006	0.001	0.001	0.02	0.049	0.084	0.176	0.588	0.895	1.011	1.078	1.111
	Corrected absorbance	0.0054	0.0009	0.0009	0.0170	0.0400	0.0817	0.1676	0.5506	0.5392	0.9951	1.0415	1.0511
Run 2	Mass of Refcoal	0.1203	0.1032	0.1154	0.1179	0.1059	0.1064	0.1039	0.1276	0.103	0.1019	0.1128	0.1128
	Absorbance @ 600 nm	0.004	0.005	0.011	0.016	0.012	0.022	0.059	0.488	0.733	0.978	1.114	1.151
	Corrected absorbance	0.0033	0.0048	0.0095	0.0136	0.0113	0.0207	0.0568	0.3824	0.7117	0.9598	0.9876	1.0204
Run 3	Mass of Refcoal	0.1018	0.1143	0.1024	0.1168	0.1146	0.103	0.1074	0.1152	0.1157	0.1036	0.116	0.1081
	Absorbance @ 600 nm	0.004	0.009	0.011	0.012	0.038	0.082	0.259	0.793	1.026	0.966	1.202	1.223
	Corrected absorbance	0.0039	0.0079	0.0107	0.0103	0.0332	0.0796	0.2412	0.6884	0.8868	0.9324	1.0362	1.1314

Table A2.2 Progress of extraction with DMAA

	Time (minutes)	0	5	10	20	30	45	60	120	180	240	300	360
Run 1	Mass of Refcoal	0.116	0.1187	0.1216	0.1036	0.121	0.1036	0.1276	0.1025	0.1102	0.1086	0.1028	0.112
	Absorbance @ 600 nm	0.004	0.014	0.025	0.063	0.099	0.206	0.432	0.715	1.015	1.135	1.149	1.282
	Corrected absorbance	0.0034	0.0118	0.0206	0.0608	0.0818	0.1988	0.3386	0.6976	0.9211	1.0451	1.1177	1.1446
	Mass of Refcoal	0.105	0.1052	0.1206	0.1179	0.1269	0.1132	0.1163	0.13	0.1196	0.1176	0.1185	0.1234
Run 2	Absorbance @ 600 nm	0.013	0.022	0.0285	0.031	0.056	0.131	0.244	0.887	1.06	1.267	1.351	1.46
	Corrected absorbance	0.0124	0.0209	0.0236	0.0263	0.0441	0.1157	0.2098	0.6823	0.8863	1.0774	1.1401	1.1831
	Mass of Refcoal	0.1242	0.1112	0.107	0.1109	0.1153	0.1102	0.1325	0.1069	0.1181	0.1157	0.1063	0.1059
Run 3	Absorbance @ 600 nm	0.015	0.032	0.073	0.375	0.948	0.992	1.186	1.025	1.131	1.143	1.07	1.13
	Corrected absorbance	0.0121	0.0288	0.0682	0.3381	0.8222	0.9002	0.8951	0.9588	0.9577	0.9879	1.0066	1.0670

Table A2.3 Small-scale extraction of Tshikondeni coal

Exp 1	Sample	Mass of Sinter Glass	Dry Mass	Mass of Residue	% Dissolution
	1	67.573	68.9594	1.3864	80.1943
	2	69.2656	70.6557	1.3901	80.1414
	3	68.652	70.155	1.503	78.5286
	4	69.5824	71.0596	1.4772	78.8971
	5	67.2718	69.3099	2.0381	70.8843
	6	68.8148	70.3586	1.5438	77.9457
	7	69.4976	70.9702	1.4726	78.9629
	8	67.491	69.474	1.983	71.6714
	9	70.3068	72.1654	1.8586	73.4486
	10	67.2254	68.578	1.3526	80.6771
Average % dissolutions			76.74159		
Exp 2	Sample	Mass of Sinter Glass	Dry Mass	Mass of Residue	% Dissolution
	1	67.477	69.0876	1.6106	76.9914
	2	67.1604	68.6374	1.477	78.900
	3	69.5212	71.469	1.9478	72.1743
	4	67.904	69.476	1.572	77.5429
	5	68.5	70.281	1.781	74.5571
	6	68.4368	70.3086	1.8718	73.2600
	7	69.981	71.7022	1.7212	75.4114
	8	70.3104	72.0056	1.6952	75.7829

	Average % dissolutions	76.79778
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Table A2.4 Small-scale extraction of Tshikondeni coal with Na₂S

	%Na ₂ S	Sample	Mass of Sinter Glass	Dry Mass	Mass of Residue	% Dissolution	Absorbance
Exp 1	0	1	67.7632	69.4974	1.7342	75.22571	0.9254
	25	2	67.1256	69.006	1.8804	73.13714	0.8465
	50	3	69.7262	71.6046	1.8784	73.16571	0.8533
	75	4	70.271	72.2498	1.9788	71.73143	0.8739
	100	5	67.2132	69.193	1.9798	71.71714	0.8032
Exp 2	0	6	67.8068	69.4804	1.6736	76.09143	0.9957
	25	7	69.5322	71.1904	1.6582	76.31143	0.8488
	50	8	67.4874	69.1288	1.6414	76.55143	0.8725
	75						0.9504
	100	10	68.77	70.7708	2.0008	71.41714	0.863
Exp 3	25	1	67.4494	69.1368	1.6874	75.89429	1.0326
	50	3	67.739	69.4656	1.7266	75.33429	0.9378
	75	5	69.66	71.5168	1.8568	73.47429	0.7911
	100	6	69.5052	71.468	1.9628	71.96	0.8614
Exp 4	25	2	67.739	69.945	2.206	68.48571	1.0238
	50	4	67.0438	68.8506	1.8068	74.18857	0.6269
	75	6	69.9514	71.9012	1.9498	72.14571	0.8756
	100	8	70.2758	72.5578	2.2820	67.4	0.8627

Table A2.5 Small-scale extraction of Moatize coal with Na₂S

	%Na ₂ S	Sample	Mass of Sinter Glass	Dry Mass	Mass of Residue	% Dissolution	Absorbance
Exp 1	0	1	68.4286	69.878	1.4494	79.29429	1.4882
	25	3	62.8314	64.2706	1.4392	79.44	1.2922
	50	5	67.8024	69.2148	1.4124	79.82286	1.207
	75	7	67.2058	68.91	1.7042	75.65429	1.2696
	100	9	70.2524	71.6872	1.4348	79.50286	1.2699
Exp 2	0	2					1.3513
	25	4	69.509	70.953	1.444	79.37143	1.2734
	50	6	68.7636	70.1104	1.3468	80.76	1.3121
	75	8	67.4874	68.9464	1.459	79.15714	1.3029
	100	10	67.76	69.5002	1.7402	75.14	1.1763

Table A2.6 Progress of extraction with C₆H₅NO₂

	Time (minutes)	0	5	10	20	30	45	60	120	180	240	300	360
Run 1(0.1%)	Mass of Refcoal	0.1203	0.1032	0.1154	0.1179	0.1059	0.1064	0.1039	0.1276	0.103	0.1029	0.1128	0.1127
	Absorbance @ 600 nm	0.004	0.005	0.011	0.016	0.012	0.022	0.059	0.488	0.733	0.978	1.114	1.203
	Corrected absorbance	0.0033	0.0048	0.0095	0.0136	0.0113	0.0207	0.0568	0.3824	0.7117	0.9504	0.9876	1.0674
	Run 2 (1%)	Mass of Refcoal	0.1107	0.1018	0.1042	0.1177	0.1156	0.1006	0.1208	0.1259	0.1217	0.1223	0.1035

	Absorbance @ 600 nm	0.001	0.003	0.004	0.009	0.024	0.026	0.052	0.111	0.215	0.455	0.656	0.972
	Corrected absorbance	0.0009	0.0029	0.0038	0.0076	0.0208	0.0258	0.0430	0.0882	0.1767	0.3720	0.6338	0.8141
Run 3 (0%)	Mass of Refcoal	0.1116	0.1164	0.114	0.1174	0.1224	0.1028	0.105	0.1068	0.166	0.1016	0.1035	0.1057
	Absorbance @ 600 nm	0.006	0.001	0.001	0.02	0.049	0.084	0.176	0.588	0.895	1.011	1.078	1.111
	Corrected absorbance	0.0054	0.0009	0.0009	0.0170	0.0400	0.0817	0.1676	0.5506	0.5392	0.9951	1.0415	1.0511

Table A2.7 Extraction with varying percentages of NaOH

	Time (minutes)	0	5	10	20	30	45	60	120	180	240	300	360
Run 1	Mass of Refcoal	0.1211	0.1064	0.1024	0.1154	0.1117	0.122	0.1064	0.154	0.1065	0.1146	0.1089	0.1035
	Absorbance @ 600 nm	0.014	0.018	0.027	0.026	0.035	0.055	0.067	0.129	0.517	0.941	1.115	1.163
	Corrected absorbance	0.0116	0.0169	0.0264	0.0225	0.0313	0.0451	0.0630	0.0838	0.4854	0.8211	1.0239	1.1237
	Mass of Refcoal	0.1375	0.1096	0.1117	0.1118	0.114	0.1158	0.1049	0.1065	0.1217	0.1144	0.1053	0.112
Run 2	Absorbance @ 600 nm	0.008	0.014	0.016	0.031	0.052	0.084	0.149	0.454	0.836	0.976	1.093	1.129
	Corrected absorbance	0.0058	0.0128	0.0143	0.0277	0.0456	0.0725	0.1420	0.4263	0.6869	0.8531	1.0380	1.0080
	Mass of Refcoal	0.1037	0.1312	0.1136	0.1092	0.1086	0.1033	0.1152	0.1146	0.1256	0.1058	0.1033	0.1121

Absorbance @600 nm	0.042	0.043	0.054	0.043	0.081	0.079	0.087	0.191	0.627	0.628	0.9631	1.0257
Corrected absorbance	0.0405	0.0328	0.0475	0.0394	0.0746	0.0765	0.0755	0.1667	0.4992	0.5936	0.9323	0.9150

Table A2.8 Determination of Na in Refcoal solution

Exp 1	Time (minutes)	0	60	120	180	240	300	360	420
	Mass of Refcoal	0.1088	0.1187	0.1005	0.1136	0.1006	0.125	0.1229	0.1245
	Absorbance @ 600nm	0.014	0.175	0.54	0.867	0.936	1.282	1.349	1.334
	Corrected absorbance	0.0129	0.1474	0.5373	0.7632	0.9304	1.0256	1.0976	1.0715
	Mass of sample	1.031	1.0408	1.1857	1.0419	1.054	1.096	1.1833	1.0728
	Sodium content (µg/ml)	0	12	16	22	26	28	31	28
	Corrected to 1.0 g	0	11.5296	13.4941	21.1153	24.6679	25.5474	26.1979	26.0999
Exp 2	Time (minutes)	0	60	120	180	240	300	360	420
	Mass of Refcoal	0.1118	0.1017	0.1076	0.1033	0.107	0.1106	0.1131	0.1293
	Absorbance @ 600nm	0.003	0.153	0.838	0.923	0.961	1.058	1.102	1.243
	Corrected Absorbance	0.0027	0.1504	0.7788	0.8935	0.8981	0.9566	0.9744	0.9613
	Mass of sample	1.0125	0.8684	1.0261	1.0304	1.0676	1.033	1.0246	1.0257
	Sodium content (µg/ml)	0	14	22	26	27	27	26	26
	Corrected to 1.0 g	0	16.1216	21.44041	25.23292	25.29037	26.13746	25.37576	25.34854

Table A2.9 Variation of Na with absorbance

Time (minutes)	0	60	120	180	240	300	360	420
Sodium content (µg/ml)	0	16.1216	21.4404	25.2329	25.2904	26.1375	25.3758	25.3485
Absorbance	0.0027	0.1504	0.7788	0.8935	0.8981	0.9566	0.9744	0.9613

Table A2.10 Extraction with lithium ethoxide

Run 1	Time (minutes)	0	20	40	60	90	120	180	240	300
	Mass of Refcoal	0.1037	0.1121	0.1181	0.1105	0.1025	0.1244	0.1142	0.101	0.1125
	Absorbance @ 600 nm	0.026	0.622	0.79	0.784	0.735	0.981	0.86	0.793	0.864
	Corrected absorbance	0.0251	0.5549	0.6689	0.7095	0.7171	0.7886	0.7531	0.7851	0.7680
Run 2	Mass of Refcoal	0.1025	0.1255	0.1139	0.1134	0.1065	0.1123	0.1044	0.1264	0.1121
	Absorbance @ 600 nm	0.169	0.909	0.937	0.979	0.913	0.988	0.926	1.1923	0.926
	Corrected absorbance	0.1649	0.7243	0.8227	0.8633	0.8573	0.8798	0.8870	0.9433	0.8260

Table A2.11 Titrations

NaOH	DMF	Water	Eqv. Pot.	NaOH	DMF + Water	Msample	Vol. HCl	mmol	% NaOH
	100	100	-70.7	2	200	1.1025	2.5178	0.252787	91.71415
	100	100	-8.1	2	200	1.107	2.4984	0.250839	91.00748

	100	100	-18.2	2	200	1.101	2.3954	0.240498	87.25557
	100	100	-21.2	2	200	1.1115	2.527	0.253711	92.04927
	100	100	-14	2	200	1.1015	2.4701	0.247998	89.97661
				NaC₂H₃O₂					% NaC₂H₃O₂
NaC₂H₃O₂	100	100	200.8	2	200	1.1164	1.3941	0.139968	50.78191
	100	100	199.9	2	200	1.1054	1.3706	0.137608	49.92589
	100	100	194.3	2	200	1.1183	1.3331	0.133843	48.55991
	100	100	191.8	2	200	1.1133	1.3491	0.13545	49.14273
	100	100	190	2	200	1.1253	1.3363	0.134165	48.67647
				DMA					% DMA
DMA	100	100	56.5	2	200	1.1311	1.2676	0.127267	46.17398
	100	100	39.9	2	200	1.1127	1.1937	0.119847	43.48208
	100	100	41.9	2	200	1.1039	1.2283	0.123321	44.74243
	100	100	37	2	200	1.119	1.1627	0.116735	42.35286

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