DESULPHURISATION OF SOUTH AFRICAN COAL USING LOW POWER MICROWAVE ENERGY

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Declaration

I declare that this dissertation is my own unaided work. It is submitted in completion of the requirements for the degree of Master of Science in Engineering at the University of the Witwatersrand, Johannesburg. It has not been previously submitted for any other degree or examination at any other University.

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Waseela Mohamed

_____ Day of _____ 2008

To my mother, father, brother, sister and loving husband.

Abstract

The effect of microwave irradiation on South African bituminous coals has been studied using various alkali solutions and particle sizes. Optimization of the treatment process was carried out on both low and high sulphur coals at varying power levels and retention times. Changes in structure and combustion characteristics after desulphurisation using a strong caustic solution were investigated.

The optimum sulphur removal time and microwave power for the high sulphur (±3.3 %) coal were difficult to determine. This is possibly due to the uneven distribution of pyrite within the coal structure and thus the samples may be biased. Coal particles of sizes 212 µm and 74 µm showed optimum sulphur removal of 40 % after an exposure time of 10 min at a power of 650 W using a sodium hydroxide solution. Decreased sulphur contents were noted with a decrease in particle size. Structural characteristics were largely unaltered as determined by XRD and Raman analysis. A slight decrease in calorific value and volatile matter was noted.

The low sulphur coal yielded a 40 % sulphur decrease depicting independence of the mode of occurrence of pyrite in the coal. Structural characteristics of the coal were apparently unaffected whilst combustion characteristics decreased to some extent.

Treatment with strong potassium hydroxide solutions as well as mixtures of sodium chloride and sodium hydroxide yielded improved desulphurisation values in comparison with that of the sodium hydroxide solution alone (40 % to 52 % sulphur decrease obtained). Conventional leaching with sodium hydroxide was found to show enhanced sulphur removal results than that of coals treated using microwave energy. Further studies are needed on the desulphurization of South African coals before a firm conclusion can be drawn.

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Contents

List of Figures

List of Tables

Chapter one: Introduction

1.1 Background

South Africa has one of the world's highest dependencies on coal as a primary source of energy, with approximately 90 % of the energy derived from coal (Horsfall, 1992). In addition to this, coal is also a major energy and reductant source for the world's metallurgical industries in which South Africa is a major player. Pollution becomes a concern with the large usage of coal in these industries. The sulphur dioxide gas released during combustion is a major source of acid rain in South Africa which poses a health issue. In addition to it being an environmental hazard, sulphur reduces the quality of coking coal and is the cause of corrosion in industrial boilers. Increasingly stringent environmental regulations force us to look at alternative or additional methods to flue gas desulphurisation (post combustion treatment). South African (2007) legislation allows an annual maximum sulphur dioxide discharge of 19 parts per billion (ppb) into the atmosphere whilst the current discharge is 30 ppb (Air Quality Act, 2004). With depleting coal reserves, it is necessary to also investigate cleaning of coal discards for utilisation in industry. Whilst at this stage, microwave treatment for coal cleaning may not be considered, in the near future it could be a feasible beneficiation process.

Of the methods employed to desulphurise coal, treatment before combustion is the most viable due to it being cost effective as the sulphur is removed before gaining entry into the process (Horsfall, 1992). This would enable the use of coal that would normally be discarded (often termed 'discard coal') thus minimizing wastage of a valuable resource. Currently most sulphur removing techniques are post combustion clean up where flue gas desulphurisation is used to treat the gas stream before purging it into the atmosphere. Whilst this method removes virtually all the sulphur dioxide

gas, it is very costly. In combustion clean up using the Limestone Injection method only allows for reductions in sulphur dioxide by 50 – 80 %.

Microwave processing of minerals has been identified as one of the emerging technologies, for ore liberation and beneficiation of minerals, by both Haque (1999) and Kingman and Rowson (1998). The primary advantage of microwave treatment is the energy and time reduction, lowering costs in the minerals processing industry (Bykov *et al.*, 2000). In terms of desulphurisation of coal using microwave energy, the selective heating property of the minerals can be exploited in order to free minerals of concern from the coal matrix.

In this dissertation, microwave energy utilization with an alkali solution for the desulphurisation of South African coal was a primary focus. A domestic microwave oven of maximum power 900 W was used to determine the optimum desulphurisation point of coal treated with an alkali. Comparison for sulphur removal was made with conventional stovetop leaching. The principle conclusion drawn was that desulphurisation on South African coal using microwave energy and a strong alkali solution is possible with a large time saving factor in comparison to conventional techniques. Further experimental investigations are required in order to increase sulphur removal yield as well as to understand the sulphur removal process using an alkali and microwave irradiation.

Based on the above findings, it was possible to conduct further experiments to investigate effects of particle size, solid to liquid ratios as well as different mixtures of alkali in order to improve desulphurisation. A mixture of sodium chloride and sodium hydroxide yielded good results on a laboratory scale, but requires further investigation in order to upgrade such a treatment in an industrial process.

The present dissertation contains five chapters.

Chapter one is an introductory chapter outlining the problem statement, aim of the project and a brief overview of the methodology.

Chapter two covers the literature survey giving a brief analysis of South African coal as well as past and current desulphurisation techniques. An overview and advantages of microwave energy in the minerals processing industry are provided, as well as desulphurisation treatment using microwaves described by various authors.

The methodology and experimental techniques carried out during this investigation are covered in chapter three. Various analytical techniques are discussed pre and post microwave treatment as well as describing the microwave treatment process in detail. Experimental methods based on the optimum findings are also considered.

Chapter four presents the experimental findings and discussion surrounding them. Comparison to the optimum desulphurisation points using conventional treatment is carried out. Manipulation of variables, particle size, alkali concentration, slurry ratio and alkali mixtures, are investigated to improve desulphurisation rates.

The dissertation ends with chapter five where the conclusions and recommendations are laid out.

1.2 Problem Statement

With increasingly stringent air pollution control laws and the need to utilize coal discards, an efficient process for the desulphurisation of coal needs to be provided, whilst at the same time preserving the heating value of the coal. South African coals have been found to be relatively difficult to

beneficiate (Mehliss, 1987). While the pyritic sulphur is removed with relative ease, the organic sulphur is typically more difficult to remove as it forms part of the coal matrix.

1.3 Research Questions

Mechanisms involving chemical dissolution of pyrite and organic sulphur in caustic solution using microwave energy, followed by magnetic separation were investigated by Rowson and Rice (1989) on UK coals as well as by Hayashi et *al*. (1990) on Japanese coal. Could this method be used to treat South African coal? If yes, how would the coal behave in comparison to treatment carried out by other authors and conventional methods? Would the microwave treatment affect coal quality and combustion characteristics? Answering these key questions with experimental evidence would demonstrate an alternate desulphurisation technique that may be industrially feasible.

1.4 Hypothesis

It is proposed that desulphurisation of South African coals using low power microwave energy (< 1 kW) in an alkali solution is feasible.

1.5 Specific Objectives

The objectives of the project are to:

- Determine optimum desulphurisation power and time using microwave energy;
- Gauge change in desulphurisation rates when varying
    - Alkali concentration
    - Solid to liquid ratio
    - Alkali used and mixtures of alkalis;

- Comparison of microwave to conventional sulphur leaching techniques;
- Comparison of high and low sulphur coal behaviour to microwave treatment and sulphur removal;

1.6 Methodology and Rationale

The methodology followed in achieving the aims and objectives of the project is based on work carried out by Rowson and Rice (1989). Microwave treatment on a high and low sulphur South African coal from the Witbank/Highveld region is considered for three different size fractions. Experiments were carried out in a multimode microwave oven operating at 2.45 GHz and maximum power of 900 W. Comparison to conventional stovetop treatment was undertaken for comparative purposes. Petrographic analysis was undertaken to determine rank and coal type. Proximate, Raman and XRD analysis had been carried out before and after treatment to determine bonding, structural and chemical changes. Calorific value and sulphur analysis were also carried out before and after treatment.

In addition to the above, the effect of the solid to liquid ratio, alkali concentration, different alkali and mixtures of these were experimented on based on the optimum desulphurisation points.

Chapter two: Literature Survey

2.1 Introduction

This chapter provides the literature survey conducted on South African coal quality and the application of microwave energy in the minerals processing sector. A basic introduction to South African coals together with mineral and particularly sulphur matter in coal is discussed. A brief overview of the different sulphur removal techniques follows. The survey goes on to give a brief overview of microwave treatment of minerals ending with a look at sulphur treatment using microwave energy and the advantages thereof.

2.2 South African Coals

South African coals and those from other Gondwana locations (including India, Australia and South America) have been found to be characteristically rich in minerals, relatively difficult to beneficiate and highly variable in rank and organic matter composition (Falcon and Ham, 1988). These characteristics can be attributed to climatic conditions and vegetation existing at the time of the coalification process. Compared to European coals, South African coals are generally less mature as a result of the time, temperature and pressures the material has been exposed to, and generally range from sub-bituminous to mid bituminous coals with the exception of locally heat affected regions according to Falcon and Ham (1988).

The South Africa Year Book reports that in 2004, 242.82 Mt of coal were produced in South Africa. Of this, 178.37 Mt were used locally while 68.94 Mt (±28 %) was exported. Approximately 51 % of South African mining is done underground while the rest is produced by open cast methods. The majority of the coal reserves are low grade with a small percentage

classified as top grade coking coal and anthracite. 75 % of South Africa's coals were found to have ash content higher than 21.5 % (Falcon, 1977). Within South Africa itself, coals vary in quality as a result of the varied origins, water levels, climate and depths of burial.

The degree of alteration is referred to as the rank of the coal, the lowest rank showing little alteration from peat while the highest rank verges on graphite (England *et al.*, 2002). Rank thus refers to the degree of maturation in any stage of the coalification process and signifies the degree of chemical change occurring in the coal. The type of coal is determined by the vegetation making up the coal at the time of formation of the peat as well as the changes taking place during the metamorphosis of the coal. Falcon (1987) defines the type of coal at two different levels: macroscopically and microscopically. On a macroscopic level, the coal can be described as dull, bright or banded. The dull, non-banded coals are identified by an even, granular surface, while the banded coals have fine alternating layers of varying brightness. Microscopically, the type of coal is determined by the proportions of different identifiable organic components known as macerals. Macerals can further be divided into two groups: chemically reactive and chemically inert macerals.

The chemically reactive macerals are divided into vitrinite and liptinite. Falcon (1987) describes vitrinite as possessing moderate volatile matter and hydrogen content relative to liptinite and inertinite. Vitrinite is largely responsible for imparting coking properties to the coal as it devolatilises fairly rapidly, becomes plastic and swells on heating. Vitrinite is physically characterized by the brilliant black bands of coal in hard specimens under a microscope. In white reflected light it appears medium dark to light grey with an occasional botanical structure (Falcon, 1978). The rank of the coal is measured by the reflectance of the polished vitrinite maceral. The reflectivity and carbon content increase with coalification while the volatile matter decreases.

Liptinite contains a high volatile and hydrogen content relative to other macerals, producing heavy tars, bitumens and hydrocarbon products. England *et al.* (2002) describes liptinite as the maceral containing the remains of plants and their seeds that are most resistant to biochemical action. These would include spore coats, leaf cuticles, waxes and resins. While liptinite itself is non-coking, it assists the coking properties of vitrinite. Falcon (1978) describes liptinite as having low reflectivity on a microscopic scale. As rank increases, liptinite increases in reflectance until it is no longer recognisable from vitrinite.

Inertinite has a lower volatile and hydrogen content in comparison to vitrinite and liptinite, and is richer in oxygen and carbon. It is generally inert in coking coals and if present in high concentrations, nullifies the coking properties of vitrinite. The inertinite macerals originate from similar plant remains to vitrinite, but oxidation occurred to a far greater extent during the biochemical stage of coalification as reported by Falcon (1978). Inertinite is the highest reflecting component in bituminous coals, and may be distinguished by a higher relief than other macerals on polished surfaces. A cell structure of wood is often observed and is referred to as fusinite which becomes harder with increasing reflectance (Falcon, 1978). Due to its dense, carbon rich structure, this component burns with an intense heat for longer periods of time and is more porous than vitrinite.

Microlithotypes are micro layers of coal made up of macerals in various proportions. South African coals are characterized by a wide range of microlithotypes, seen both vertically and laterally within a seam, and regionally. They are generally typified by much higher inertinite rich associations (Falcon and Falcon, 1983). The key microlithotypes are vitrite, inertite, and intermediates, clarite and durite. Falcon (1978) describes the vitrite and inertite as mono-maceral types, while clarite is composed of vitrinite and liptinite, and durite is a mixture of liptinite and inertinite,

which are bi-maceral types. A tri-maceral microlithotype exists which is an intermediate between the microlithotypes and is termed trimacerite. The chemical properties of microlithotypes are alike to those of the macerals of which they predominantly consist (Falcon and Snyman, 1986). The physical properties are related to those of the macerals as well as the combined effect of their associations.

Maceral associations in the coal are important in understanding the coal structure and changes brought about in the structure due to chemical treatment. Ideally, pyrite removal should occur with minimal structural and coal matrix changes in order to preserve the heating value of the coal.

2.3 Mineral matter in Coal

Mineral matter is the inert, solid material in coal and remains behind in a slightly altered form as ash after coal combustion. The mineral matter finds its way into the peat bed during the formation of the coal (syngenetic) and can be included during mining in terms of roof and floor inclusions. Table 2.1 summarises the minerals commonly occurring in coal.

Mineral matter can be divided into either inherent or extraneous mineral matter. England *et al.* (2002) defines inherent mineral matter as the matter intimately mixed with the coal. This consists of minerals present in the original vegetation, from which the coal was formed, as well as clays and materials carried into the swamp by water and wind. This mode of occurrence is unlikely to be removed by simple coal preparation techniques.

Mineral Group	Mineral	Idealised Formula
Clay	Kaolinite	$Al_2SiO_5(OH)_4$
	Muscovite Illite	$KAl_2(Si_3Al)O_{10}(OH)_2$ $K_{1-1.5}Al4[Si_{7-6}Al_{1-1.5}O_{20}](OH)_4$
	Smectite	$(Na,Ca{\cdot}nH_2O)(Al_{2\gamma}Mg_{\gamma})(OH)_2(Si_{2x}Al_x)O_{10}$
Oxides	Quartz	SiO_2
	Rutile Anatase	TiO_2
Carbonates	Calcite Aragonite	$CaCO_3$
	Dolomite	$CaMg(CO_3)_2$
	Ankerite	$Ca(FeMg)CO_3$
	Siderite	$FeCO_3$
	Rhodochrosite	$MnCO_3$
Feldspars	Orthoclase Microcline	$KAlSi_3O_8$
	Plagioclase	$Na[AlSi_3O_8]$-$Ca[Al_2Si_2O_8]$
Scapolite	Analcime	$NaAlSi_2O_6{\cdot}H_2O$
Sulphides	Pyrite Marcasite	FeS_2
Phosphates	Apatite	$Ca_5(PO_4)_3(F, Cl, OH)$
	Crandallite	$CaAl_3(PO_4)_2(OH)_5{\cdot}H_2O$
	Gorceixite	$BaAl_3(PO_4)_2(OH)_5{\cdot}H_2O$
	Goyazite	$SrAl_3(PO_4)_2(OH)_5{\cdot}H_2O$
Sulphates	Gypsum	$CaSO_4{\cdot}2H_2O$
	Alunite	$KAl_3(SO_4)_2(OH)_6$
	Jarosite	$KFe_3(SO_4)_2(OH)_6$

Table 2.1: Mineral Matter in Coal (Van Alphen, 2005)

Clays, quartz, carbonate and pyrite group minerals are examples of inherent mineral matter occurring in varying quantities in South African coals. The extraneous mineral matter can be more readily removed using coal preparation techniques as it typically occurs in large particles or cleats. Extraneous mineral matter occurs as partings and lenses in the coal seam, as well as shale, sandstones and intermediate rocks introduced during the mining of the coal bed. In addition to the above, pyrite, ankerite and calcite can exist as forms of extraneous mineral matter deposited in the coal seam after its formation. The following summarises the major mineral groups present in South African coals as described by Falcon and Snyman (1986) and as viewed petrographically:

Clay accounts for approximately 60 to 70 % of mineral intergrowths and occurs as minute grains, small lenses, microscopically visible bands, infillings in cell cavities and as veins. It has a variable appearance and can appear petrographically from almost white to orange-brown with an uneven granular texture to black with an even texture. Clays commonly occurring in South African coal are: kaolinite, illite/muscovite and montmorrillonite. The clays are a principal source of ash in washed coal and the association and distribution of clay in coal is important for beneficiation.

Quartz occurs in small quantities and is a coarse mineral blown or washed into coal swamps. The quartz is freed during breakage of the coal and can be easily removed by washing. Under reflected light and oil immersion, quartz appears glassy-black to clear. As the refractive index of the quartz is very close to that of the oil, it should first be viewed without the oil where it would appear a darker gray than coal. This would give an indication if quartz is present or not.

Carbonate minerals occur as nodules, usually of siderite, and as veins and cell fillings of calcite, ankerite and dolomite. Siderite typically occurrs as round, flattened or irregular concretions while calcite occurs epigenetically in veins. In reflected light, under oil immersion, carbonates are brownish grey while calcite exhibits a crystalline twinning.

Pyrites occur in relatively small quantities in South African coals but are important owing to the harmful effects on the environment as well as on industrial equipment. Pyrite can occur as inherent and extraneous forms and where abundant, petrifications and nodules may also be present. Pyrite is identified by the bright yellow colour observed in reflected light under oil immersion.

2.4 Sulphur in coal

Coal, when broken down into it's chemical constituents, consists of carbon, hydrogen, nitrogen, sulphur, oxygen and a variety of other trace elements. Sulphur, although occurring in small percentages (on average below 2 % in South African coals), is of great concern owing to the harmful effects it may have in boilers where sulphates cause corrosion, as well as reducing the quality of metallurgical coal and polluting the atmosphere. Mehliss (1987) reports that at 1 % sulphur the coal burnt in major industrialized countries have the potential of releasing 19.6 Mt of sulphur dioxide or 30.6 Mt of sulphuric acid annually into the atmosphere. This poses a serious environmental problem.

Raask (1985) discusses that, as sulphur is a vital element of plant life, it is only natural to find sulphur compounds existing in coal deposits and associated mineral strata. Coal deposits occurring in brackish marine areas are usually rich in ash, sulphur and nitrogen, while iron sulphides formed as a result of anaerobic bacteria. Raask (1985) further discusses the principal iron and sulphur bearing minerals of coal as pyrite and marcasite containing an approximate formula of FeS_2, while pyrrhotite (FeS_x), chalcopyrite ($CuFeS_2$), galena (PbS) and sphalerite (ZnS) have been identified in coal as sulphur containing compounds.

Sulphur occurs in coals mainly as pyritic, organic and sulphatic sulphurs. The pyritic sulphur is derived from pyrite and marcasite and is relatively

simple to remove. The organic sulphur forms part of the coal and is derived from the plant material during the formation of the coal. Pyrite can occur as microscopic crystals, intimately associated with the coal macerals, as thin layers on joints and bedding planes, as well as discrete masses occurring up to half a metre in diameter. Sulphatic sulphur is mainly derived from the sulphates of calcium and iron and occurs in small quantities in unweathered coals. Both the organic and sulphatic sulphurs are difficult, sometimes impossible, to remove (Mehliss, 1987).

2.5 Sulphur Removal from coal

Horsfall (1992) discusses the methods of sulphur removal from coal:

1. Post-combustion removal: Post-combustion clean up suggests the use of flue gas desulphurisation where virtually all the sulphur dioxide gas is removed as well as some of the nitrogen dioxide emissions. The disadvantage of the method is the high cost associated with it.
2. In combustion clean up: This uses the Limestone Injection Multiple Stage Burner method where limestone is injected into the combustion chamber and combined with the sulphur dioxide gas. Approximately 50 to 80 % of the sulphur is removed. The limestone addition is only feasible if the cost associated with delivery is minimal and plant capacity is small. Koper (2004) and Horsfall (1992) are of the opinion that the limestone injection method is technically feasible but economically unrealistic.
3. Pre-combustion coal treatment is the most attractive treatment option due it being cost effective. Koper (2004) discusses the various pre-combustion options available as:
    a. Biological treatment methods: the use of bacteria;
    b. Chemical treatment methods: temperature, catalysts, pressure and reactions;

c. Physical treatment methods: most widely used form of beneficiation.

Biological, chemical and physical treatments are explored further below.

2.5.1 Biological treatment

Coal depyritisation was found to be possible using bacteria as a metal sulphide-oxidising agent. Pyritic sulphur, when treated with a micro-organism, has been found to oxidize abiotically in aqueous, oxygenated solutions, resulting in the dissolution of the mineral. Clark *et al.* (1993) studied the kinetics of pyrite oxidation by *Metallosphaera Sedula* as well as *Acidianus Brierleyi* and *Thiobacillus ferro-oxidans*. The pyrite in the coal was found to oxidize more rapidly with an increase in temperature.

Sukla *et al*. (2001) experimented with microbial desulphurisation using a *Thiobacillus ferro-oxidan* culture. Optimization of the process occurred at a pH of 1.5, particle size -45 µm, pulp density at 2 % (w/v), a residence time of 30 days, while the temperature was kept at 35 °C and stirring at 140 rpm. Using the same micro-organism, Juszczak *et al*. (1995) optimised the desulphurisation process at a pH of between 2 to 3, particle size less than 0.06 mm, pulp density of 2.4 wt%, residence time of 7 days, temperature at 35 °C at an initial concentration of 15g Fe^{2+} ions/dm^3.

Although the above methods were proven to be successful in removing finely disseminated pyrite from coal, which is difficult to achieve using physical methods, the depyritisation process was found to be too slow, as well as costly, as further dewatering and drying methods need to be employed before such a coal can be used in industry.

2.5.2 Chemical Treatment

Various processes employing catalysts, heat, pressure and chemicals have been developed and implemented both on a bench and pilot scale.

Koper (2004) discusses methods developed on a pilot scale production by Pittsburgh Energy Technology Centre (PETC), Ames, TRW and ARCO which use selective oxidation of sulphur compounds in a pressurised, hot environment with the aid of promoters. Whilst these have been found to have good sulphur removal results, the residence time ranges from 10 min up to several hours with a particle size of less than 6 mm. Energy balances under these conditions show that the energy input required for the combined processes of preparation and product upgrading, is close to or exceeding the energy content provided to the consumer.

Mukherjee and Borthakur (2001) investigated washing pulverized coal (-212 μm) using aqueous sodium hydroxide followed by a hydrochloric acid treatment on a bench scale. Using a 16 % sodium hydroxide solution and a 10 % hydrochloric acid, all the inorganic sulphur and 10 % of the organic sulphur was removed after 8 hrs of stirring. Furthermore, it was found that the aqueous sodium hydroxide alone had a very small effect on the reduction of the ash content. Demineralization of the coal was found to decrease with increase in alkali concentration, whereas desulphurisation was found to increase with an increase in alkali concentration.

Araya *et al.* (1981) studied the treatment of sub bituminous coals using sodium hydroxide solutions while varying time, temperature, alkali concentration, and particle size. The pulverized coals were treated for up to 16 hrs in sodium hydroxide solutions prepared using distilled water. Ash and sulphur content was reduced using hot (80 °C) caustic solutions of concentration 100 g/dm^3. Elimination of ash and sulphur was found to increase with hydrolysis time, temperature, alkali concentration, and a

decrease in particle size. This method does not remove the organic and sulphatic sulphurs.

2.5.3 Physical Treatment

Physical coal treatment has been the most widely used pre-combustion coal cleaning method in the industry. Whilst various technologies are available to beneficiate coal, selection of these technologies is dependent on the type of coal, efficiency of method, and costs associated with the methods employed. New and improved technology is made available on a regular basis with the underlying principles of beneficiation largely modelled on basic principles of coal washing. Historically, the methods employed were jigging, flotation, and dense medium separation. Outlined below are some beneficiation methods, also discussed by England *et al*. (2002).

2.5.3.1 Simple Coal Washers

Basic Coal washers can be divided into two simple types: the barrel washer and an upward current washer. The barrel washer works well on coal that is free of middlings or when deshaling is to be carried out at a density where little or no near density material is present. This type of washer introduces feed together with water into the shale discharge end so as to carry the shale for a few meters in relatively clean water. Clean coal flows out at the end of the discharge together with the water whilst the shale is discarded at the feed end. This has been proven to be a cheap way of re-treating discard dumps.

The basic principle of the upward current washer is to allow particles of lower relative density to lift with a rising current of water, more readily than those of a higher relative density. In this way, the coal rises with the current while the discard sinks. Table 2.2 highlights the different coal type and pyrite relative densities. Pyrite with an approximate relative

density of 5 will sink whilst the light coal particles will float. The difficulty with coal washing arises when the pyrite is bound within the coal substance. In South Africa, this method has been proven to be unsuccessful.

	Relative Density
Bituminous coal	1.32
Anthracite	1.47
Sub Bituminous	1.30
Lignite	1.29
Pyrite	4.9 ~ 5.2

Table 2.2: Relative density of different coals and pyrite (Perry, 7th edition)

2.5.3.2 Coal Jigging

The basic principle of jigging is based on the principle of a fluidised bed. Mitchell (1950) describes jigging as the stratification of a mass of solid particles in upward and downward pulsating movements. The lighter fractions then migrate to the top of the bed whilst the dense fractions sink to the bottom. A principle advantage of jigging is the low operational cost but due to its low efficiency, in comparison to alternative, available separation equipment, jigging is not commonly used in industry. It would only be economically viable when dealing with material that has little or no near gravity material.

The application of jigs in South Africa has only recently started, with extensive test work showing this method to be viable.

2.5.3.3 Dense Medium Separators

Osborne (1988) reports that dense medium separation is a highly accurate method of coal separation yielding greater efficiencies than other methods. Dense medium separation is based on the principle of float and sink analysis and operates efficiently between densities of 1.30 and 1.80. Float and sink analysis involves separating a coal sample into

two or more relative density fractions by means of a liquid of relative density between that of the pure coal and the purities associated with it. The type of liquid employed should be cost effective, immiscible in water, stable, non-toxic, low in viscosity, as well as chemically inert. The current liquid mediums employed in coal preparation are:

1. organic liquids: these are commercially unviable due to the cost associated with them
2. solutions of salts in water
3. aerated solids: industrially not viable for treating mist coals
4. suspensions: a mixture of a solid and liquid. The solid particles are ground so finely that they do not settle in the liquid but rather remain uniformly distributed throughout e.g. magnetite

Dense Medium Separators employs a centrifugal force to create rotational fluid motion, which in turn causes the relative movement of the materials suspended in the fluid, allowing separation of the materials. Separations employing these methods are usually rapid for particles with appreciable differences in relative densities, whilst for small particles with small relative density differences, the separation is slow. Thus efficient separation does not occur. It is for this reason that dense separation mediums are not employed for coal particles smaller than 6mm.

2.5.3.4 Fine Coal Cleaning Methods

Fine coal is defined as less than 0.5 mm in size. Approximately 15 % of the coal mined in South Africa is fine coal. The major methods of treating fine coal are spiral beneficiation, froth flotation, oil agglomeration and to some extent, dense medium beneficiation.

Spiral beneficiation is based on gravity separation. The heavy material stays on the inside while the lighter material moves to the outside of the

spiral as material flows down. Separation of the product is achieved by adjustable blades positioned to remove the product.

Froth flotation: fractions less than 0.15 mm are available for froth flotation as a result of the introduction of spirals. This method depends on a principle where some minerals attach themselves to air bubbles while others attach themselves to water. Coal is hydrophobic while the mineral is hydrophilic. This method proves to be ineffective in pyrite removal due to its hydrophobic nature.

Oil agglomeration is a process whereby the fine coal slurry is mixed with fuel oil and stirred in an agglomerating tank. The coal particles form balls or spheres whereby water is excluded. In this manner the fine coal is beneficiated while at the same time dewatering occurs. This method is currently dormant due to its uneconomical nature with regard to the oil price.

Dense medium beneficiation: for fine coal beneficiation, cyclones with smaller diameters operating at high pressure have been found to be effective

2.6 Microwave Processing

Microwave processing is an emerging technique used in minerals processing for ore and coal beneficiation. The following section provides a brief introduction to the microwave unit and its use in minerals processing industries.

2.6.1 The microwave oven

Microwaves are a form of electromagnetic radiation with a frequency range from around 0.3 GHz to 300 GHz. The microwaves are transmitted, absorbed or reflected depending on the type of material as depicted in Figure 2.1. The microwave heating process generates heat internally within the

material as opposed to conventional heating which generates heating externally (Haque, 1999).

The principle behind microwave heating is relatively simple. Materials that absorb microwave radiation are referred to as dielectrics thus microwave heating is also referred to as dielectric heating. A dipole has two equal but opposite charges separated by a finite distance. For example, the covalent bond in a water molecule provides a dipole movement and is non-symmetric. The molecule with the electric polarity then tends to align itself with an electric field, inducing a temporary dipole movement, and reverting to its original position once the field is removed. This movement generates friction inside the dielectric material with the energy dissipated as heat. (Jones *et al*., 2002)

The heat generation in the volume element of the material is thus dependant on the electric field strength, frequency and dielectric properties of the material. The following section highlights the above phenomena in industrial applications.

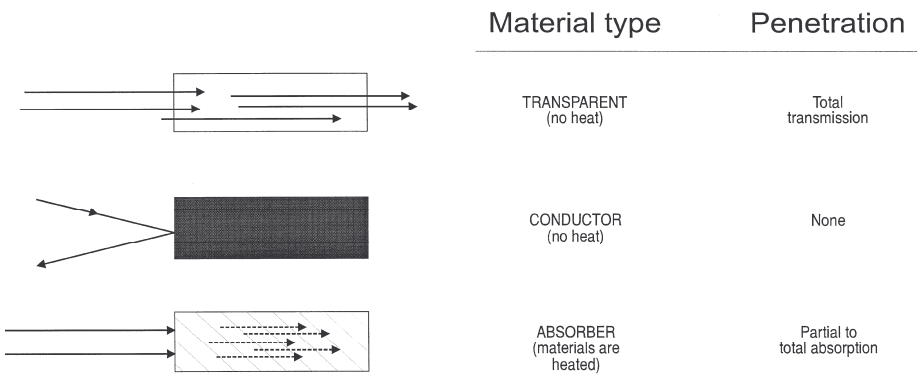


Figure 2.1: Microwave interaction with materials (Haque, 1999)

2.6.2 Microwave applications in Minerals Processing

Bykov *et al.* (2000) reviewed the advantages of microwave processing of materials. Amongst the benefits of utilising microwave energy is the specificity of microwave energy absorption. In comparison to commonly used methods of thermal heating, microwave energy allows volumetric heating of materials. Heat penetrates the inside of the sample, thus the heating rate would be limited by the microwave power source. The temperature inside the sample will always be higher than on the surface, although heat is dissipated through to the surface.

The principle advantages of microwave heating are:

- Reduced energy consumption and process time: Costs are reduced significantly, in comparison to other treatments, specifically in high temperature processes as heat losses increase with an increase in process temperature;
- Economic viability: microwave processing is capable of improving the product quality which leads to results that cannot be achieved conventionally;
- Rapid and controllable rate of heating: high heating rates lead to a reduction in process time as well as energy reduction;
- Selective heating is increased with microwave energy as it becomes easier to form a spatial distribution of heat sources and to control their power;
- Microwave heating also provides an alternate method to surface treatment of materials utilising the intense energy flow and penetration depth provided by the microwave source.

Mockovčiaková *et al.* (2002) used microwave radiation to intensify the magnetic separation and leaching of copper ores. The ores were samples of chalcopyrite and tetrahedrite heated in a microwave oven of maximum power 900 W. Microwave heating caused phase changes of the sulphides and modifications of the magnetic properties of the chalcopyrite. This

resulted in the thermic decomposition of the ores with a formation of a new phase. The treated ores were crushed to a grain size below 0.5 mm and subjected to magnetic separation. The increase in the magnetic susceptibility of chalcopyrite due to microwave irradiation enhanced magnetic separation. The tetrahedrite formed a strong magnetic phase of ferrites. Microwave leaching of the chalcopyrite became effective only after the leaching temperature exceeded 100 °C. A decrease in the concentration of antimony, arsenic and mercury occurred when the tetrehedrite underwent microwave leaching. With an increase in the exposure time, ore recovery was found to increase significantly.

Hwang *et al.* (2002) carried out a similar study on leaching of a copper sulphide mineral under hydrothermal conditions (i.e. water at elevated temperature and pressure), and found that the microwave induced super heating of the copper ions thus promoting fast leaching kinetics. This becomes significant as the leaching temperature rises.

Higher recoveries of copper was attained by Al-Harahsheh *et al.* (2005) when microwave leaching chalcopyrite using sulphuric acid and ferric sulphate. The surface of the chalcopyrite particles were found to heat up faster than that of the leach solution, causing a positive temperature gradient between the liquid and the solid. This assisted the reaction kinetics as the reaction is highly temperature dependent.

Beeby (1992) patented the process for the recovery of a valuable species in an ore that contains materials that absorb microwave energy, with particular emphasis on gold bearing ores containing sulphides (commonly pyrite and arsenopyrite). This involves treating the ore using microwave energy for duration of one hour, in intervals of 10 s to 20 min making it easier to cause a mechanical breakdown of the ore. Microwave exposure resulted in increased gold recovery of up to 62 %, possibly due to the large extent of mechanical changes. The ore underwent thermal expansion due the

formation of a high temperature internal gas phase, as well as crystallographic transformation of materials in the ore, inducing stress and strains which ultimately lead to the breakdown of the ore. An added advantage of the above process is the reduced sulphide and arsenic emissions. Beeby (1992) carried out further experiments on a complex lead-zinc ore which yielded results similar to that produced by the gold ore microwave leaching.

Clark *et al.* (2000) discussed processing materials using microwave energy ranging from 0.3 MHz to 300 GHz frequencies. Microwave sintering of alumina and microwave processing of glasses were primarily investigated. Microwave sintering of alumina was carried out using microwave hybrid heating. The samples were exposed to microwave energy using a 300 W oven at 2.45 GHz and exposed to temperatures ranging from 1200 ºC to 1500 ºC for approximately 30 min to an hour. In comparison to conventional heating techniques using a furnace, the microwave sample achieved a higher density at a lower temperature due to the internal heating phenomenon associated with microwave heating. Microwave processing of glasses involved using microwave energy as a heat source for ion-exchange reactions to achieve surface modifications in the glass. This enhanced the rate of ion-exchange and allowed for thicker ion exchange layers to be formed. Furthermore, microwave energy aided in converting amorphous glass into polycrystalline glass-ceramic. The crystal growth rate achieved in microwave heating was greater than that in conventional heating due to the selective heating of the microwave energy.

Long *et al.* (2002) used a combination of electric heating and microwave processing in the clinkering of sulfoaluminate cement. The experiment involved heating the prepared samples to critical temperatures of 1000 ºC, 1100 ºC and 1200 ºC in an electric furnace and then transferring to a microwave cavity to allow for microwave processing. Microwave clinkering occurred for approximately 2 min which resulted in a dense, hard

material, with the f-CaO content decreasing. In comparison to conventional clinkering processes, microwave aided clinkering sped the process up approximately 100 times.

Potgieter *et al*. (2003) studied the effect of microwave curing on strength development in cement mortars (Ordinary Portland cement and sand mixtures with varying water/cement ratios and time intervals) and found that intermittent heating using microwaves produces better results than continuous microwave heating which evolves steam. Further investigation is required in order to optimize the process. In addition to the above, Fang *et al*. (1996a) microwave sintered cement samples at 900 W and 2.45 GHz in a multimode microwave oven. This was found to enhance the clinkering reaction to some extent in both the ordinary Portland cement as well as the coloured cements. Lower clinkering temperatures were observed, thus making the process economically viable.

Fang *et al*. (1996b) also looked at the microwave sintering of fly ash. An increase in temperature resulted in increased sintering yielding higher density and strength than the conventionally sintered samples thus enhancing the sintering process.

Microwave reduction of oxidised ilmenite concentrates were studied by Kelly and Rowson (1995). The study entailed heating the ilmenite concentrate in a furnace at 1000 ºC to allow the iron to oxidise into a ferric state. The cooled sample was then mixed with carbon and reduced in a muffle furnace for approximately 16 hrs, and subsequently, in a microwave for 10 to 15 min. Reduction using microwave techniques occurred at a faster rate than that of conventional furnace reduction. The removal of titanium and iron from the microwave reduced samples, increased proportionally to the extent of reduction at varying powers together with the surface areas and porosity of the concentrate.

Kingman *et al.* (2004) investigated the influence of microwave treatment on mineral ore breakage. The ore used was a lead-zinc ore which underwent microwave pre-treatment using both a multimode as well as a single-mode unit prior to strength and breakage testing. Using 15 kW multimode oven, strength of the ore was significantly reduced after exposure for 0.5 s. Reductions of approximately 15 % were achieved in the energy required for comminution. Using a single-mode cavity, strength reductions of 50 % at 10 kW and 0.1 s exposure occurred. Kingman *et al.* (2004) concluded that the change in strength using multimode cavities is related to the applied microwave level. For microwave pre-treatment to be economically viable, high values of electric field are required, with an even distribution across the ore.

2.6.3 Microwave applications in pyrite removal

Huang and Rowson (2001) investigated the heating characteristics and decomposition of pyrite and marcasite using microwave energy. Pyrite and marcasite were found to occur together, and, while having the same chemical composition, have different crystals structures. Sulphide minerals were found to have a strong ability to absorb microwave energy and heat preferentially while either the gangue or precious minerals were found to be transparent to the microwave radiation. The experiment involved exposing pyrite and marcasite samples to microwave radiation at varying power levels. The rate of heating and decomposition was found to increase with an increase in power levels. Marcasite heated and decomposed at a slightly increased rate compared to pyrite, which suggests that crystal structure has an influence on the heating characteristics. Larger particles heated up faster than the fine samples as a result of a decreased energy loss from the surface of the large sample. Microscopic examination of both samples revealed that pyrite and marcasite decomposed into porous pyrrhotite-like phases and elemental sulphur when exposed to microwave radiation in a nitrogen atmosphere.

Atalay *et al.* (2003) undertook a similar study to investigate the effect of microwave heating on magnetic separation of pyrite at 2.45 GHz. The pyrite sample used was a copper deposit milled to different size fractions, exposed to microwave energy at 850 W, whilst varying the exposure time. An optimum was obtained at 420 µm size fraction and 850 W, allowing the temperature to reach 860 ºC in 495 s. As the treatment temperature is increased, a larger portion of the microwave treated pyrite changes structure to become magnetic. The study concludes that microwave treatment has a significant effect on the mineralogy, heating characteristics and magnetic processing of the pyrite mineral.

2.6.4 Microwave applications in coal processing

Marland *et al.* (1999) exposed coals of various ranks to microwave radiation in order to quantify its effect on coal grindability. The experimental procedure involved milling the microwave treated and non-treated samples in order to compare the effect of microwave radiation on coal grindability. Coal samples were exposed to microwave radiation for up to 8 min. An optimum was obtained after 5 min of exposure to microwaves, with a reduction of approximately 50 % of the relative grindability of the coal in comparison to conventional drying techniques (heating the sample to 250 ºC in a muffle furnace). This comes about as a result of the water contained in the coal which is a good absorber of microwave energy and when exposed to microwave radiation, heats up and expands due to the internal pressures created, weakening the coal structure. The effect of microwave radiation on the calorific value of the coal was minimal and is comparable to that obtained by conventional drying techniques. In addition to the above, Marland *et al.* (1998) found that the selective heating obtained by microwave exposure allowed pyrite to heat to 250 – 300 ºC causing the

pyrite to convert to a magnetic enhanced pyrrhotite. This allowed for a sulphur removal using magnetic separation.

Mockovčiaková *et al.* (2004a) investigated the effect of microwave radiation on the triboelectrostatic separation of coal. The experimental study involved heating coal samples of less than 3mm in a microwave oven for 10 min, utilising a nitrogen atmosphere to avoid oxidation with air. Microwave heating prior to triboelectrostatic separation was found to be advantageous as the volatile content increased from 30 to 44 wt% while the ash decreased from 49 to 18.3 wt%. In addition to the above, Mockovčiaková *et al.* (2004b) studied the modification of magnetic properties of siderite ore using microwave energy and its influence on the subsequent low-intensity separation. The outcome of the treatment was increased ore faulting resulting in decreased strength whilst reducing the energy required for comminution as well as enhancing mineral separation.

2.7 Desulphurisation of coal using Microwave Energy

Desulphurisation of coal using microwave energy (1 kW, 915 MHz and 2.45 GHz) has been experimented by Zavitsanos and Golden (1982). This method utilises the difference in magnetic susceptibility of coal and iron bearing minerals to liberate the minerals. Course granules of ±6 mm were microwave treated and then crushed and magnetically separated. The microwave treatment converts the pyrite to another phase, typically phyrrhotite ($Fe_{1-x}S$), which has a greater magnetic susceptibility than pyrite, if the medium is air or argon. The extent of conversion is 10 % and in some cases, more. This technique showed significant liberation of iron and sulphide phases.

Uslu and Atalay (2003) undertook a similar experiment. Magnetite was added to coal sample and microwave heated for 300 s before undergoing magnetic separation and mineralogical analysis. The magnetite was

essential for increasing the medium temperature to sufficiently heat the pyrite. The pyritic sulphur was found to decrease by 55.1 %, ash by 21.5 % while the calorific value increased by 20.4 %. Conventional stovetop heating resulted in a decrease of 22.3 % and 15.8 % for pyritic and ash respectively.

Rowson and Rice (1989) investigated desulphurisation of coal using low power microwave energy (500 W and 2.45 GHz). Using untreated high sulphur coal and microwave treatment at 500 W and 2.45 GHz, sulphur rich gases and magnetically enhanced pyrite did not form as with a high power microwave experiment carried out by Zavitsanos and Golden (1982). Dry desulphurisation of coal is appeared not to be possible using low power microwave energy. An alternate method using strong caustic (300 g/L sodium hydroxide or potassium hydroxide) solution, pulverized coal and radiating the sample for 60 s in an air atmosphere was employed. After microwave treatment, the sample was washed to remove soluble sulphides and sulphates and then underwent magnetic separation. The method was repeated a number of times to obtain up to 70 % total sulphur removal.

Hayashi *et al.* (1990) studied the effect of molten caustics in coal desulphurisation using microwave energy. Whilst it was easy to remove the pyritic sulphurs by alternate means such as wet washing or magnetic separation, it was almost impossible to remove the organic sulphurs other than with the molten caustic methods. The study involved mixing the pulverized coal particles with water and equal amounts of sodium hydroxide and potassium hydroxide and pre-heating it to allow the alkali to dissolve. The mixture was then exposed to microwave radiation. Sulphate and pyritic sulphurs were found to be removed during the pre-heating period while the organic sulphur content remained unchanged with the rate limiting step of molten caustics into the coal matrix mass transfer limiting.

Chemical desulphurisation of coal using hydroiodic acid was reported by Yürüm *et al.* (2002) to be successful as well. The chemically treated pulverized coal (-65 mm) samples underwent microwave treatment for 20 min in an inert atmosphere. The reaction mixture was then cooled to room temperature, washed with water and the different forms of sulphur analysed according to ASTM methods. This method removed all the pyritic sulphur and 70 % of the organic sulphur but was not cost effective as concluded by Yürüm *et al.* (2002).

Andrés *et al.* (1995) investigated chemical desulphurisation of low rank coal using HI acid as a desulphurizing agent with microwaves as the energy source. The experiment involved exposing the coal and hydroiodic mixture to microwaves in an inert argon atmosphere. After 10 min of exposure time, approximately 99 % of the pyritic sulphur was removed, and an organic sulphur removal of 64.7v% was detected after 20 min of irradiation. Together, this allowed 80 % of the total sulphur to be removed. Andrés *et al.* (1995) describes the treatment of low rank coals with caustics as difficult due to the high amount of phenolic and humic materials released during the desulphurizing treatment.

Jorjani *et al.* (2003) desulphurised coal using a combination of microwave irradiation and peroxyacetic acid. Microwave irradiation was carried out on a pulverized sample for 50, 80, and 110 s at powers of 600, 800, and 1000 W. The sample was then treated with peroxyacetic acid. This was done by heating the coal in glacial acetic acid to the required temperature and then adding H_2O_2. Using microwave desulphurisation alone removed 19 % of the sulphur. The peroxyacetic acid washing increased the sulphur removal to 35.9% after exposure for 30 min, which increased with an increase in residence time. A decrease in the particle size yielded an increase in the rate of sulphur removal.

Bodman *et al.* (1997) also looked at the role microwave heating played in the desulphurisation process with different solutions. Coal containing a total sulphur content of 2.2 % was desulphurised using copper (II) chloride as well as tri-iron dodecacarbonyl. Pulverized coal was mixed with a 50 % aqueous solution of copper (II) chloride and exposed to microwave radiation for duration of 1 hr in varying increments. Precipitation of copper crystals occurred with the sulphur content of the sample decreasing to 0.8%. Desulphurisation of coal using the tri-iron dodecacarbonyl reduced the total sulphur content to 1 %.

2.8 Summary

In summary, it is clear from this discussion that microwave processing of minerals in general, and coal in particular, has a number of advantages and can be fruitfully exploited further. The investigation described in more detail in the following chapters (3 and 4) will determine the advantages of using microwave technology as well as its effect and behaviour on South African coals. South African coals differ in relation to composition and nature, from materials as described in literature. The focus will be specifically on the efficiency and approach to desulphurise South African coals.

Chapter Three – Methodology and Experimental

3.1 Introduction

In this chapter the analytical procedures used in the experimental study are discussed. Studies by other authors are adapted to suit South African coal as well as availability of instruments. A high sulphur coal was supplied by Mintek while a low sulphur coal was received from Sasol. The high sulphur coal was received as large lumps with the pyrite bands visible on the outside of the coal. The low sulphur coal was received with particle size of approximately 6 cm particles. Coal samples required further preparation before utilisation in the experiments, as outlined in Section 3.2. Figure 3.1 provides a flowsheet sequence of the experimental methods.

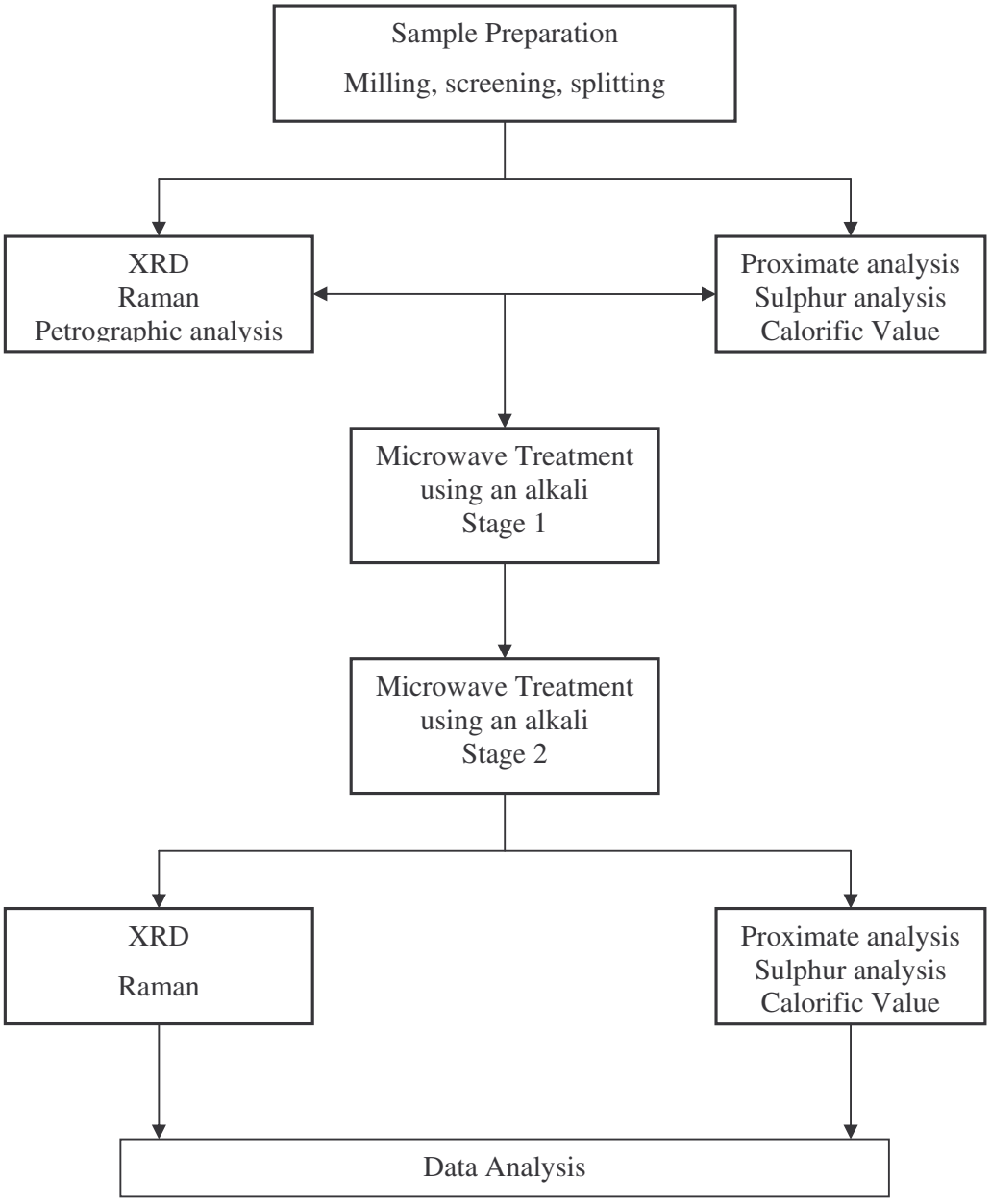


Figure 3.1: Experimental Flowsheet

3.2 Sample preparation

Sample preparation is an important stage in the experimentation and analysis process and is thus dependent on the type of analysis to be carried out. For most analytical and experimental processes the sample as received from industry requires a reduction in mass and size. Quantitative analysis requires the sample to be as representative of the parent source as possible. Proximate analysis uses a below 200 µm particle while the petrographic analysis requires the sample to pass a 1 mm sieve and minimising the fines (below 75 µm particles). Splitting of the sample should be carried out before and after grinding to ensure a homogenous sample.

3.2.1 Crushing and grinding

The objective of size reduction is to produce a coal that meets the experimental requirements whilst not over crushing and producing excess fines. Industry supplied the coal in large lumps that required further breakdown. A jaw crusher was used in the primary size reduction of the coal as large feed openings (approximately 2.5 × 2.5 m) were available. Particle size could be varied by adjusting the width of the outlet gap. The material is crushed by stressing it between a stationary and reciprocating jaw driven by an eccentric shaft.

For medium-coarse size reduction, a cone crusher was used following the jaw crusher. The basic principle is of an eccentrically driven rotor crushing material against a stationary mantle. The particle size could be varied by changing the clearance between the rotor and mantle. For coal crushing, the rotor was set to discharge a product of approximately 4 mm.

A rod mill consisting of a rotating hollow cylinder, partially filled with rods extending the length of the mill, was used to achieve fine particle sizes. Size reduction is achieved by the combined action of rolling and lifting of the balls or rods against each other. The grinding action allows high stress to be

applied to the particles so that a large portion of fines are produced. Milling of the coal samples was carried out for approximately 13 min to achieve even size fraction splits of +600 µm, +212 µm and -74 µm. Excess ultra fine particle production was minimized by continuous screening and re-milling. Advantages of this type of milling are the low power consumption as well as cost installations. In addition to this, the mill is suitable for materials of varying hardness.

3.3 Petrographic Analysis

Falcon (1978) describes coal petrography as the study of the organic and inorganic materials that make up coal. Emphasis is placed on the need to identify organic constituents of coal, as well as to recognise mineral matter present in the coal. The technological behaviour of coal is predicted from its petrographic composition making petrographic analysis an integral part in evaluation and assessment procedures.

Petrographic analysis involves coal evaluated under a polarised reflected light microscope with oil immersions. The type of coal can be determined macroscopically (hand specimen) where the coal is described as dull, bright or banded, as well as microscopically where the type of coal is determined by the proportions of different organic components termed macerals (discussed in Section 2.2). The analysis is referred to as maceral group analysis and determines the proportions of vitrinite, liptinite and inertinite (as well as subgroups). These are expressed as a percentage by volume basis (% volume). Rank is the measure of the maturity of the coal and is determined by the proportion of light reflecting off the surface of the vitrinite maceral group. It is referred to as a reflectance analysis and the results are expressed as a % RoV (reflectance of vitrinite, mean random %).

As well as determining the type, grade and rank, observations were made on the mode of occurrence of pyrite within the coal matrix. The analysis

was conducted within the School of Chemical and Metallurgical Engineering, University of the Witwatersrand, by Dr. N. Wagner.

A solid block consisting of crushed and screened particles (-1000 μm - +74 μm) was bound in resin and prepared for petrographic analysis as per ISO 7402/2. A Zeis Universal petrographic microscope with a Swift point counter was used for the maceral, microlithotype and mineral group analysis as well as the rank analysis and were carried out in accordance to the ISO standards – ISO 7404. The sample was scanned using a magnification of 400X, and a total of 500 points was counted.

3.4 Empirical analysis

Empirical analysis characterises the coal in terms of its physical or chemical properties. The analytical classifications are further broken down into proximate and ultimate analysis, which provide details of the chemical composition.

3.4.1 Proximate Analysis

Summarised from lecture notes, proximate analyses constitute the following:

- *Inherent moisture* consists of the water that has remained in the pores of the coal after all the surface moisture has been removed. This affects the energy value of the coal as an increase in moisture content decreases the calorific value of the coal. In South African coals, moisture values are typically between 2 – 6 %.
- *Ash content* is the residue remaining after complete combustion of the coal and consists of iron oxides, aluminium, calcium, magnesium and silica. South African coals typically consist of 25%

to 35% ash, which can be considered to be unsuitable for most applications. It is thus necessary to clean the coal to decrease its mineral content. Various beneficiation techniques were discussed in Section 2.5.

- *Volatile matter* is derived from the organic and mineral matter in the coal. This determines the ease with which the coal will ignite and burn, which is important when the burning rate needs to be varied. On combustion, organic matter produces tars, oils, hydrocarbon gases, hydrogen and oxides of carbon. Certain mineral matter can produce incombustible volatiles, which, if present in sufficient quantities, affect the performance of coal.
- *Fixed carbon* is determined from the difference of the ash, moisture, and the volatile component deducted from a 100. It is not an analysis thus errors occurring during other analysis may manifest in the fixed carbon value. The fixed carbon value is useful when comparing coals. Generally the carbon value ranges between 50% and 60% and is utilised by chemical and metallurgical processes.

3.4.2 Sulphur Analysis

According to Lazar (1978), the total sulphur is determined by one of the following methods:

1. Eschka method
2. Bomb method
3. High temperature combustion method

The classic system is the Eschka method. The sulphur content is determined by mixing the sample of coal with an Eschka mixture (2 parts magnesium oxide to 1 part sodium carbonate) which is the heated to 800 °C and allowed to oxidise. The oxides released are absorbed by the Eschka mixture and leached out as a sulphate, which is then precipitated as a barium sulphate. From the mass of precipitate, the percentage sulphur can be

determined. The disadvantage of the manual sulphur determining method is the high percentage error associated with it.

The LECO analyser is a more precise, automated method of determining the total sulphur in the sample. For these reasons, it was selected as the preferred sulphur determining method throughout the project. The LECO Carbon/Sulphur Determinator, as shown in Figure 3.2, is a microprocessor based software driven instrument for measurement of carbon and sulphur content in metals, ores, ceramics and various other inorganic materials. The instrument utilises an induction furnace and measures carbon and sulphur by infrared absorption. The sample gases are swept into a carrier stream where sulphur is measured as sulphur dioxide in the first infrared cell. A small amount of carbon monoxide is converted to carbon dioxide in the catalytic heater assembly; sulphur dioxide is converted to sulphur trioxide and removed from the system in a cellulose filter. Carbon is measured as carbon dioxide in the infrared cell as gases flow through the infrared cells.

Sulphur form analysis looks at the quantities of mineral sulphate, sulphatic sulphur and organic sulphur within a representative sample. In Section 2.4, the difficulty in removing sulphatic and organic sulphur is discussed. For this reason, it is important to determine the quantity of sulphatic and organic sulphur in the coal. Sulphur form analysis was carried out according to the ISO 157 standard.

Figure 3.2: LECO Carbon/Sulphur Determinator

3.4.3 Calorific Value

In addition to determining the sulphur content of coal, of great importance is the calorific value which can be defined as the measure of heat or energy content of coal (Falcon, 1987). A bomb calorimeter is used to determine the calorific value of coal. The method as described by Lazar (1978) is briefly outlined: the coal is burnt in a pressure vessel filled with oxygen at 3.0 MPa. This vessel is then placed in a water jacket whose temperature can be accurately determined before, during and after combustion. The calorific value is then calculated from the observed temperature rise.

Proximate, sulphur and calorific value analysis were conducted by the author in the Department of Extractive Metallurgy, University of Johannesburg.

3.5 X-Ray Diffraction

X-Ray powder diffraction (XRD) is a technique used to identify minerals as well as other crystalline materials and is particularly useful for identifying fine grained minerals that may not be identified by other techniques. Identification of the minerals occurs by diffraction of the mineral depending on the type of atoms that make up the crystal lattice and how the atoms are arranged, enabling the prediction of inorganic and organic variability within coal samples (Flohr, 1997). Vassilev and Tascon (2003) describe the principal advantage of XRD analysis as the detection of occurrence and degree of crystallinity of forming major and some minor crystalline phases in coal independently from the size. The purpose of including XRD analysis in the project was to detect the type of mineral matter present in the coal before treatment. XRD analysis was also used to gauge formation of new mineral phases on the microwave and alkali treated samples, if any.

A Philips Analytical X-Ray B.V. Diffractometer of type PW1710 based with PC-APD diffraction was used. The operating conditions were as follows: copper anode tube, 40 kV generator tension, 20 mA generator current, 1º divergence slit, 0.1 receiving slit, start angle of 10° and end angle of 80°. A step scan mode was used. Mineralogical phases were identified using various literature resources (De Abreu *et al*. (2007), Wang *et al*. (2007), Caldiera *et al*. (2003), Reyes *et al*. (2003), Štyriaková *et al*. (2003), Komnitsas *et al*. (2001), Fajardo *et al.*, (1999), and Eymery (1999)). XRD analyses were conducted within the School of Chemical and Metallurgical Engineering, University of the Witwatersrand, by the author.

3.6 Raman Spectroscopy

Raman spectroscopy is a technique used to study low frequency modes in a system. It relies on Raman or inelastic scattering of monochromatic light usually from a laser in the visible, near infrared or ultraviolet range, due to vibrational and rotational modes in a molecule (Godoi *et al*., 2006).

Preparation of the sample blocks were done according to the ISO 7404/2 standard discussed in Section 3.4. The samples were analysed using a BRUKER SENTERRA micro Raman spectrometer coupled with a TE-cooled CCD detector. Excitation was provided using a 532 nm line of a frequency double Nd:YAG laser, of which the power density was varied between 0.2 to 20 mW according to the laser sensitivity of the sample spot analysed. Samples were scanned over a spectral range from 75 – 3000 cm^{-1} . Spectral resolutions of approximately 3 cm^{-1} using 1200 line mm^{-1} were achieved. The acquisition time for each scan varied from 2 to 10 s whilst the number of accumulations varied from 1 to 5. Spectra were obtained using 20 × and 50 × magnification objectives. Power was regulated from 0.2 mW to 10 mW to prevent the coal from burning out. Data acquisition was carried out using OPUS Software packages. Spectral analysis was done by comparison with an in-house library.

Raman analyses were conducted by Prof. S. Potgieter-Vermaak and Ms. N. Maledi within the School of Chemistry, University of the Witwatersrand.

3.7 Microwave Treatment

A detailed discussion on microwave technology and the studies determined in literature is presented in section 2.6. The underlying section provides the experimental methods of microwave treatment of coal samples for the purpose of desulphurisation used in this study.

A domestic LG microwave oven (Figure 3.3) of varying power levels with a frequency of 2.45 GHz was used to conduct the treatment on the samples. The microwave unit was of a multimode type where the microwave signal is coupled through a slot and is subject to multiple reflections. This allowed for a uniform heat distribution. The maximum power level was at 900 W with additional power levels occurring at 100 W, 200 W, 400 W and 650 W. The maximum treatment time the microwave allowed for was an hour. The microwave treatment was carried out in two stages for the high sulphur coal, the first being the determination of an optimum desulphurisation point. The second stage involved further experimental work on the optimum points in order to achieve a better sulphur removal. Treatment on low sulphur coal was carried out to gauge behaviour and response to treatment.

Figure 3.3: Microwave oven used for experiments

The microwave experiments were conducted by the author at the University of Johannesburg, department of Extractive Metallurgy.

3.7.1 Stage 1: Determination of the Optimum Desulphurisation Rate

For stage 1 treatment a standard strong caustic solution made up as follows, was used:

- A 300 g mass of sodium hydroxide pellets was measured to two decimal places and placed in a beaker;
- Using a 1.00 L cylinder, and as accurately as possible, a litre of de-ionized water was dispensed into the beaker with sodium hydroxide pellets;
- The de-ionized water was added to the sodium hydroxide pellets gradually, as the reaction is exothermic;
- Using a spatula, the mixture was stirred until all solids were dissolved. The prepared mixture is a thick syrupy solution;
- The mixture was left to cool down before using.

The coal sample had been screened into size fractions +600 µm, +212 µm and -74 µm as discussed in Section 3.2.1. Microwave treatment on the coal samples to determine the optimum is as outlined below:

- A 15 g coal sample was mixed using a 25 weight % solids to 75 weight % liquid ratio, and stirred until a slurry formed;
- Before actual experimentation was carried out, the ignition time at each power level was required. This was done by microwave treating a +600 µm prepared sample, at each power level and noting the time at which the sample began sparking;
- A 15 g sample from each size fraction was then microwave treated in increments of 2 min, until the ignition time. This was done for each power level;
- Treated samples were cooled down, filtered and washed using de-ionized water until all traces of alkali were removed. This was tested for using red litmus paper;
- Overnight drying (±8 hrs) occurred in an oven set at 50 °C;

- After oven drying, samples were exposed to the atmosphere for two days to allow moisture to be regained;
- Change in sulphur concentrations was determined using LECO analysis as outlined in Section 3.5.2;
- Proximate analysis after treatment was carried out to determine change in coal characteristics;
- Raman and XRD analysis was performed to gauge structural and mineralogical phase change;
- Based on the sulphur reduction, an optimum power and time for each size fraction was selected.

The same procedure was carried out on the low sulphur coal, with Raman analysis omitted.

3.7.2 Stage 2: Further Experimental Work

Based on the optimum desulphurisation points determined for each size fraction, further experimental work was undertaken as follows:

1. Effect of increased alkali concentration was investigated
    - A 400 g/L sodium hydroxide solution was prepared using the same procedure as preparation for the 300 g/L solution;
    - A 15 g sample from each size fraction was prepared and the slurry microwave treated at the corresponding optimum time and power;
    - After treatment, the sample was filtered, washed, and dried as per stage 1;
    - Change in combustion characteristics, and sulphur was determined using proximate and LECO analysis respectively.
2. Varying the solid to liquid ratio
    - The solid to liquid ratio was increased from a 75 wt% liquid to an 80 wt % liquid ratio;
    - Treatment was carried out at the optimum conditions;

- The sample was filtered, washed and dried as per stage 1;
- Change in combustion characteristics, and sulphur was determined using proximate and LECO analysis respectively.

3. Comparison to conventional stovetop leaching
    - The samples were prepared for treatment using the 300 g/L sodium hydroxide solution as described in stage 1;
    - To determine the efficiency of the stove in comparison to the microwave unit, an identical quantity of water was boiled in the microwave as well as on the stove. Efficiency of the microwave was taken as 1. Correlating the time taken for the water to boil and the energy balance, as estimate of the efficiency of the stove can be determined;
    - Stovetop heating occurred at a time corresponding to that of the optimum microwave conditions whilst taking into account the efficiency of the stove;
    - Filtering, washing, drying, and analysis of the treated samples is as per point 2.
4. Effect of using different alkali and mixtures of alkali
    - Potassium hydroxide, calcium hydroxide, and sodium chloride: preparation of sample, treatment, and analysis is as per stage 1 with the relevant alkali replacing the use of sodium hydroxide;
    - Mixture of sodium chloride and sodium hydroxide solutions (300 g/L) were prepared individually as per preparation of sodium hydroxide in stage 1. The mixtures were then combined in a mass ratio of sodium chloride: sodium hydroxide, 30:70. Solid to liquid ratio was kept at 25:75 as in stage 1;
    - Treatment and analysis was carried out as per stage 1 with the exclusion of Raman analysis.

3.8 Summary

High volatile bituminous coals with sulphur contents between 0.5 % and 3.6 % were used in the study. Based on work carried out by Rowson and Rice (1990), size fractions +600 µm, +212 µm and -74 µm were treated with a strong alkali solution in a 2.45 GHz, variable power (maximum 900 W) microwave unit.

Typically, during microwave treatment, 15 g of coal was mixed with a 300 g/L of sodium hydroxide solution, solid to liquid ratio 25:75, and microwave treated at various powers and times to determine the optimized desulphurisation point as well as to gauge size fraction reaction to treatment. After treatment the mixture was filtered and washed until all traces of the alkali were removed. Extent of desulphurisation was determined by sulphur analysis using a Leco analyzer, on the treated and untreated coal. Change in structure and bonding was determined using XRD and Raman analysis before and after microwave irradiation. Optimum power and time found using the high sulphur coal and 300 g/L sodium hydroxide solution were used as a basis in the following experimentation:

1) Effect of increased alkali concentration (400 g/L) was investigated;
2) Varying solid to liquid ratio effect;
3) Comparison to conventional stovetop leaching;
4) Effect of using different alkali: potassium hydroxide, calcium hydroxide, sodium chloride, and a mixture of sodium chloride and sodium hydroxide.

Chapter Four - Results and Discussion

Chapter four discusses the findings of the experimental work carried out. Comparison is made to work carried out by other authors on different coals as well as to conventional sulphur removal techniques.

4.1 High Sulphur Coal

4.1.1 Petrographic Analysis

The main purpose of undertaking petrographic analysis was to determine the type, rank and mode of occurrence of pyrite in the coal. The high and low sulphur coals were characterized as low to medium rank bituminous coals as seen from the reflectance value in Table 4.1.

The high sulphur coal was found to contain a high proportion of vitrinite whilst a mineral group analysis showed the mineral component to consist mainly of quartz/clays, carbonates and pyrite. The carbominerite rock was found to constitute 17 % of the sample mineral matter. A relatively high degree of purity is reflected by the vitrite content.

The mineral group analysis showed high percentages of pyrite particles larger than 50 μm, signifying pyrite is found loosely in the coal rather than embedded in the matrix. Pyrite occurred as epigenetic in-filled particles with a greater part not bound in the organic matter. In terms of treatment using an alkali, it would signify that the pyrite could be easy to remove. Figure 4.1 shows pyrite occurrence in the high sulphur coal.

Petrographic Analysis: High sulphur coal										
Mean Random Reflectance (% RoVmr)					0.6					
Standard Deviation					0.06					
Maceral Group Analysis (%)										
Vitrinite	Liptinite	SF[1]	Fusinite		Inertodetrinite					
74.5	5.3	13.1	3.2		3.9					
Microlithotype Group Analysis (%)										
Vitrite	Intermed[2]	SF/Fus[3]	Carbominerite				Sapropelic			
			(OM+MM)[4]	(>60% MM)			Ce[5]	Te[6]	De[7]	
50.1	16.8	8.3	7.8	9.2			4.1	3.6	0	
Mineral Group Analysis (%)										
Quartz/Clay			Pyrite			Carbonates			Clean Coal	
<25	25-50	>50	<25	25-50	>50	<25	25-50	>50		
11.6	2	2	0.4	1.2	2	1	2	5.8	72	

Table 4.1: Petrographic analysis of the high sulphur coal

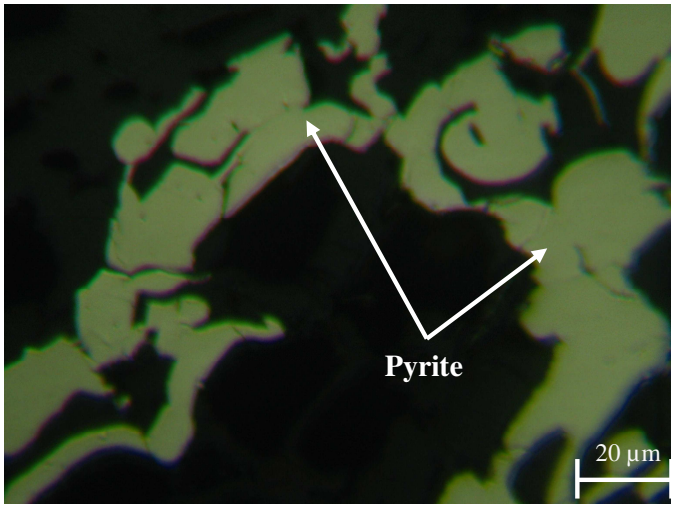


Figure 4.1: Pyrite occurrence in the high sulphur coal

*Instrument: Leitz MPV-2 with Canon digital camera, reflected light, oil immersion lens x500

[1] SF = Semi-Fusinite
[2] Intermed = bi and tri maceral
[3] Fus = Fusinite
[4] OM = Organic matter/ MM = Mineral matter
[5] Ce = Clarite
[6] Te = Trimacerite
[7] De = Durite

4.1.2 Proximate Analysis

The proximate analysis indicates the parent coal to be a moderate ash, high volatile bituminous coal. Table 4.2 summarises the proximate analysis of the high sulphur coal as per received basis and the size fractions.

Proximate, Sulphur Analysis (wt %) and CV				
	Average Parent Coal	**600 µm**	**212 µm**	**74 µm**
Moisture	4.0	4.0	4.0	4.2
Ash	18.5	20.5	15.3	19.8
Volatile Matter	32.0	31.0	33.2	30.8
Fixed Carbon	45.5	44.5	47.5	45.2
Total Sulphur (S)	3.3	3.5	3.2	3.3
Mineral	2.6	2.9	2.6	2.4
Sulphatic S	0.1	0.1	0.1	0.2
Organic S	0.6	0.5	0.5	0.7
CV (MJ/kg)	24.6	24.6	25.0	24.3

Table 4.2: Proximate, CV and S analysis – High Sulphur Coal before treatment

The 212 µm coal fraction was found to be the 'cleanest' coal fraction in comparison to the other size fractions. This can be seen from the moderate ash content exhibited as well as increased volatile matter content, hence increased fixed carbon content. The 600 µm particle size was found to contain large pyrite particles randomly scattered throughout the sample making representative sample selection difficult. The LECO analyzer used a maximum mass of 2 mg, thus the large particles offset the analysis when splitting to obtain a representative sample. From the sulphur form analysis, it is noted that at least 80 % of the sulphur is pyritic sulphur.

4.1.3 Stage 1: Microwave Treatment

Detailed background to microwave treatment is provided in Section 2.6. The experimental methods are described in Section 3.8. Figure 4.2 shows the prepared sample for treatment.

Figure 4.2: Sample ready for treatment

Table 4.3 gives the ignition times for each power level using the 600 μm particle size.

Power Level (W)	Ignition time (s)
900	407
650	615
400	660
200	960
100	1500

Table 4.3: Ignition time as a function of Power

Appendix A shows experimental data and observations of stage 1 microwave treatment to determine the optimum desulphurisation point.

Figures 4.3, 4.4 and 4.5 show total sulphur values after treatment for the different size fractions 600 µm, 212 µm and 74 µm respectively, treated at varying power and time to determine an optimum desulphurisation point with a caustic solution. Raw data for the graphical construction is presented in Appendix B.

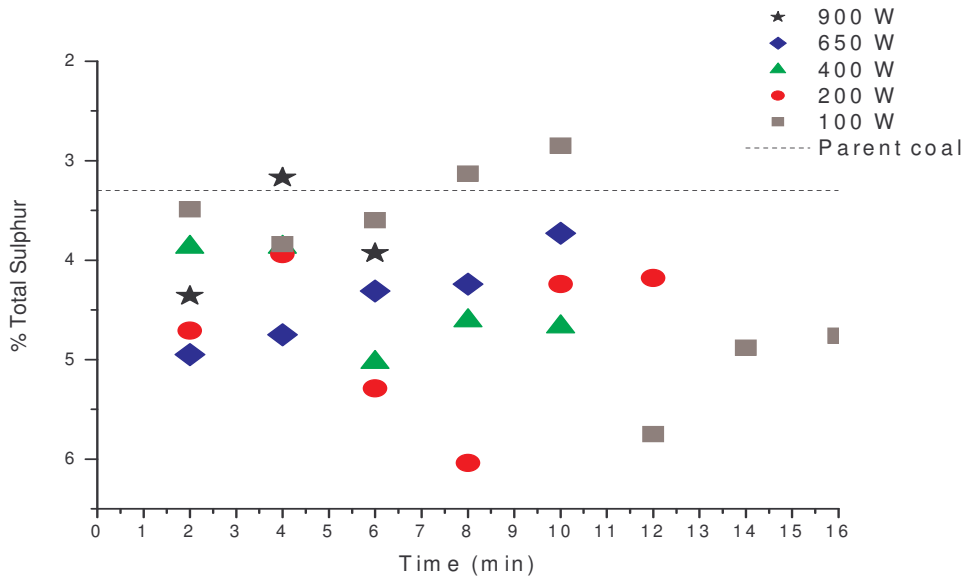


Figure 4.3: 600 µm microwave treated samples

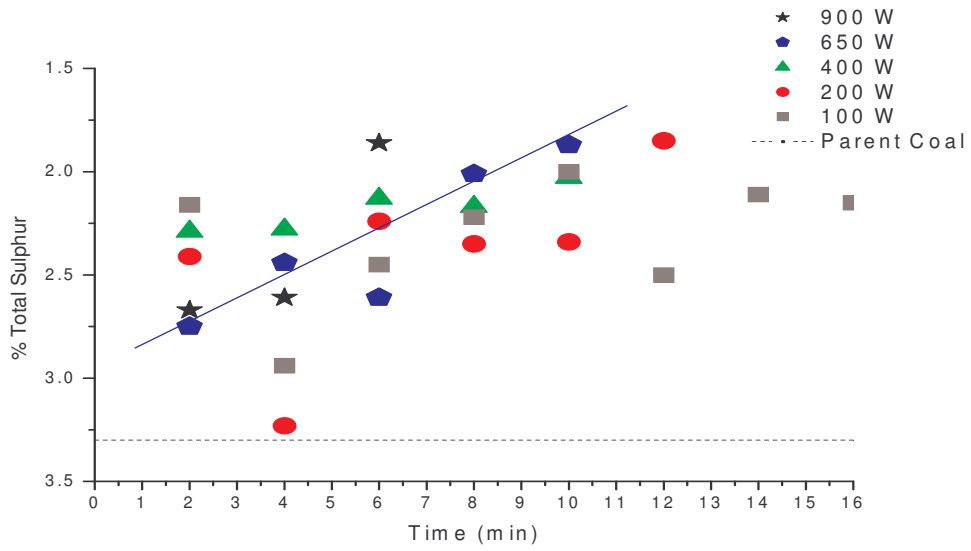


Figure 4.4: 212 µm microwave treated samples

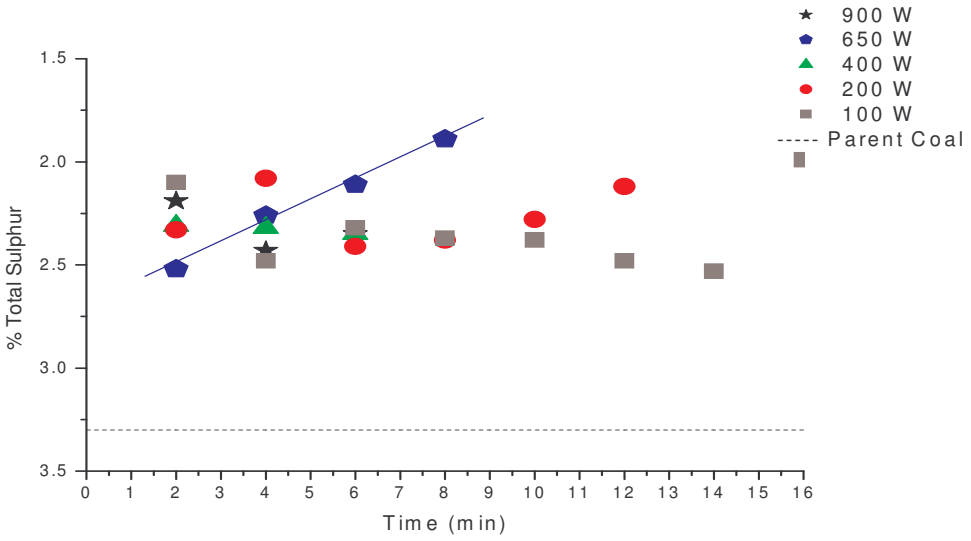


Figure 4.5: 74 µm microwave treated samples

Microwave treatment results show scattered power and time desulphurisation rates for all size fractions. This is particularly noticeable in the 600 µm size fraction (Figure 4.3) and may be due to the pyrite

occurrence in the coal. Bulk of the treated samples shows sulphur contents greater than that of the untreated parent coal. The small mass (2 mg) of sample used in the LECO sulphur analysis is a contributing factor in increasing error. Sulphur analysis of the 600 µm fraction produced sulphur rates higher than that of the untreated sample, clearly signifying error in the homogeneity of the sample, neglecting the 1 % instrumental error. Whilst every effort was made to produce a homogenous sample as possible, pyrite distribution within the coal made it very difficult to optimise the 600 µm size fraction.

The 212 and 74 µm size fractions produced better desulphurisation trends, showing a steady increase in desulphurisation with increase in time. An optimum power and time was determined at 650 W and 10 min for the 212 µm size fraction, whilst the 74 µm showed an optimum desulphurisation at 650 W and 8 min, both occurring at a time just before ignition. Sulphur was found to decrease by approximately 40 % after treatment. Sulphur contents analysed for after treatment for the 650 W, shows a roughly linear trend whilst treatment at other power levels are undefined. Further investigation of the coal and sulphur removal at different power levels is needed in order to draw a firm conclusion.

Table 4.4 summarises the proximate analysis carried out on the optimum treated samples. Negligible changes were noted in the ash content after treatment whilst the volatile matter and calorific value of the treated coal decreased. The benefit of decreased sulphur needs to be weighed against a loss in calorific value and volatiles.

An important characteristic noted during the treatment of samples was formation of 'hotspot' regions in the coal slurry treated. Jones *et al.* (2002) discusses the phenomenon as a region of very high temperature occurring due to non-uniform heating, which is a characteristic of microwave heating. Thermal instability arises as a result of the non-linear dependence of the

electromagnetic and thermal properties of the material on temperature. The formation of 'hotspots' could be minimized by keeping the sample in mixing or fluidized conditions (Haque, 1999).

In comparison to the 212 and 600 µm samples, the 74 µm sample formed hotspots after treatment for a shorter period of time. This is possibly due to the smaller voids between the particles allowing for a quicker evaporation rate of alkali solution, at the surface of the slurry.

Proximate Analysis (wt% after treatment)			
	Parent Coal	**212 µm**	**74 µm**
Moisture	4.0	7.8	7.0
Ash	18.5	17.9	20.6
Volatile Matter	32.0	27.6	27.4
Fixed Carbon	45.5	46.6	45
Total Sulphur	3.3	1.9	1.9
CV (MJ/kg)	24.6	22.4	22.6

Table 4.4: Proximate analysis of optimum treated sample

4.1.4 XRD Analysis

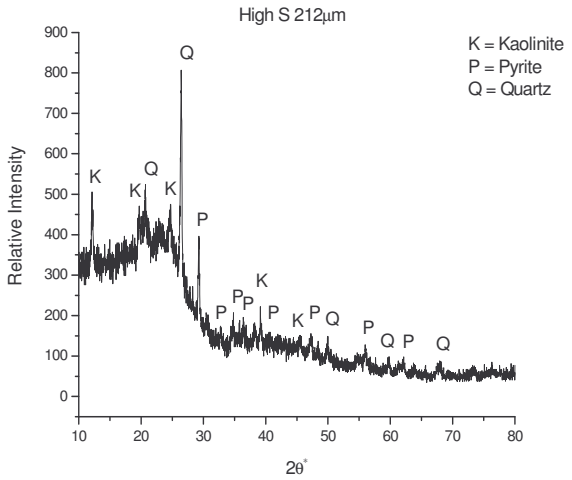


Figure 4.6: XRD of 212 µm before treatment

*Bragg's Law where θ is the angle of incidence of the X-ray beam

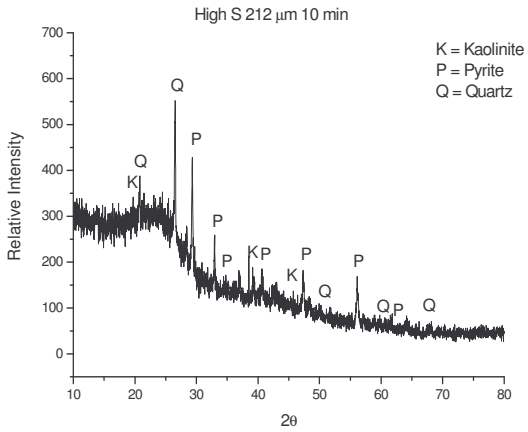


Figure 4.7: XRD of 212 μm after treatment

XRD analysis was undertaken before and after treatment to detect change in mineralogical phases or structure. Figures 4.6 and 4.7 show XRD patterns obtained for the untreated and treated coals respectively where peaks of kaolinite, quartz and pyrite were identified. The broad baseline occurring from 10 to 30 2θ is typical of coal patterns rich in organic matter (amorphous phase) and low in mineral matter (Reyes *et al.,* 2003). This decrease after treatment indicates a decrease in mineral matter. XRD patterns for the other size fractions are shown in Appendix C. From the XRD patterns, no change in structure or mineralogical phases appears to have occurred. Essentially, this implies that the coal does not undergo any changes during treatment. A percentage of the pyrite is leached into the solution largely unaltering the coal mineralogy. Further investigation regarding pyrite interaction with an alkali under irradiation is needed before a conclusion can be drawn.

4.1.5 Raman Analysis

Raman analysis was carried out to detect a change in the coal structure as well as mineral phase changes brought about by increased temperature. Detailed instrumentation specifications and operating conditions are discussed in section 3.7. Figure 4.8 gives the Raman spectra of the

untreated and treated samples in comparison to the in house pyrite spectrum.

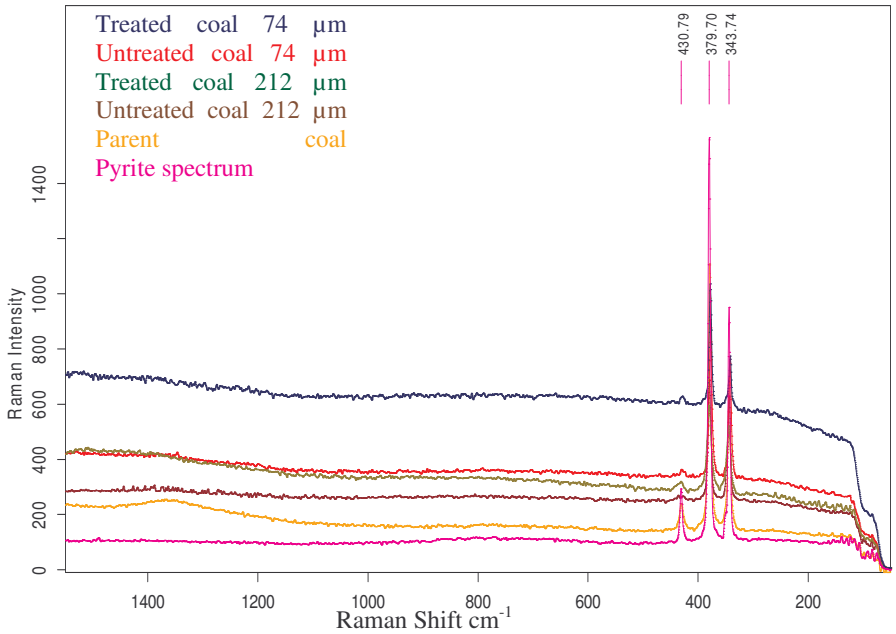


Figure 4.8: Raman analysis of the High Sulphur Coal

Raman analysis, as with the XRD analysis, did not pick up new mineral phases thought to have occurred during treatment. The temperature of the sample reaches approximately 130 °C when undergoing treatment. Particularly minerals located at the surface of the sample could experience a high temperature gradient resulting in a phase change. Due to limitations in temperature measurements and isolation of the mineral in the sample, it was not possible to measure temperatures. Sources from literature, (Rowson and Rice, 1990 and Zavitsanos and Golden, 1982) report that the pyrite is converted to pyrrhotite after microwave treatment, thus increasing the magnetic susceptibility of the coal and making it easier to desulphurise using magnetic separation. From the Raman scan in Figure 4.9, no pyrrhotite was detected or any formation of new mineral phases, with all scans corresponding closely to that of the parent coal. Mossbauer Spectroscopy was undertaken to determine change in the Fe-S structure, but

due to instrument problems, no pyrite or change in pyrite structure was detected.

The pyrrhotite scan, as seen in Figure 4.9, has peaks closely related to that of the pyrite peaks making detection of the pyrrhotite very difficult. Pyrrhotite and pyrite scans were obtained from the RRUFF database (Downs, 2006), which is based on experimental work of various individuals. Wang *et al*. (1998) reports that magnetic pyrrhotite has a major peak near 430 cm^{-1} which distinguishes it from the pyrite peaks.

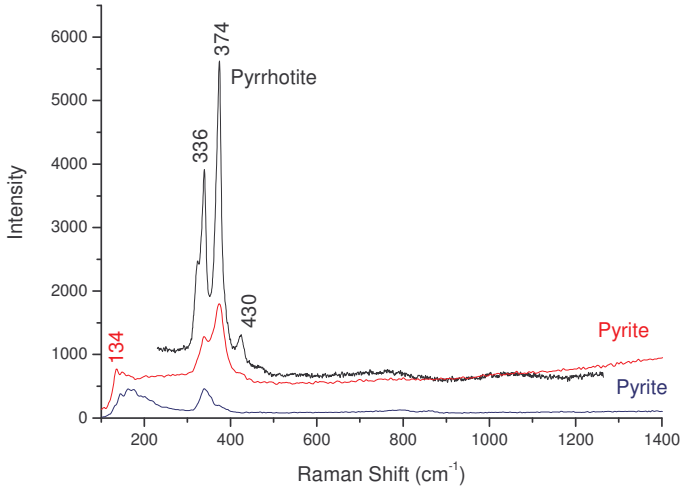
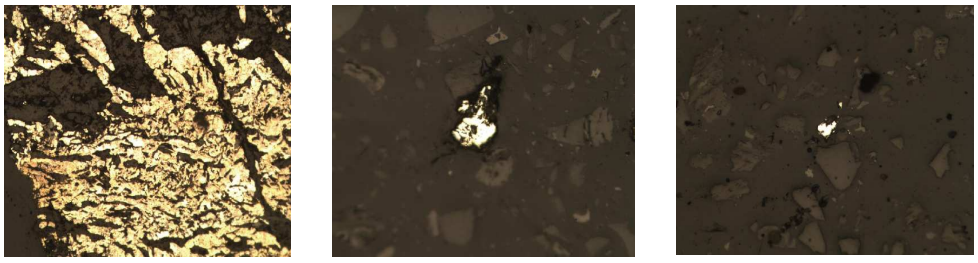


Figure 4.9: Raman scan of pyrrhotite vs. pyrite (Downs, 2006)



(a) Parent Coal (b) Untreated 74 µm Coal (c) Treated 74 µm Coal

Figure 4.10: Variation of pyrite occurrence in the coal*

*Olympus BX51 coupled to the Raman Bruker Senterra

Figure 4.10 shows the pyrite variation in the parent coal in comparison to the untreated and treated 74 µm size fraction. The parent coal was found to contain large lumps of the pyrite loosely bound to the outer coal body whilst the milled and screened coal contains pyrite particles found within the sample. The treated coal as seen in Figure 4.10(c) shows even tinier pyrite particles. Further experimental work is required to determine whether the pyrite is dissolving in the caustic solution whilst the core of the particle remains intact.

4.1.6 Theoretical phase changes with temperature

Haque (1999) reports that after a treatment time of 6.76 min, the pyrite reaches a maximum temperature of 1019 ºC, heating at a rate of 20 ºC/s. It is further reported that pyrrhotite attains a maximum temperature of 886 ºC in just 1.75 min. At a power of 500 W the pyrite was found to reach a temperature of 698 ºC after treating for 7 min whilst pyrrhotite reached 380 ºC in 4 min at the same power. These temperatures were measured for the isolated minerals. Relating data from literature to the coal samples treated during this research investigation and from the phase diagram in Figure 4.11, it is noted that above a temperature of 743 ºC, pyrite changes form and other Fe-S compounds occur. As it was not possible to measure the temperature of the pyrite in the coal sample, due to equipment availability and time constraints, pyrite structural and phase changes are difficult to predict. However, it could be postulated that at the maximum attained sample temperature of 136 ºC, with a 40 % sulphur decrease, the pyrite had to structurally adapt to form a small percentage of pyrrhotite and bcc (body centred cubic) iron as per phase diagram. Further experimentation, with accurate temperature measurements, is required in order to detect mineralogical phase changes in the treated sample.

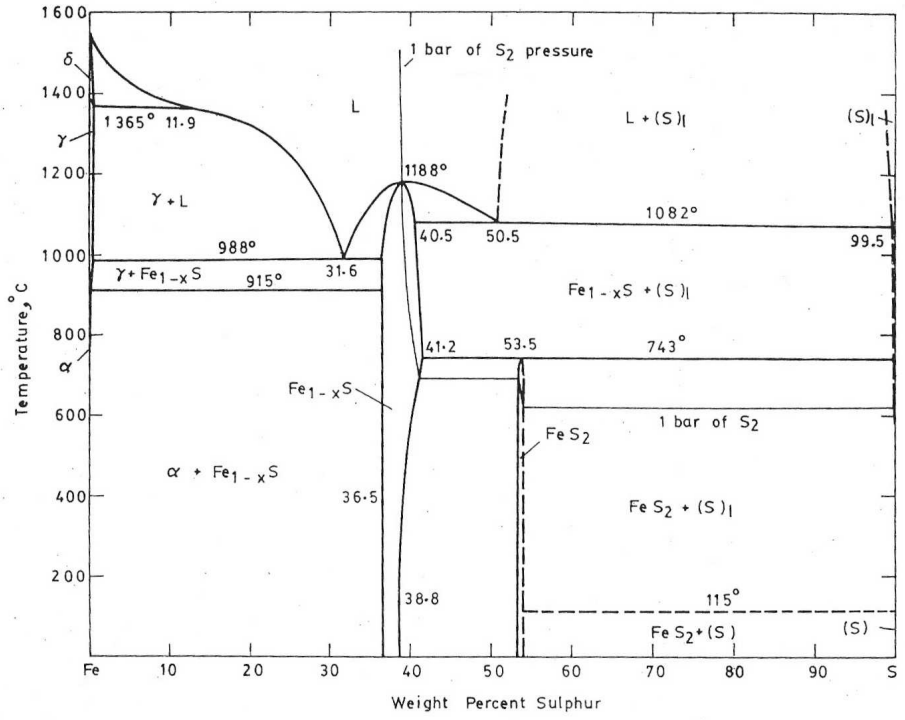


Figure 4.11: Phase Diagram of the Fe-S System (Raghavan, 1981)

4.1.7 Summary

In summary, optimization of the high sulphur coal occurred at 650 W and 10 min for the 212 µm size fraction whilst an optimum for the 74 µm size fraction was detected at 650 W and 8 min (Table 4.5). This allowed for an approximate sulphur removal of 40 %. No phase or structural changes were detected whilst calorific value and volatile matter decreased.

Size Fraction (µm)	Power (W)	Time (min)
600	-	-
212	650	10
74	650	8

Table 4.5: Optimum desulphurization points detected

4.2 Low Sulphur Coal

4.2.1 Petrographic Analysis

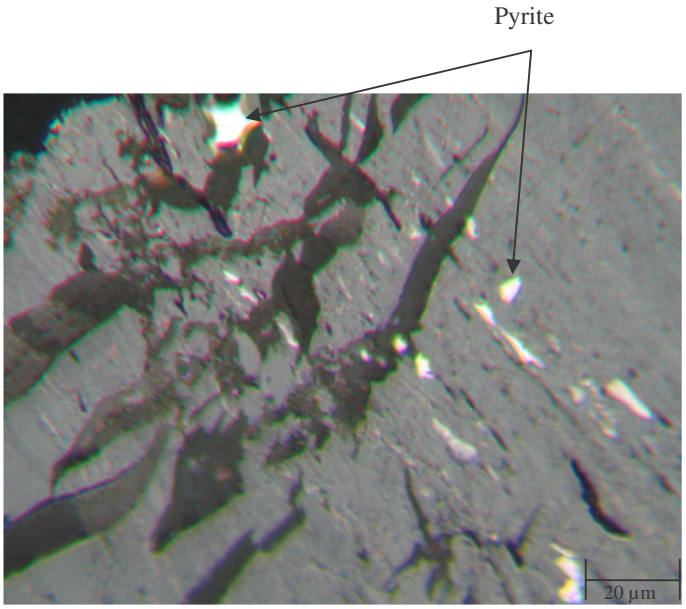


Figure 4.12: Pyrite occurrence in low sulphur coal

*Instrument: Leitz MPV-2 with Canon digital camera, reflected light, oil immersion lenses

From Figure 4.12 it can be noted that the pyrite occurrence in the low sulphur coal is bound within the organic matrix with most particles occurring smaller than 25 µm. This would indicate that it might be difficult to desulphurise the coal due to the nature of pyrite within the coal.

The low sulphur coal was identified as a high volatile bituminous coal based on proximate analysis. In terms of petrographics, the low sulphur coal is typical of a South African coal and classified as a medium rank C bituminous coal with vitrinite found in small quantities. Mineral group analysis showed the coal consisted of a high percentage of quartz and clays smaller than 25 fraction, attributing to high ash content. Table 4.6 summarizes the petrographic analysis on the low sulphur coal.

Petrographic Analysis: Low sulphur coal								
Mean Random Reflectance (% RoVmr)			0.69					
Standard Deviation			0.07					
Maceral Group Analysis (%)								
Vitrinite	Liptinite	SF[8]	Fusinite			Inertodetrinite		
18	6.8	38	4.8			32.4		
Microlithotype Group Analysis (%)								
Vitrite	Intermed[9]	SF/Fus[10]	Carbominerite			Sapropelic		
			(OM+MM)[11]	(>60% MM)		Ce[12]	Te[13]	De[14]
7.2	13	54.6	15.2	6.8		0	0.6	2.6
Mineral Group Analysis (%)								
Quartz/Clay			Pyrite			Carbonates			Clean Coal
<25	25-50	>50	<25	25-50	>50	<25	25-50	>50	
41.6	13.4	6.4	0.4	0	0	13	1.8	1.8	22

Table 4.6: Petrographic analysis of the Low sulphur coal

4.2.2 Microwave Treatment

Based on evidence from the high sulphur coal where the 600 µm size fraction results showed a large percentage error, only the 212 and 74 µm samples were analysed and used in the experimental study. Table 4.7 shows results for the average low sulphur parent coal. The proximate analysis 212 and 74 µm carried out on the low sulphur coal is combined to obtain the average for the parent sample and is shown in Appendix D.

[8] SF = Semi-Fusinite
[9] Intermed = Bi and Tri- maceral
[10] Fus = Fusinite
[11] OM = Organic matter/ MM = Mineral matter
[12] Ce = Clarite
[13] Te = Trimacerite
[14] De = Durite

The low sulphur coal has high mineral matter content as observed from the ash content of the sample even though the sulphur content was low. Decreased volatile matter content impacted on the coal quality decreasing the calorific value.

Proximate, Sulphur Analysis (wt % as received) and CV						
	Parent Coal	**212 µm**	**212 µm**	**212 µm**	**74 µm**	**74 µm**
Treatment Time (min)	-	8	6	4	6	4
Moisture	4.2	6.6	6.5	6.8	6.7	7.1
Ash	24.9	26.4	26.1	24.8	24.6	24.7
Volatile Matter	22.1	19.6	19.7	19.7	19.8	19.8
Fixed Carbon	48.8	47.4	47.7	48.7	48.9	48.4
Total Sulphur	0.55	0.38	0.33	0.31	0.35	0.31
CV MJ/kg	21.1	20.0	19.9	20.5	20.5	20.6

Table 4.7: Proximate analysis of treated low sulphur coal at 650 W

The low sulphur coal underwent microwave treatment for times in the region of the high sulphur coal optimum determined in Section 4.1.3 and summarised in Table 4.5. This was done to eliminate unnecessary experimentation whilst at the same time, monitoring low sulphur coal behaviour. 'Hotspot' formation was found to occur quicker than that of the high sulphur coal, with a maximum treatment time of 8 min for the 212 µm fraction and 6 min for the 74 µm fraction being possible. Selective heating property of the microwave attributed to the formation of the hotspots with the minerals heating at a faster rate than the coal thus causing the surrounding coal to ignite as minerals were found to be bound within the coal matrix rather than loosely situated. From this it is noted that regardless of the low volatile matter content and calorific value, the low sulphur coal ignited at a lower treatment time than that of the high sulphur coal.

From Table 4.7 we see that that an optimum desulphurisation point occurs at a time of 4 min with high sulphur content noted at a higher treatment time. After a treatment time of 4 min, the sample was still in a slurry form

whilst at 6 min and longer, the sample began to dry up. It could be postulated that the sulphur in the caustic solution dried up to a solid form at higher treatment times and was not removed after washing the sample with water to remove the caustic. Further investigation regarding this is required as the marginal error of the LECO analyzer was no more than 2 %. The homogeneity of the sample sent for analysis is also questionable.

In summary, a percentage reduction in sulphur of approximately 43 % using the caustic solution, for both coals was possible. The low sulphur coal did not desulphurise further after long treatment times but requires additional investigation to determine accurate desulphurisation behaviour.

4.2.3 XRD Analysis

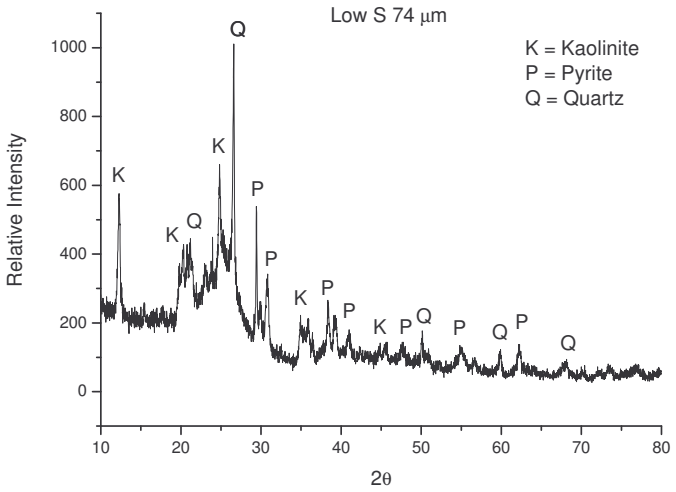


Figure 4.13: XRD analysis before treatment on the low sulphur coal

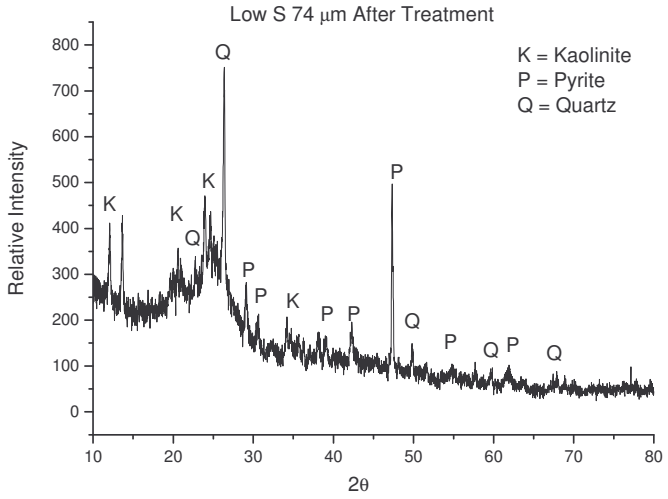


Figure 4.14: XRD analysis after treatment on the low sulphur coal

As with the high sulphur coal, no formation of new minerals or phases is observed (Figures 4.13 and 4.14). The broad baseline indicating the organic matter amorphous phase undergoes some change as seen with the shift in the XRD pattern after treatment. Further investigation of the structural characteristics of the organic matter phase is required.

4.2.4 Raman Analysis

Due to difficulty in locating the pyrite in the sample, Raman spectroscopy was carried out on a representative parent coal. Figure 4.15 shows the Raman scan of the low sulphur coal, together with the in-house pyrite spectrum and the high sulphur parent scan for comparative purposes.

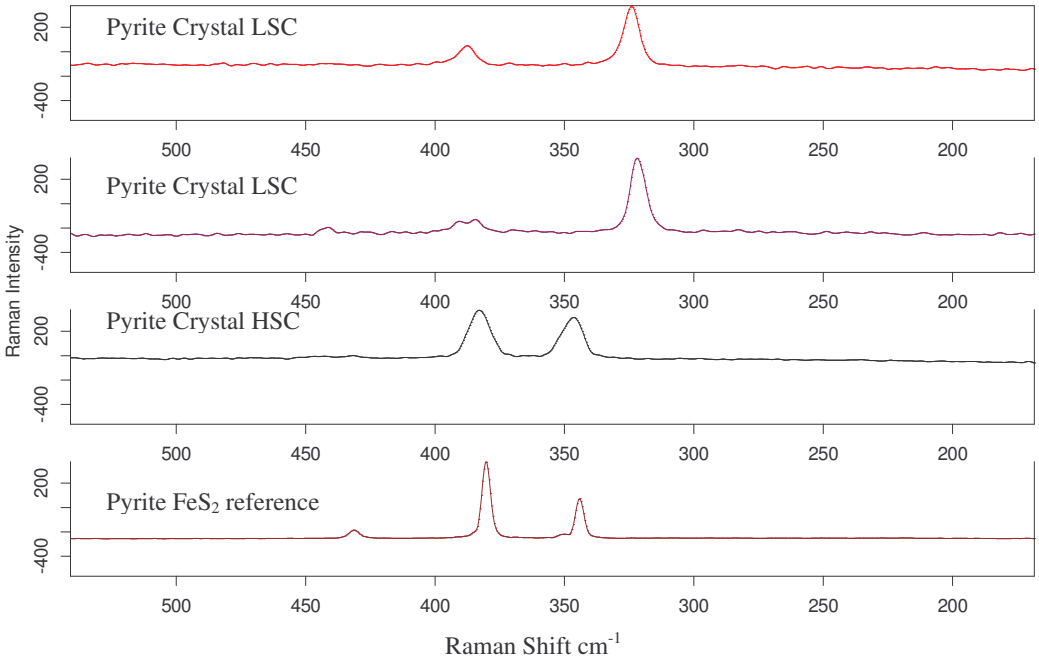


Figure 4.15: Raman scan of Low Sulphur coal

The low sulphur coal Raman scans showed shifts in the pyrite scans indicating a possible difference in the iron to sulphur ratio.

4.3 Stage 2: Further Experimental Work

The optimum desulphurisation rate as determined in Section 4.1.3 and summarised in Table 4.5 is 650 W and 10 min for the 212 µm size fraction and 650 W and 8 min for the 74 µm size fraction. Based on these optimum desulphurisation points, treatment using different alkali and mixtures thereof, as described in Section 3.8.2, were experimented with to increase the desulphurisation rate of coal. Increased solid to liquid ratio and alkali concentration were also considered. Table 4.8 summarises the results of the various microwave treatments undertaken.

Treatment	Potassium hydroxide[15]		Sodium hydroxide[16]		S:L 20:80[17]		Sodium chloride[18]		Calcium hydroxide[4]	
Temperature ºC	141	120	122	121	120	128	78	61	82	65
Particle size µm	212	74	212	74	212	74	212	74	212	74
Moisture %	9.7	9.8	8.5	8.0	12.4	11.9	5.4	-	-	-
Ash %	18.6	20.0	17.5	16.0	17.5	16.5	14.7	-	-	-
Volatile Matter %	26.0	26.9	27.9	28.7	26.9	26.8	30.9	-	-	-
Fixed Carbon %	45.7	43.3	46.1	47.3	43.2	44.8	49.0	-	-	-
Sulphur %	1.39	1.81	1.61	1.87	1.86	1.74	2.25	-	2.37	-
CV(MJ/kg)	22.8	22.2	23.6	24.0	22.5	22.8	24.6	-	-	-
% Reduction	58	45	51	43	44	47	32			

Table 4.8: Various microwave treatment results – stage 2

Utilization of potassium hydroxide as an aid in the desulphurisation process yielded a significant (average 51 % sulphur reduction) increase in sulphur removal from the treated coal. The potassium hydroxide solution was found to ignite at approximately 6 min into the treatment time and results thus presented, indicate sulphur removal for a treatment time of 5 min. Process time was reduced by half. This is a key factor in terms of energy (thus cost) savings.

The 400 g/L sodium hydroxide solution yielded a marginally lower sulphur removal compared to the standard treated coal but again ignited at a treatment time of 5 min. Viability of using increased solution concentration needs to be weighed against cost ratio of decreased process time. Effect of the increased solid to liquid ratio on the coal was found to be minimal.

[15] Experimental conditions: 650 W, 5 min
[16] 400 g/L NaOh used, experimental conditions: 650 W, 4 min
[17] 300 g/L sodium hydroxide used, experimental conditions corresponding to optimum power and time obtained per size fraction
[18] 300 g/L alkali used, experimental conditions corresponding to optimum power and time obtained per size fraction

Treatment with sodium chloride was found to lower the maximum treatment temperature significantly with no ignition of the coal occurring as well as very little impact on the sulphur value of the coal. Although the boiling point of sodium chloride is significantly higher than that of the other alkali used, the driving factor behind the no ignition theory was found to be a formation of a 'blanket' layer on the coal slurry thus preventing combustion from taking place as well as decreasing vaporization rate of the solution. From Table 4.8, a large decrease in the ash content of the coal when treated with sodium chloride solution only is noted. The question arises to whether sodium chloride plays a role in the removal of mineral matter or specific components and would require further investigation.

Treatment with the calcium hydroxide solution yielded results similar to those obtained using the sodium chloride solution. The difficulty of washing the coal was encountered, as calcium hydroxide is not water soluble and thus difficult to separate from the coal. Treatment using sodium chloride and calcium hydroxide solutions on the 74 µm particle size yielded a solid mass that could not be washed or analyzed.

Following the above results, a mixture of sodium chloride (300 g/L) and sodium hydroxide (300g/L), solid to liquid ratio of 30:70 was used to treat a 15 g coal sample (Results shown in Table 4.9). The addition of sodium chloride to the sodium hydroxide solution lowers the overall temperature whilst forming the 'blanket' layer as seen with the sodium chloride solution only. This allows the solution to be gradually heated thus increasing contact time between the coal and alkali. XRD analysis (Figures 4.16 and 4.17) did not detect formation of new minerals.

	Parent Coal	Sodium chloride and Sodium hydroxide
Temperature ºC	-	136
Particle size µm	Average	212
Moisture %	4.0	9.3
Ash %	18.5	17.0
Volatile Matter %	32.0	27.4
Fixed Carbon %	45.5	46.3
Sulphur %	3.3	1.37
CV (MJ/kg)	24.6	22.5
% Reduction	-	52

Table 4.9: Sodium chloride and Sodium hydroxide microwave treatment results on high sulphur coal

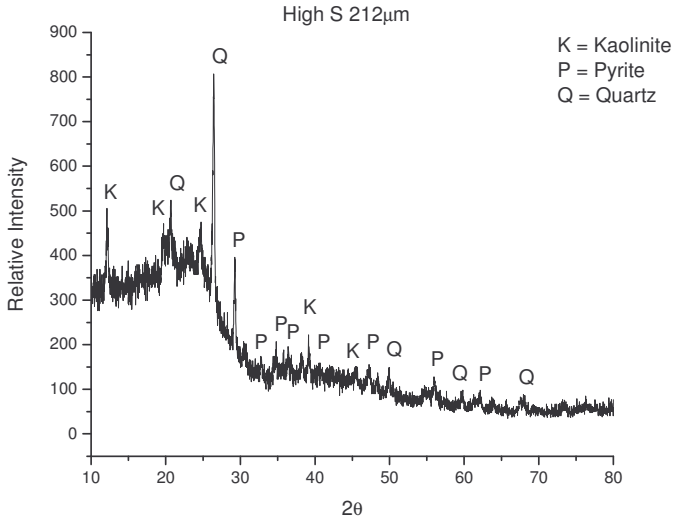


Figure 4.16: XRD Scan of 212 µm before treatment

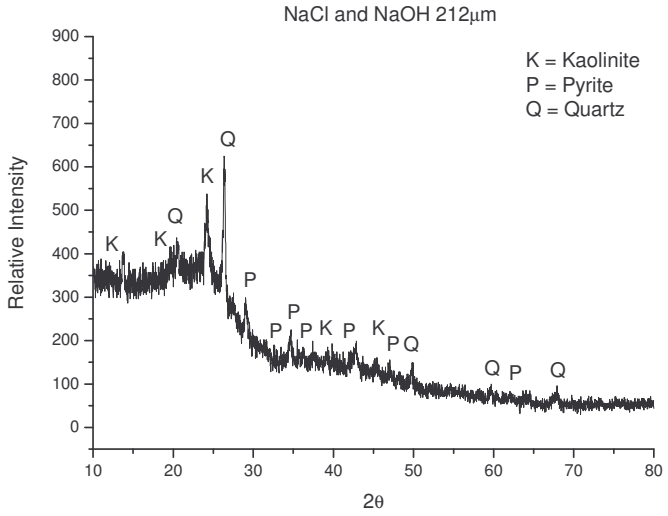


Figure 4.17: XRD Scan of 212 μm after treatment with sodium chloride and sodium hydroxide

4.4 Conventional Leaching

Conventional leaching (Table 4.10), carried out on a stovetop (625 W, 50 Hz, efficiency of 0.38), and using energy inputs corresponding to that of the microwave, yielded good desulphurisation results. This is possibly due to the gradual increase in temperature thus allowing the alkali to penetrate the coal to a large extent which in turn allows the sulphur located within the coal structure to be more readily removed.

Further experimental work has been proven to be successful using potassium hydroxide treatment and a mixture of sodium hydroxide and sodium chloride. These yielded average sulphur reductions of 52 %. Additional experimental work is required in order to optimize the treatment using potassium hydroxide as well as the mixture of alkali.

	Microwave treatment		Conventional treatment	
	212 µm	**74 µm**	**212 µm**	**74 µm**
Temperature ºC	-	-	120	115
Moisture %	7.8	7.0	12.0	9.0
Ash %	17.9	20.6	17.9	18.6
Volatile Matter %	27.6	27.4	27.0	28.1
Fixed Carbon %	46.6	45	43.1	44.3
Sulphur %	1.87	1.89	1.30	1.43
Calorific Value (MJ/kg)	22.4	22.6	21.8	23.0
Treatment Time (min)	10	8	28	22
% Reduction	43	43	61	57

Table 4.10: Conventional leaching results

Chapter Five: Conclusion and recommendations

5.1 Conclusion

The focus of the project was to desulphurise South African coal using low power microwave energy. Optimum desulphurisation points for different size fractions were determined by treating the coal together with an alkali in a microwave oven. Time and power were varied in increments of 2 min and 20 % power reduction respectively, until ignition occurred. After treatment the samples underwent analysis to determine extent of desulphurisation and change in coal characteristics.

The use of microwave energy to desulphurise coal has been proven to be feasible on South African coal operating at a power of 650 W and frequency of 2.45 GHz in a multimode applicator. The high and low sulphur coals showed an approximate sulphur removal of 40 %. The volatile matter and calorific value decreased by 14 % and ±1 MJ/kg respectively, impacting on the coal quality. An optimum desulphurisation point at 650 W and 10 min occurred for the high sulphur coal whilst the low sulphur coal was found to desulphurise significantly after a treatment time of 4 min at the same power. This suggests that increased sulphur content of the coal makes it longer and more difficult to desulphurise.

The comparitive sulphur removal values for the high and low sulphur coals indicate that the mode of occurrence of pyrite in the coal does not appear to affect desulphurisation, in this instance. In comparison to conventional treatment, the microwave process showed an improved process time but decreased sulphur removal. Treatment time was reduced by a third when using the microwave unit.

Rowson and Rice (1990) showed that a 60 % sulphur removal is possible after irradiating the coal for two 60 s exposures using a 300 g/L caustic

solution and a microwave power of 500 W. This is a very short treatment time at a lower power compared to what was possible on the two South African coals tested here.

La Union (Chile) coals studied by Araya *et al.* (1981) yielded a 30 % sulphur decrease after conventional leaching for 8 hrs. South African bituminous coals yielded a sulphur removal of over 40 % after approximately 25 min of treatment.

Further experimental work was carried out based on the optimum conditions, in order to further improve the sulphur reduction. Treatment using potassium hydroxide and mixtures of sodium chloride and sodium hydroxide yielded higher sulphur removal than that of the caustic solution but requires further investigation in order to optimize the desulphurisation process. In comparison to coals investigated by other authors, South African coal requires longer microwave treatment times whilst yielding lower sulphur removal.

5.2 Recommendations

The primary focus of the present study was to determine the response of South African coal to desulphurisation using microwave energy and the extent of desulphurisation. Whilst this proved to be feasible, potential exists for improvement in the desulphurisation treatment in order for the process to be industrially (and economically) viable. Further experimental studies using mixtures of alkali are required, in order to determine optimum desulphurisation points. Mossbauer spectroscopy, which had not been undertaken due to time constraints and the limited availability of the instrument while under repairs, is recommended in order to accurately determine change in the Fe-S structure. Sulphur form analysis after treatment requires further investigation to evaluate sulphur removal from coal. Further experimental analysis in order to gauge pyrite and alkali

interactions under microwave irradiation is required together with particle size and microwave power effects. In addition to this, kinetics and penetration depth of the alkali into the coal particle will further assist in improving the desulphurisation process whilst preserving the coal quality.

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Appendix A: Experimental observations

Time min	2	4	6	8	10	12	14	16	18
600 µm									
900 W				X	X	X	X	X	X
650 W						X	X	X	X
400 W						X	X	X	X
200 W			56 ºC[19]	62 ºC	67 ºC	80 ºC	114 ºC	X	X
100 W	38 ºC	43 ºC	46 ºC	54 ºC	30 ºC	61 ºC	45 ºC	65 ºC	X
212 µm									
900 W				X	X	X	X	X	X
650 W						X	X	X	X
400 W						X	X	X	X
200 W			60 ºC	68 ºC	74 ºC	109 ºC	X	X	X
100 W	32 ºC	34 ºC	40 ºC	30 ºC	34 ºC	42 ºC	64 ºC	70 ºC	X
74 µm									
900 W				X	X	X	X	X	X
650 W						X	X	X	X
400 W						X	X	X	X
200 W			68 ºC	82 ºC	94 ºC	98 ºC	X	X	X
100 W	42 ºC	32 ºC	60 ºC	72 ºC	30ºC	36 ºC	86 ºC	119 ºC	X

Table A1: Matrix of experimental data

X = ignited

[19] Temperature measured with a laser gun. Readings are inaccurate due to the angle of reflection not constant. During early stages of the experimental, Laser gun had not been available

Appendix B: Raw Data for Graphs

	600 µm	212 µm	74 µm
Time	**% Sulphur (total)**		
900 W			
2	4.36	2.67	2.19
4	3.17	2.61	2.43
6	3.93	1.37	2.35
650 W			
2	4.95	2.75	2.52
4	4.75	2.02	2.26
6	4.31	2.60	2.11
8	4.24	2.01	1.89
10	3.73	1.87	
400 W			
2	3.87	2.29	2.31
4	3.87	2.28	2.32
6	5.03	2.13	2.35
8	4.61	2.17	
10	4.67	2.03	
200 W			
2	4.71	2.41	2.33
4	3.94	2.47	2.08
6	5.29	2.24	2.41
8	6.04	2.35	2.38
10	4.24	2.34	2.28
12	4.18	1.85	2.12
100 W			
2	3.47	2.16	2.10
4	3.56	2.94	2.48
6	4.05	2.45	2.32
8	2.41	2.22	2.37
10	2.48	1.84	2.38
12	5.75	2.50	2.48
14	4.88	2.11	2.53
16	4.76	2.15	1.99

Appendix C: XRD High Sulphur Coal

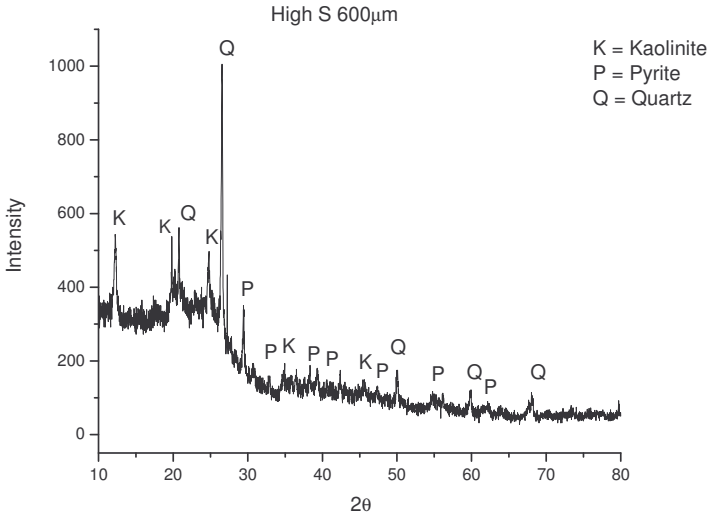

Figure C1: XRD Scan of 600 μm before treatment

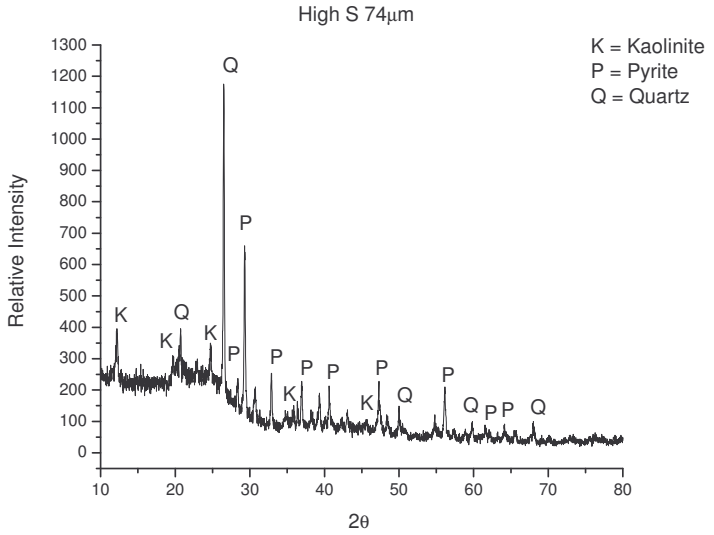

Figure C2: XRD Scan of 74 μm before treatment

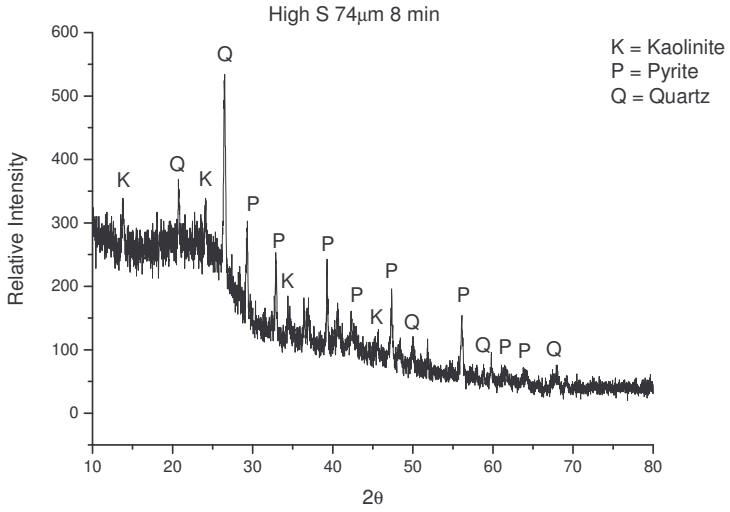

Figure C3: XRD Scan of 74 μm after treatment

Appendix D: Proximate Analysis data for the Low Sulphur Coal

Proximate Analysis (wt % as received)			
	Average Parent Coal	**212 µm**	**74 µm**
Moisture	4.2	4.5	3.9
Ash	24.9	25.2	24.6
Volatile Matter	22.1	22.0	22.2
Fixed Carbon	48.8	48.3	49.3
Sulphur	0.55	0.59	0.50
CV (MJ/kg)	21.1	21.1	21.2

Table D1: Proximate analysis for the Low Sulphur Coal