Sulphur self-retention and sulphur dioxide capture with active calcium minerals in mineral-rich coals

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Dissertation submitted in partial fulfilment of the requirements for the degree of Master of Engineering at the Potchefstroom Campus of the North-West University.

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July 2011
Potchefstroom
“In a world where there is so much to be done, I felt strongly impressed that there must be something for me to do.”

Dorothy Dix
DECLARATION

I, Dursman Mchabe do hereby declare that the dissertation with the title: Sulphur self-retention and sulphur dioxide capture with active calcium minerals in mineral-rich coals, submitted in partial fulfilment of the requirements for the degree of Master of Engineering at the Potchefstroom Campus of the North-West University is my work and has not been submitted at any other university either in whole or in part.

Signed at Potchefstroom on the .......... day of .............................................2012

..............................................
D. Mchabe
ACKNOWLEDGEMENTS

I would like to recognise, with gratitude, the support received from all those who assisted me in making this research a success. In particular, I would like to thank the following:

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ABSTRACT

In order to provide information for the development of clean coal technology, the sulphur self-retention and sulphur dioxide capturing properties of minerals present in low grade coals was investigated. This study consisted of detailed mineral analyses of coal and ash samples using results obtained from QEMSCAN and separate retention (coal) and capture (ash) experiments with laboratory scale reactors. Typical South African coal samples were used in this study. The ash content varied between 37.0 wt % and 47.9 wt % with active calcium oxide (from calcite and dolomite) present between 1.22 wt % and 4.92 wt %. The total sulphur content ranged between 0.60 wt % and 1.90 wt % and was distributed between sulphate minerals, pyrite and organically associated minerals in the coal macerals. The calcium to sulphur ratio based on the active calcium ranged from 0.64 to 3.20. Sulphur self-retention experiments (using powders of particle sizes ranging from 212 µm to 300 µm) were carried out in a Packed Bed Balance Reactor at 900 ºC at atmospheric pressure with dry air for a period of 12 h. Transformation of a large fraction of the calcium bearing minerals to sulphates was evident with total sulphur self-retention between 22.9% and 66.9% and the formation of calcium containing non-crystalline phases.

Thermogravimetric Analyzer experiments using 1 mm diameter coal particles were carried out with the ash prepared (in situ with air) prior to the actual sulphation determinations. After attaining a stable ash mass, the gas stream was changed to the sulphur dioxide containing mixture (3000 ppm SO₂, 8.0% CO₂, 8.0% O₂ and 83.7% N₂) and the increase in mass as a result of the reaction of sulphur dioxide (and oxygen) with calcium oxide (calcite and dolomite) was recorded. Conversion of active calcium bearing phases in the presence of sulphur dioxide containing gas mixture, similar to the gas released during fluidised bed combustion, was employed to evaluate the desulphurisation potential of the coal ashes, and it was found that nearly 40% of the active calcium oxide was converted after 90 min reaction time at 900 ºC and that no blocking of pores occurred as a result of solid phase changes. A mathematical model based on the shrinking core model with diffusion through the product layer as the determining mechanism was found to describe the overall reaction rate.
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
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<tbody>
<tr>
<td>A, B</td>
<td>Dimensionless parameters in the USC model</td>
<td>-</td>
</tr>
<tr>
<td>b</td>
<td>Stoichiometric ratio</td>
<td>-</td>
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<tr>
<td>C_{SO_2}</td>
<td>SO_2 concentration</td>
<td>mol/m^3</td>
</tr>
<tr>
<td>c_{CaO_{Active_Ash}}</td>
<td>Active CaO in ash</td>
<td>wt %</td>
</tr>
<tr>
<td>c_{CaO_{Active_Coal}}</td>
<td>Active CaO in coal</td>
<td>wt %</td>
</tr>
<tr>
<td>c_{Ca_{Active_Ash}}</td>
<td>Active Ca in ash</td>
<td>wt %</td>
</tr>
<tr>
<td>c_{Ca_{Active_Coal}}</td>
<td>Active Ca in coal</td>
<td>wt %</td>
</tr>
<tr>
<td>D_{eff}</td>
<td>Effective diffusivity</td>
<td>m^2/min</td>
</tr>
<tr>
<td>k_s</td>
<td>Reaction rate constant</td>
<td>m/min</td>
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<td>M(CaCO_3MgCO_3)</td>
<td>CaCO_3MgCO_3 molecular weight</td>
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<tr>
<td>M(SO_3)</td>
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</tr>
<tr>
<td>n_{SO_2}</td>
<td>SO_2 molar flow rate</td>
<td>mol/min</td>
</tr>
<tr>
<td>R_p</td>
<td>Ash particle radius</td>
<td>m</td>
</tr>
<tr>
<td>S_{Ash}</td>
<td>Sulphur content in ash (on coal basis)</td>
<td>mg/100 mg coal</td>
</tr>
<tr>
<td>S_{Coal}</td>
<td>Sulphur content in coal</td>
<td>mg/100 mg coal</td>
</tr>
<tr>
<td>t</td>
<td>Time to achieve conversion X</td>
<td>min</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>t_{dif}</td>
<td>Diffusion time scale (product layer)</td>
<td>min</td>
</tr>
<tr>
<td>t_{kin}</td>
<td>Chemical kinetics time scale</td>
<td>min</td>
</tr>
<tr>
<td>W_0</td>
<td>Weight of sample before introducing reaction gas</td>
<td>wt %</td>
</tr>
<tr>
<td>W_t</td>
<td>Weight of sample at a given time</td>
<td>wt %</td>
</tr>
<tr>
<td>c_{CaMgO}</td>
<td>Mass fraction of CaMgO</td>
<td>wt %</td>
</tr>
<tr>
<td>c_{CaO}</td>
<td>Mass fraction of active CaO (equivalent)</td>
<td>wt %</td>
</tr>
<tr>
<td>c_{X_{CaO}}</td>
<td>Degree of conversion of active CaO</td>
<td>-</td>
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</tbody>
</table>
Greek Letters

$\varepsilon$  
Sorbent particle porosity  
m$^3$/m$^3$

$\rho_{\text{Ash}}$  
Density of ash  
g/m$^3$

$\rho_{\text{CaO}}$  
Density of CaO  
g/m$^3$

$\rho_{\text{CaO mol}}$  
Molar concentration of CaO  
 mol/m$^3$

Subscripts

0  
Initial

dif  
Intra-particle diffusion

eff  
Effective

kin  
Kinetics

mol  
Molecular

Abbreviations

ACT  
Advanced Coal Technology

AEP  
Ash Effect Predictor

AFBC  
Atmospheric Fluidised Bed Combustion

ASTM  
American Society for Testing and Material

BFBC  
Bubbling Fluidised Bed Combustion

C & C  
Capital charge

CCSD  
Cooperative Research Centre for Coal in Sustainable Development

CCSEM  
Computer Controlled Scanning Electron Microscope

CCT  
Clean Coal Technologies

CFBC  
Circulating Fluidised Bed Combustion

CSIRO  
Commonwealth Scientific and Industrial Research Organisation

D-R  
Dubinin-Radushkevich data analysis method

ECE-UN  
Economic Commission for Europe of the United Nations

EDX  
Energy Dispersive X-ray

Eskom  
Electricity supply commission

FBC  
Fluidised Bed Combustion

FGD  
Flue Gas Desulphurisation

HTTFIR  
High-temperature tube furnace and infrared detection

ICP – AES  
Inductively Coupled Plasma Atomic Emission Spectrometry

ICP – MS  
Inductively Coupled Plasma Mass Spectrometry
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>IGCC</td>
<td>Integrated Gasification Combined Cycle</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LCFB</td>
<td>Lurgi Circulating Fluidised Bed</td>
</tr>
<tr>
<td>NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Nitrogen Oxides</td>
</tr>
<tr>
<td>O &amp; M</td>
<td>Operation and maintenance</td>
</tr>
<tr>
<td>PBBR</td>
<td>Packed Bed Balance Reactor</td>
</tr>
<tr>
<td>PFBC</td>
<td>Pressurised Fluidised Bed Combustion</td>
</tr>
<tr>
<td>QEMSCAN</td>
<td>Quantitative Evaluation of Mineralogy by Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SABS</td>
<td>South African Bureau of Standards</td>
</tr>
<tr>
<td>SCM</td>
<td>Shrinking Core model</td>
</tr>
<tr>
<td>SDS</td>
<td>Spray dry scrubber</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Sulphur Oxides</td>
</tr>
<tr>
<td>*SSR</td>
<td>Sulphur Self-Retention</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analyser</td>
</tr>
<tr>
<td>USC-VED</td>
<td>Unreacted Shrinking Core model with Variable Effective Diffusivity</td>
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<tr>
<td>VAC</td>
<td>Van Alphen Consultancy</td>
</tr>
<tr>
<td>WLS</td>
<td>Wet limestone scrubber</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray florescence</td>
</tr>
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</table>

* - Defined in glossary

Nomenclature for petrographic analysis is provided in respective tables
GLOSSARY

Only very important definitions are provided.

**Active calcium oxide in coal** (CaO\(_{\text{Active,Coal}}\)): is the equivalent calcium oxide that can be found in the calcium carbonate and dolomite of coal. It is considered to have the potential to react with sulphur dioxide according to equation 5.1. Its evaluation is discussed in Section 4.4.2, and Equation A1 (Appendix A) was employed. The results are presented in Figure 4.4, Tables 4.12 and A1 (Appendix A), and discussed in Section 4.4.2.

**Active calcium oxide in ash** (CaO\(_{\text{Active,Ash}}\)): is the equivalent calcium oxide formed as the product of the thermal decomposition of calcium carbonate and dolomite during coal combustion. It is considered to have the potential to react with sulphur dioxide according to equation 5.1. Its evaluation is discussed in Section 4.4.2, and Equation A2 (Appendix A) was employed. The results are presented in Figure 4.4, Tables 4.12 and A1 (Appendix A), and discussed in Section 4.4.2.

**Active calcium in coal** (Ca\(_{\text{Active,Coal}}\)): the equivalent calcium found in the active calcium oxide of coal. The basis of its evaluation is discussed in Section 4.4.2, and Equations A5 was employed. The results are presented in Table A1.

**Active calcium in ash** (Ca\(_{\text{Active,Ash}}\)): the equivalent calcium found in the active calcium oxide of ash. The basis of its evaluation is discussed in Section 4.4.2, and Equations A6 was employed. The results are presented in Table A1.

**Conversion of active CaO** (X): the ratio of moles of product calcium sulphate to moles of reactant active calcium oxide (equivalent) during sulphur dioxide capture. Its evaluation is discussed in Section 5.4. The results are presented in Figures 5.4 – 5.8 and discussed in Sections 5.4.1 - 5.4.2.

**Sulphur dioxide capture**: the heterogeneous reaction of the gaseous sulphur dioxide (in the presence of oxygen), occurring in the ambient gas mixture inside the reactor,
with the (sorbent) solid active mineral(s) (e.g. active CaO) in order to produce stable sulphur compounds that remain in coal ash (e.g. CaSO₄, according to equation 5.1).

Sulphur self-retention %: the percentage of the sulphur retained in coal ash after coal has been combusted. Its evaluation is discussed in Section 4.4.4, and Equation A9 was used. The results are presented on Figure 4.6 and Table A1, and discussed in Section 4.4.4. The same approach was used by Grubor and Manovic (2002) to evaluate SSR% on the Kolubara coal.
LIST OF PUBLICATIONS
(Conference proceedings)


“In the universe, there are things that are known, and things that are unknown, and in between, there are doors.”

William Blake
1 GENERAL INTRODUCTION

This chapter presents an introduction to the research undertaken using ashes from low grade coals for the removal of sulphur (as sulphur dioxide). The background and motivation is presented in Section 1.1, with emphasis on the sulphur self-retention and sulphur dioxide capture using ashes derived from coal.

The main objective and auxiliary objectives are presented in Section 1.2. This covers investigating the parameters influencing sulphur self-retention and sulphur dioxide capture while also identifying and quantifying the mineral phases that are involved in sulphur self-retention and sulphur dioxide capturing during coal combustion and desulphurisation. It also includes determining and evaluating the reaction rate model. The scope of the study is presented in Section 1.3.

1.1 BACKGROUND AND MOTIVATION

Fossil fuels (especially coal) are largely considered to be the main source of energy and will most likely remain so for the foreseeable future, despite endeavours to utilise alternative renewable sources of energy. Fossil fuels will continue to supply energy for power generation, transportation, industry and domestic requirements (Ashman & Mullinger, 2005). Unfortunately, the generation of pollutants is normally associated with coal combustion and gasification and can influence the final economics of the process.
South African coals, which are in large supply (mined and discards) with relatively large amounts of sulphur compounds, also have a high inertinite content, inertinite being an inert maceral whose combustion and gasification efficiencies are poor. The combustion of such coals in pulverised coal combustion boilers is not efficient due to low ignition and burnout properties of the inertinite, the high ash content, and the production of pollutants such as sulphur and nitrogen compounds necessitating uneconomical down-stream processing (Kaitano, 2008). Coal discards are produced as a by-product from the beneficiation processes of different grades of mined bituminous coal, where good quality coal is for export and some for local consumption. The lowest grade of material which has been discarded presents a challenge to all coal-based industries (power and liquid fuels). New technologies incorporating Clean Coal Technologies (CCTs) need to be developed and implemented in order to utilise these discards. The poor quality discards are usually associated with high sulphur and ash content (Kaitano, 2008). However, in order to meet the anticipated growth in energy demand, South Africa will have to use inferior quality fuels, coal discards and low grade coals which may be available at lower cost for economic electrical power generation (Mukondiwa, 2007).

There is a great need to regulate emissions from coal combustion systems. Owing to both the global and national clean energy drive, the removal of sulphur and nitrogen compounds (SO$_2$, H$_2$S and NO$_x$) from coal combustion and gasification needs to be addressed seriously (Mukondiwa, 2007). A variety of technologies may be used to eliminate sulphur dioxide emission from power plants, namely coal pre-cleaning technologies and technologies promising in situ sulphur dioxide reduction by added sorbents and cleaning of flue gas (Manovic et al., 2006).

Calcium containing minerals present in coals can retain sulphur compounds (sulphur self-retention) during combustion at mild temperatures as in fluidised bed combustion (750 ºC to 900 ºC) and thus decrease the amount of added sorbents (dolomites) required to reduce the emission of sulphur dioxide (Fuertes et al., 1992; Manovic et al., 2006). Sulphur self-retention is dependent on the composition and physical structure of the minerals and the operating conditions. It is a complex system since the minerals’ properties change during combustion (Vuthalu & French, 2008), and the
decomposition of sulphur (organic and inorganic forms) compounds in the coal is highly variable.

It has been reported that calcium oxide (from carbonates, calcite, dolomite) and organically associated calcium (exchangeable ions) are active minerals for sulphur dioxide retention (Grubor & Manovic, 2002; Sheng et al., 2000 & 1998) while the calcium present in clays and silicates is inactive (e.g. CaFe-aluminosilicates) (Conn et al., 1993). The reactivity of the base oxides (MgO+Na₂O+K₂O) has also been examined under a wide range of conditions and found to be negligible under fluidised bed conditions (Grubor & Manovic, 2002; Sheng et al., 2000). The transformation of minerals during combustion can be significant and the resulting effect on the distribution of the available calcium between the active and inactive calcium minerals needs to be examined. Thus, for a meaningful study involving sulphur removal using the minerals in coal, a complete assessment and classification of calcium minerals present would be necessary.

The determination of minerals in coals and coal ash can be accomplished using mainly X-ray diffraction (XRD), Computer Controlled Scanning Electron Microscope (CCSEM) and Quantitative Evaluation of Mineralogy by Scanning Electron Microscopy (QEMSCAN) (Gupta, 2007; Liu et al., 2005 & 2007a). These techniques have been used for studies involving the effect of high concentrations of minerals in coal on the physical operation of high temperature combustion and gasification processes. From reviews on the applicability of the different methods available (Vuthaluru & French, 2008; Van Alphen, 2007; Liu et al., 2005 & 2007a), Quantitative Evaluation of Mineralogy by Scanning Electron Microscopy (QEMSCAN) can be considered the most suitable technique for examining mineral behaviour in coals and ashes. This method includes the measurement of mineral/organic matter association, crystalline and amorphous minerals.

The use of coal ash for sulphur dioxide capture from gases (desulphurisation) produced by coal processes is both economic and environmentally attractive given that it will be produced in large quantities in the future as more low grade coals are used. Coal ashes from combustion and gasification with residual calcium minerals (after retention of sulphur) can be used either with or without added sorbents to
remove sulphur dioxide from flue gases (Grubor et al., 2003; Lee et al., 2005; Mukondiwa, 2007; Fernández et al., 1997). The initial active calcium content of the ash and the associated transformation of all minerals affecting the distribution during the sulphation process are also very important. There have been many studies on sulphation with limestones and dolomites that have a high concentration of calcium oxide and carbonates. In these studies calcium was predominately in the active form, which is very different from coal ashes (Iisa et al., 1992; Yrjas et al., 1995). There are numerous publications on sulphur dioxide capture using coal ash or coal ash with other sorbents, but very few consider the effect of the different forms of the calcium (Lee et al., 2005, Mukondiwa, 2007; Zhang et al., 2003).

Modelling of the overall reaction kinetics of sulphur dioxide capture with dolomites based on the shrinking core concept with diffusion through the product layer and chemical reaction on the surface of the core has been successfully accomplished. Zevenhoven et al. (1998) considered the increased volume resulting from the conversion of calcium oxide to calcium sulphate and calculated a variable effective diffusion co-efficient based on diffusion through pores and the product layer. Modelling of sulphur dioxide capture with coal ashes (low calcium content) using the shrinking core model has been published (Grubor et al., 2003; Lee & Koon, 2009).

1.2 OBJECTIVES OF INVESTIGATION

The overall objective of this investigation was to examine the sulphur removal performance of mineral-rich coals and ashes (with suitable calcium containing minerals) at moderate temperatures (750 °C to 900 °C) in order to contribute to the development of fluidised bed combustion with minimal sulphur dioxide emission. To achieve this objective the sulphur retention performance during coal combustion and the sulphur dioxide capture performance of ashes were investigated separately. The specific objectives are listed as follows:

(1) The determination of detailed chemical, physical, petrographic and mineralogical properties of the selected coal and ash samples to provide a thorough characterisation of the samples used.
(2) The determination of the sulphur self-retention properties of the coals based essentially on the mineral analysis (QEMSCAN) of the coals and ashes together with combustion experimentation carried out in a laboratory Packed Bed Balance Reactor (PBBR).

(3) The determination of the sulphur dioxide capture properties of coal ashes following combustion and the determination of a suitable reaction rate model. This consisted of the assessment of the conversion of active calcium oxide (equivalent) to calcium sulphate with a thermogravimetric analyser using a dilute mixture of sulphur dioxide.

Typical South African coal samples and their corresponding ashes, with active calcium oxide concentrations (equivalent) less than 10 wt % were selected for this study.

1.3 SCOPE

The effective design and operation of coal combustion systems is heavily dependent on the complementary design and operation of efficient gas cleaning systems, including particulates, SO\textsubscript{x} and NO\textsubscript{x} capture systems. Along with consideration of clean coal technologies (CCTs) for the utilisation of low grade coal, there is great need to investigate the sulphation capacity of coal ashes under atmospheric conditions and rate their effectiveness as sorbents.

In Chapter 2, an overview of the available literature on fluidised bed combustion and sorbent sulphation is presented. Review of clean coal technology, sulphur compounds in coal and the mineral analysis are given. Sulphur self-retention and capture as well as modelling of sulphation results are also reviewed.

The experimental apparatus and the methods used are described in Chapter 3. A Packed Bed Balance Reactor (PBBR) and Quantitative Evaluation of Mineralogy by Scanning Electron Microscopy (QEMSCAN) were used to investigate sulphur self-retention. A high temperature (maximum temperature of 1700 °C) thermogravimetric analyser (TGA) was used to investigate sulphation. In this process, the coal sample
was first combusted and the resulting ash was sulphated with a simulated flue gas mixture containing a low concentration of SO₂.

In Chapter 4, the coal and the corresponding ash characterisation and sulphur self-retention results are presented and discussed. Chapter 5 presents the coal combustion and sulphur dioxide capture results and modelling. The results of the experiments are then discussed with respect to findings from other researchers. The validity of the shrinking core model with diffusion through the product layer is also demonstrated in Chapter 5. Finally, in Chapter 6 conclusions on the results of the study, contributions to the knowledge base of coal science and technology and subsequent recommendations are given.
“In literature as in love, we are astonished at what is chosen by others.”

Andre Maurois
LITERATURE SURVEY

2.1 INTRODUCTION

In this literature chapter, a review of current developments in the utilisation of coal as a primary source of energy is given. The related environmental effects and the possibility of sulphur self-retention and sulphur dioxide capture under fluidised bed combustion conditions using coal ashes as sorbent are explored. An overview of clean coal technology is presented in Section 2.2, which focuses on the advantages of clean coal technologies (CCTs) and fluidised bed combustion (FBC). Section 2.3 gives an overview of the types of sulphur found in coal, that is, organic and inorganic based sulphur. Section 2.4 gives a review of coal and ash mineralogy and mineral analysis techniques. Sections 2.5 and 2.6 present a review of sulphur dioxide retention and capture respectively. Finally, Section 2.7 gives a review of models which can be applied to explain the sulphur dioxide capture results.

2.2 CLEAN COAL TECHNOLOGY

Pulverised coal combustion leads to production of undesirable sulphur based gaseous pollutants. Abatement of these gases has become a key factor in determining the continued use of coal as a source of energy. Coal usage needs to address the current stringent environmental protection drive and legislation. Thus, clean coal technology has given a new lease of life to coal based energy sources. The answer to various environmental concerns linked to the use of coal as a source of energy is seen in clean coal technologies (CCTs). These technologies offer a route to a low emission future.
while allowing the continued sustainable usage of the most abundant and affordable of all fossil fuel, coal (WCI, 2005).

The interest in the research and development of technologies for lowering the emission of pollutants like nitrogen and sulphur oxides is quite advanced and well documented (Manovic et al., 2006). Some (SO$_2$ and CO$_2$) of the clean coal technologies that are at different stages of development and application are:

- **Post Combustion Capture**, which occurs when gases and particulates are removed from the flue gas before it is discharged into the atmosphere. This is generally an expensive exercise and the equipment used for flue gas desulphurisation is usually large. The desulphurisation systems can be classified as either regenerable or non-regenerable. Typical non-regenerable FGD systems include limestone/gypsum systems (Nygaard et al., 2004) and seawater scrubbing processes (Williams, 1999). Regenerable systems include the Wellman-Lord Process (Buzek et al., 1998).

- **Oxy-coal combustion**, which tries to eliminate the expensive process of post treatment of gases by using oxygen instead of air for the combustion process. The flue gas produced is concentrated with CO$_2$, which can be easily stored following liquefaction.

- **Circulating fluidised bed combustion**, in which limestone and dolomite are added to the circulating fluidised bed combustors for the removal of SO$_2$ in-situ. If coal ash has high calcium content self-retention of SO$_2$ is believed to take place and the retention process is dependent on characteristics such as Ca/S ratio and combustion conditions (Conn et al., 1993; Sheng et al., 2000).

- **Integrated gasification combined cycle technology** (IGCC), which is based on the fact that maximum efficiency and energy is produced from both gasification and combustion processes. This process can produce electricity at efficiencies as high as 50%, a substantial improvement over the roughly 35% that is typical of conventional power stations (Pruschek & Oeljeklaus, 1977). Since this method uses less coal, less CO$_2$ and SO$_2$ is produced per MW of electricity generated.
• Ultra supercritical pulverised coal combustion, which involves the use of ultra supercritical steam conditions in order to increase the efficiency of conventional pulverised coal combustion boilers by as much as 10%. As a result less CO$_2$ and SO$_2$ is produced per MW of electricity generated.

The removal of SO$_x$ from the flue gas released during the combustion of fossil fuels has been a worldwide concern since the 1970s (Xu et al., 2000). There are two common ways of desulphurisation, namely, fluidized bed combustion (FBC) technology and flue gas desulphurisation (FGD) process. FBC is practically a type of dry desulphurisation, and desulphurises simultaneously with combustion under dry conditions in furnace, whereas FGD is a wet desulphurisation and needs specific exteriorized FGD equipments for desulphurising along with wet conditions (Gong & Yang, 2011).

Flue gas desulphurisation technologies (FGD) can be primarily categorized into three different types, namely, wet scrubbers, semi-dry processes (such as spray drying and sorbent injection), and dry processes (including regenerable techniques and combined SO$_x$/NO$_x$ removal systems) (Miller, 1986 & Soud, 1995).

In wet FGD processes, flue gas is brought into contact with a slurry consisting of a sorbent in an aqueous medium, such that the flue gas is cooled to the adiabatic saturation temperature. Wet scrubbers are considered to be reliable for a variety of fuels, and have been widely commercialized in the industry for achieving SO$_x$ removal in excess of 95% (Soud, 1995). However, this kind of technology generates a huge amount of wet solid waste and requires the treatment of waste water. It also involves complex designs and costly operation (Yeh et al., 1982 and Miller, 1986).

Dry and semi-dry FGD processes involve the injection of solid sorbent or sorbent slurry into the furnace or flue gas duct (Ersoy-Meriçboyu, 1999). Dry FGD systems are attractive in principle, as compared to wet scrubbers, in terms of cost, since they do not call for water and reheating energy (Koballa and Dudukovic, 1978 & Kiel et al., 1992). The desulphurisation efficiency and the sorbent utilization are considered to be lower for the semi-dry FGD processes than for wet scrubbers. This can be
ascribed to the short residence time of the $\text{SO}_x$ sorbent (Irabien et al., 1990 & Jiang et al., 1995).

Zevenhoven and Kilpinen (2001) compared the cost of wet, semi-dry and dry processes (Table 2.1) on basis of 90% $\text{SO}_2$ removal efficiency over 30 years. The costs were broken down into fixed and variable operation & maintenance (O & M) costs and fixed capital charge (C & C) costs.

Table 2.1: Cost comparison for wet, semi-dry and dry FGD processes, 1995 (Zevenhoven & Kilpinen, 2001)

<table>
<thead>
<tr>
<th>Plant size, (MW_{Electricity})</th>
<th>Coal Sulphur Content (wt %)</th>
<th>FGD process</th>
<th>Fixed O &amp; M (US$/tonne $\text{SO}_2$)</th>
<th>Variable O &amp; M (US$/tonne $\text{SO}_2$)</th>
<th>Fixed C &amp; C (US$/tonne $\text{SO}_2$)</th>
<th>Total Costs (US$/tonne $\text{SO}_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>2.6</td>
<td>WLS</td>
<td>79</td>
<td>90</td>
<td>183</td>
<td>352</td>
</tr>
<tr>
<td>200</td>
<td>2.6</td>
<td>SDS</td>
<td>40</td>
<td>143</td>
<td>134</td>
<td>317</td>
</tr>
<tr>
<td>200</td>
<td>2.6</td>
<td>LCFB</td>
<td>15</td>
<td>140</td>
<td>123</td>
<td>277</td>
</tr>
<tr>
<td>500</td>
<td>4.3</td>
<td>WLS</td>
<td>20</td>
<td>76</td>
<td>83</td>
<td>178</td>
</tr>
<tr>
<td>500</td>
<td>4.3</td>
<td>SDS</td>
<td>11</td>
<td>131</td>
<td>69</td>
<td>211</td>
</tr>
<tr>
<td>500</td>
<td>4.3</td>
<td>LCFB</td>
<td>3</td>
<td>130</td>
<td>63</td>
<td>196</td>
</tr>
</tbody>
</table>

WLS - Wet limestone scrubber
SDS - Spray dry scrubber
LCFB - Lurgi CFB

The dry process (Lurgi CFB) is observed to be the most economical process (total cost of 277 US$/tonne $\text{SO}_2$) on small plants (200 MW) running on low sulphur (2.6 wt %), while the wet process (Wet limestone scrubber) was the most economical on the large plants (500 MW) running on high sulphur coals (4.3 wt %).

Fluidised bed technology has been widely applied in the chemical industry since the early 1920s and during the oil crisis of the 1970s its development for combustion application was accelerated (Partanen, 2004). Coal combustion through fluidised bed technology has demonstrated improvement in $\text{SO}_2$ removal. Limestone and dolomite additives have been successfully used to capture sulphur dioxide under atmospheric fluidised bed combustion (AFBC) and pressurised fluidised bed combustion (PFBC) conditions (Basu, 2006). FBC is so versatile that it can handle organic material of
different nature; it is also possible to blend coal with any other carbon-rich fuels such as biomass.

The SO$_2$ removal process can be achieved by adding sorbent in the form of limestone, leading up to 90% removal of SO$_2$ in the form of CaSO$_4$ (Nolan, 1998). FBC units are favourable compared to pulverised combustion units due to superior sorbent efficiency which results in a great reduction in emission of pollutants such as SO$_2$ and NO$_x$ during the combustion of fuel with high sulphur content (Anthony et al., 2003).

The active calcium compounds in ash are believed to be able to retain sulphur dioxide. The low temperatures of operation in fluidised coal combustion help keep the ash in its solid form thereby aiding the SO$_2$ removal process (Mukondiwa, 2007). Another added advantage of the lower temperature (850 °C) of operation is that there is relatively low NO$_x$ production and emission.

Circulating Fluidised Bed Combustion (CFBC) is most favourable in the fossil fuel and co-combustion applications due to its higher fuel flexibility, combustion efficiency, excellent heat transfer, lower NO$_x$ production and more efficient sulphur removal (Partanen, 2004). For low grade fuels such as biomass or waste derived fuels, the best technology to utilise is the bubbling fluidised bed combustion (BFBC); this is due to its simpler design and it’s low investment and maintenance costs (Partanen, 2004).

### 2.3 SULPHUR IN COAL

During coal combustion a fairly large amount of sulphur is released leading to environmental pollution problems. The coal linked sulphur is found to exist in two different forms: organic sulphur; and inorganic sulphur. Organic sulphur exists as aliphatic thiols, aromatic sulphides and thiophenes, while inorganic sulphur is mainly found as pyritic sulphur and sulphates (Miftahul et al., 2006; Chen et al., 2000). The inorganic sulphurs generally occur as mineral inclusions whereas the organic sulphurs are relatively uniform throughout the coal structure (Telfer & Zhang, 1998). Aliphatic sulphurs are part of volatile matter which is liberated during pyrolysis and aromatic
sulphurs are part of the products that are driven off during coal combustion. Pyrite releases around 30% of its sulphur at temperatures of about 650 °C to become pyrrhotite (Miftahul et al., 2006; Chen et al., 2000). Borgwardt and Harvey (1972) suggested that the acyclic sulphur, pyrite, thiophene and sulphate in the coal decompose within the temperature ranges of 300-400 °C, 400-450 °C, 480-500 °C and above 1100 °C, respectively.

Cheng et al. (2004a) investigated the dynamic sulphur release in Shenmu coal during combustion and observed that when a coal sample is brought to a high-temperature (about 800 °C), loose organic sulphur (such as mercaptan and sulphides) and a little pyrite thermally decompose to form SO₂ gas. However, organic sulphur (such as thiofuran) and pyrite intensively decompose to form SO₂ at high temperatures (about 1200 °C). Iron sulphide (FeS) is only stable up to temperatures of 1000 °C after which it transforms into other iron-sulphur compounds (Grubor & Manovic, 2002).

Functional groups containing organic sulphur decompose over a range of temperatures. Aliphatic thiols decompose at 200-300 °C, sulphides and disulphides at around 350-400 °C, cyclic and aromatic sulphides at 700-800 °C and thiophenes at above 800 °C (Telfer & Zhang, 1998). During devolatilisation pyrite transforms according to the chemical reaction:

\[
\text{FeS}_2 \rightarrow \text{FeS} + \text{S} \tag{2.1}
\]

This reaction starts around 550-600 °C and when the temperature reaches 1000 °C, only FeS is left. This is independent of coal rank and pyrolysis conditions (Gryglewicz, 1995). Calcium sulphides (CaS) contained within the ash at the bottom of a fluidised combustor in an oxygen starved environment accumulate within particles, but if the conditions alternate between reducing and oxidising conditions a complete sulphur release occurs (Hoteit et al., 2007). Under oxidising conditions and temperatures of around 800-950 °C the following reaction takes place:

\[
2 \text{CaS} + 3 \text{O}_2 \rightarrow 2 \text{CaO} + 2 \text{SO}_2 \tag{2.2}
\]
This reaction prevents the accumulation of CaS within the ash particle. A high CO concentration will increase the rate of sulphate decomposition during the reduction phase of the reaction.

2.4 MINERAL ANALYSIS

Mineral analysis (coal and ash) is important for understanding both the sulphur self-retention by minerals in coal and the sulphur dioxide capture capabilities of the minerals in ash. The transformation of ash-forming inorganic matter in coal is thus vital to understand the chemical behaviour of the formed ash.

2.4.1. Mineral analysis techniques

Several techniques exist for the characterisation of ash and coal. Some of the widely used techniques are X-ray diffraction (XRD), Inductively Coupled Plasma Mass Spectrometer (ICP - MS), Inductively Coupled Plasma Atomic Emission Spectrometer (ICP - AES) Computer Controlled Scanning Electron Microscope (CCSEM) and Quantitative Evaluation of Mineralogy by Scanning Electron Microscopy (QEMSCAN) (Matjie, 2008; Saikia & Ninomia, 2011; Liu et al., 2005). A combination of analytical data obtained from these techniques gives a relatively accurate account of the mineral to ash transformation that can be a vital tool in predicting the behaviour of the ash under various conditions, including reaction with sulphur and related elements/compounds (Gupta, 2007).

QEMSCAN is an integrated system originally designed by CSIRO (Skorupska & Couch, 1993) for base and precious metals analysis in the mining industry, it has been adapted to analyse the mineral matter in coal and ash (Van Alphen, 2007; Creelman et al., 1993; Creelman & Ward, 1996; Gottlieb et al., 1991). Knowledge of the association of mineral matter with organic matter is important for coal utilisation processes such as coal combustion and gasification. Advanced analytical instruments such as QEMSCAN afford the ability to measure the mineral/organic matter
association on a particle-by-particle basis (Liu et al., 2007a, Gottlieb et al., 1991; Creelman & Ward, 1996).

There are three major ways in which QEMSCAN can be used to predict and provide information on mineral transformation (Liu et al., 2007a):

- Statistical graphs and tables generated using iDiscover™ software make it possible to observe individual mineral grains and allows comparison between coals and the deduction of impacts.
- Images obtained from QEMSCAN analysis can be converted to CCSEM-like analysis data via software developed by CCSD. The data is then interpreted by a University of Newcastle developed ash prediction model. Finally a CCSD Ash Effect Predictor (AEP) model is applied (Liu et al., 2005).
- Ash prediction can also be done directly from QEMSCAN analysis; the technique takes into account the effect of mineral-mineral association on ash properties (Liu et al., 2005).

The Computer Controlled Scanning Electron Microscope (CCSEM) technique characterises minerals in terms of size, shape, abundance and association. Mineral grains are located and sized by their cross-sectional area. Their elemental composition is then monitored by several x-ray channels by Energy Dispersive X-ray (EDX) and this makes it possible to identify most commonly occurring minerals in coals (Liu et al., 2007a; White et al., 1972).

Measurements by X-ray diffraction (XRD) are based on the effect of the crystalline structure of minerals on X-rays. A standard sample of specific minerals of known composition, against which measurements of the sample under investigation are compared, is required. The Bragg’s equation describes the interaction between inter-planner spacing crystals and the incident X-ray (Rao & Gluskoter, 1973).

2.4.2. Active calcium bearing mineral phases (coal and ash)

The distribution of various forms of calcium in Kolubara B coal ashes is presented in Figure 2.1. About 60% of the calcium takes part in the sulphur self-retention process.
More than half of that 60% comes from carbonates while the balance occurs as exchangeable ions in the coal matrix (Grubor & Manovic, 2002). The mineral matter that is found in coal ash is responsible for self-retention SO$_2$ as it evolves from coal during the combustion process (Grubor et al., 2003).

![Figure 2.1: Distribution of the various forms of calcium in Kolubara B coal ash (Grubor & Manovic, 2002)](image)

Conn et al. (1993) studied the reactivity of different calcium forms in poor quality coals and found that calcium present in clays and silicates cannot react with SO$_2$ at FBC conditions. However, in comparison with other alkaline elements found in coal (such as Mg, Na and K) the Ca/S ratio was found to have the highest correlation coefficients between sulphur self-retention and molar ratios of alkaline elements to sulphur. This suggests that calcium has the greatest effect on sulphur self-retention of laboratory prepared ash (Sheng et al., 2000).

### 2.5 SULPHUR SELF-RETENTION

The use of ash as sorbents for the sulphur self-retention process has been stimulated by the development of fluidised bed combustion technology due to its favourable
conditions (Manovic et al., 2006). The operational conditions such as low temperature and high pressure are conducive to the sulphur self-retention process (Grubor & Manovic, 2002). Grubor et al. (2003) reported that tests performed on fluidised bed combustors have shown that some coals retain substantial amounts of sulphur without the injection of limestone.

The mineral matter in coal ash reacts with the SO$_2$ released during combustion to form stable compounds. The key compound formed for sulphur self-retention is CaO derived from CaCO$_3$, CaMg (CO$_3$)$_2$, and calcium containing organic groups (Grubor & Manovic, 2002). Manovic et al. (2006) reported that the process due to which part of SO$_2$ is retained in ash is designated as inherent SO$_2$ capture or self-retention and is affected by coal characteristics and combustion conditions (Sheng et al., 2000; Conn et al., 1993; Fuertes et al., 1992; Gray, 1986; Raask et al., 1985). The percentage of sulphur retained by an ash sample increases with increasing Ca/S molar ratio of the parent coal (Sheng et al., 2000). Sheng et al. (2000) demonstrated that there is no obvious correlation between coal rank and sulphur self-retention. However, there is a slight tendency for a decrease in sulphur self-retention as the coal rank increases.

Although a reasonable amount of work has been done in determining the mechanism of SO$_x$ capture, the sorbent’s (limestone) interaction with NO$_x$ reduction is still under scrutiny (Rajaram, 1999). Anthony et al. (2003) simplified the CaO formation and sulphur self-retention process chemical reactions as follows:

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \\
\text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{CaSO}_4 \\
\text{CaCO}_3 \cdot \text{MgCO}_3 & \rightarrow \text{CaCO}_3 \cdot \text{MgO} + \text{CO}_2 \\
\text{CaCO}_3 \cdot \text{MgO} & \rightarrow \text{CaO} + \text{MgO} + \text{CO}_2
\end{align*}
\]

Some ashes are known to retain up to 32% of the coal sulphur (Mukondiwa, 2007). However, not all calcium in coal is capable of capturing sulphur. Table 2.2 gives a summary of some of the relevant sulphur self-retention work covered in literature.
Fuertes *et al.* (1992) examined SO$_2$ retention by coal ashes during the fluidised bed combustion of four bituminous coals with high ash content (>47 wt %) and moderate sulphur content (≈1 wt %). It was reported that sulphur retention at low temperature (700 °C) take place by direct sulphation of calcite, whereas at elevated temperatures, sulphur is retained by CaO.

The self-retention of SO$_2$ by different Kolubara lignite coal ashes was examined by Grubor & Manovic (2002) using three sieved fractions. It was reported that particle size had no significant effect on the sulphur self-retention efficiency, but that most sulphur self-retention occurs in less dense particles and only 60% of the total calcium was reported to be active in relation to sulphur self-retention capability.

The experimental investigation on sulphur self-retention of four coals was conducted by Grubor *et al.* (1999), who reported the sulphur self-retention efficiency ranging from 17% to 49%, and that the efficiency increased with the increasing temperature and C$_{lv}$/vol ratio. Grubor *et al.* (2003) used coals of different ranks, content of sulphur forms and molar Ca/S to investigate the influence of temperature, coal particle size and the surrounding conditions, on sulphur self-retention efficiencies. It was reported that sulphur self-retention does not occur during devolatilisation.

Li *et al.* (2008) investigated sulphur self-retention in a 1MW tangentially-fired furnace while varying the air stoichiometric ratio of the primary combustion zone and the relative location of the over-fire air injection ports. It was reported that sulphur self-retention increased when the air stoichiometric ratio of the primary combustion zone was 0.85 to 0.95. SSR was also observed to increase relative to the location of the over-fire air injection ports.

A grain model approach had been employed by Manovic *et al.* (2002) to model the sulphur self-retention of the combustion of Bogovina and Kolubara coals. Manovic *et al.* (2006) also modelled the sulphur self-retention during the combustion of three Serbian coals. In both cases, the model’s parametric analyses were also done and experimental results were used to verify the model.
Table 2.2: Summary of sulphur self-retention investigations done by other researchers

<table>
<thead>
<tr>
<th>Researcher(s)</th>
<th>Reactor</th>
<th>Sample</th>
<th>Sample Particle size</th>
<th>Temperature (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuertes et al. (1992)</td>
<td>0.14 m (i.d) fluidised bed reactor</td>
<td>Bituminous coals</td>
<td>Not available</td>
<td>700 and 900</td>
</tr>
<tr>
<td>Grubor &amp; Manovic. (2002)</td>
<td>Laboratory oven</td>
<td>Kolubara coal</td>
<td>1-1.6, 2.5-3.2, and 4.76-7 mm</td>
<td>750</td>
</tr>
<tr>
<td>Grubor et al. (1999)</td>
<td>80 mm (i.d) fluidised bed reactor</td>
<td>Not available</td>
<td>4-7, 7-10, and 10-13 mm</td>
<td>750, 800 and 850</td>
</tr>
<tr>
<td>Grubor et al. (2003)</td>
<td>78 mm (i.d) fluidised bed reactor and in a laboratory oven</td>
<td>Kolubara and Bogovina coals</td>
<td>4-7, 7-10 and 10-13 mm</td>
<td>750, 800 and 850</td>
</tr>
<tr>
<td>Li et al. (2008)</td>
<td>1 MW fired-coal furnace</td>
<td>Shenmu coal (a Chinese bituminous coal)</td>
<td>11.4-160 µm</td>
<td>Not available</td>
</tr>
<tr>
<td>Manovic et al. (2002)</td>
<td>Fluidised bed reactor and in a laboratory oven</td>
<td>Kolubara and Bogovina coals</td>
<td>Not available</td>
<td>Not available</td>
</tr>
<tr>
<td>Manovic et al. (2006)</td>
<td>Laboratory fluidised bed reactor</td>
<td>Low rank Serbian coals</td>
<td>4-7, 7-10, and 10-13 mm</td>
<td>750, 800 and 850</td>
</tr>
<tr>
<td>Okasha (2007)</td>
<td>100mm (i.d) and 300mm (i.d) FBC</td>
<td>CaO integrated rice straw-bitumen biomass pellets</td>
<td>12, 15 and 18 mm</td>
<td>800</td>
</tr>
<tr>
<td>Sheng et al. (2000)</td>
<td>Chamber electric furnace, pulverised coal-fired boilers ranging from 50 to 300 MWe, and pilot scale combustor</td>
<td>Chinese coals (ranks from low volatile anthracite to lignite)</td>
<td>less than 0.2mm</td>
<td>815</td>
</tr>
</tbody>
</table>
Okasha (2007) investigated the sulphur self-retention efficiency of ashes produced during the combustion of CaO-integrated biomass pellets. The same author reported that this technique is efficient in enhancing sulphur self-retention and that the ash which remains after the pellets are completely combusted works as an efficient sorbent for sulphur dioxide capture within the combustor.

Sheng et al. (2000) compared the sulphur self-retention capabilities of coal ashes in the laboratory ashing procedure; in a pulverised coal-fired combustor; and in a fluidised bed combustor. They reported that sulphur retention behaviour in the laboratory ashing procedure was comparable with that in the fluidised bed combustor. It was, however, significantly different to that of the pulverised coal-fired combustor. Calcium was observed to play an important role in the sulphur retention and the percentage of sulphur retention generally increased as an exponential function of Ca/S molar ratio of the parent coal. Contributions of other alkaline elements may be limited to high rank coal.

2.6 SULPHUR DIOXIDE CAPTURE

Table 2.3 presents a summary of some of the sulphur dioxide capture work done by different researchers. The feed gas composition contained mainly between 1000 and 3000 ppm SO$_2$ concentration in O$_2$ and CO$_2$, with the bulk of the gas being mainly N$_2$. Most of the work was done at the relatively low temperatures that are typical of fluidised bed combustion.

The sulphur dioxide capture of different sorbents (Omyacarb limestone and two calcium hydroxides) was reported to be influenced by parameters related to the product layer diffusion, namely, the value of the product layer diffusion coefficient - normally related with the impurity content of the sorbent; and the product layer thickness - normally dependent on the porous structure of the sorbent (Adánez et al., 2000).
Table 2.3: Summary of sulphur dioxide capture investigations done by other researchers

<table>
<thead>
<tr>
<th>Researcher(s)</th>
<th>Reactor</th>
<th>Sample</th>
<th>Sample mass</th>
<th>Temperature (ºC)</th>
<th>Feed gas composition</th>
<th>CaO utilisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adánez et al. (2000)</td>
<td>Drop Tube Reactor</td>
<td>Calcium-based sorbents</td>
<td>100 mg</td>
<td>950-1250</td>
<td>2000 ppm SO₂, 15.0% H₂O, 2% O₂, 15.0% CO₂ and bal N₂</td>
<td>-</td>
</tr>
<tr>
<td>Cheng et al. (2004b)</td>
<td>Fluidised bed reactor</td>
<td>Limestone and seashell</td>
<td>-</td>
<td>800-950</td>
<td>2200 ppm SO₂ and bal air</td>
<td>-</td>
</tr>
<tr>
<td>Govender (2006)</td>
<td>Fluidised bed reactor</td>
<td>Limestone and dolomite</td>
<td>20 g</td>
<td>800-900</td>
<td>1100 ppm SO₂ and bal air</td>
<td>-</td>
</tr>
<tr>
<td>Iisa &amp; Hupa (1990)</td>
<td>TGA</td>
<td>Limestone and Dolomite</td>
<td>150-300 mg</td>
<td>750-950</td>
<td>3000 ppm SO₂, 4% O₂, 15% CO₂ and bal N₂</td>
<td>-</td>
</tr>
<tr>
<td>Lee et al. (2005)</td>
<td>Fixed bed reactor</td>
<td>Malaysian fly ash and English CaO + CaSO₄</td>
<td>0.70 g</td>
<td>60-300</td>
<td>1000 ppm SO₂, 500ppm NO, 5% O₂, 12% CO₂ and bal N₂</td>
<td>53.6-244mg SO₂/g CaO</td>
</tr>
<tr>
<td>Mukondiwa, (2007)</td>
<td>TGA</td>
<td>Coal, Limestone and Dolomite</td>
<td>100 mg</td>
<td>750-900</td>
<td>2000 ppm SO₂, 5.30% O₂, 10.0-20.0% CO₂ and bal N₂</td>
<td>13-49%</td>
</tr>
<tr>
<td>Ngeleka, (2005)</td>
<td>TGA</td>
<td>Dolomite</td>
<td>300 mg</td>
<td>750-950</td>
<td>2500 ppm SO₂, 6.80% O₂, 10.0-8.00 &amp; 25.0% CO₂ and bal N₂</td>
<td>23-40%</td>
</tr>
<tr>
<td>Zevenhoven et al. (1998)</td>
<td>TGA</td>
<td>Limestone and Dolomite</td>
<td>100 mg</td>
<td>850-950</td>
<td>3000 ppm SO₂, 4.0% O₂, 20.0% CO₂ and bal N₂</td>
<td>15-88%</td>
</tr>
<tr>
<td>Zhang et al. (2003)</td>
<td>TGA</td>
<td>Chinese coal ash</td>
<td>10 mg</td>
<td>850</td>
<td>1000 ppm SO₂, 10% O₂ and bal N₂</td>
<td>-</td>
</tr>
</tbody>
</table>
Cheng et al. (2004b) investigated the effect of the characteristics of three limestones and two seashells on sulphur dioxide capture capability. Pore size and specific surface area were reported to have a great influence on the sulphur capturing ability of these sorbents.

Govender (2006) studied the desulphurisation capability (under fluidised bed combustion) of eight South African commercially mined sorbents (4 limestones and 4 dolomites). The optimum temperature and particle size were reported to be 850 °C and 425-500 µm, respectively.

Lee et al. (2005) worked at unusually low temperatures, 60 - 300 °C. However, the findings were generally similar to those at high temperatures; there was an increase in sorbent desulphurisation activity with reaction temperature and surface area.

Mukondiwa (2007), in an investigation carried out under atmospheric pressure, found calcium conversion of between 22-44% for dolomite, 37-49% for limestone and 13-28% for coal ash (after 180 min). The same author reported that while the reactivity of dolomites and coal ash started off relatively fast followed by a sudden decline after 16-20% conversion, the reactivity of limestone did not show any decline. The decline can be attributed to two sequential mechanisms: first, the surface controlled reaction of the solid surface (during which a product layer develops and changes chemical composition); and second, diffusion through the product layer. Generally, Mukondiwa (2007) observed conversion to increase with increasing temperature, with limestone and coal ash reaching maximum at 850 °C, and then declining at 900 °C due to sintering and loss of surface area.

Ngeleka (2005) investigated the sulphur dioxide capturing behaviour of two typical industrial-type dolomites (A and B) from a South African dolomite mine. It was reported that conversion of CaO to CaSO$_4$ over very long periods of time (500 min) did not show any blocking-off of pores so that conversion was ever increasing (at a decreasing rate).

Zevenhoven et al. (1998) investigated the sulphur dioxide capturing behaviour of five limestones and two dolomites at 850 °C, 1.5 MPa and 950 °C, 1.5 MPa. CaCO$_3$
conversion to CaSO₄ ranging from 15 to 88% was reported, and was described by competing reaction kinetics control and diffusion inside the particle, with the diffusion mechanism mainly controlled by product layer diffusion.

Zhang et al. (2003) investigated the sulphur dioxide capturing behaviour of ashes derived from two Chinese coals with added limestone and calcium acetate. They reported that the sulphur removal efficiency of ash could be the same as that of natural limestone.

The main sorbents believed to be the key for sulphur dioxide capture are calcium based or magnesium based. At elevated temperatures, calcite is calcined into CaO and dolomite to CaMgO and these are the compounds that participate in sulphur dioxide capture during desulphurisation. Up to temperatures of 400 °C, MgCO₃ is very stable but decomposes to MgO and CO₂ at temperatures over 400 °C. Moss (1970) suggested that sulphation occurs via two mechanisms, namely the formation of CaSO₃ and SO₃. These mechanisms can be represented by:

\[
\text{CaO} + \text{SO}_2 \rightarrow \text{CaSO}_3 \quad (2.7)
\]

\[
\text{CaSO}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4 \quad (2.8)
\]

or

\[
\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3 \quad (2.9)
\]

\[
\text{CaO} + \text{SO}_3 \rightarrow \text{CaSO}_4 \quad (2.10)
\]

The CaSO₃ mechanism is favoured at lower temperatures (≤850 °C), whereas the SO₃ mechanism is favoured at higher temperatures (≥850 °C). This is because of the thermal instability of CaSO₃ (Moss, 1970; Moss, 1975). The SO₃ mechanism route was questionable due to the fact that the SO₃ is mainly formed catalytically over surfaces at levels well below the equilibrium levels, which is about 10-5% conversion of SO₂ (Anthony & Granatstein, 2001; Dennis & Hayhurst, 1988). Allen and
Hayhurst (1996) concluded that sulphation occurring through the CaSO₃ mechanism includes the formation and utilisation of CaS in the following reaction:

\[
4\text{CaSO}_3 \rightarrow \text{CaS} + 3\text{CaSO}_4 \tag{2.11}
\]

\[
\text{CaS} + 2\text{O}_2 \rightarrow \text{CaSO}_4 \tag{2.12}
\]

Sulphation is believed to proceed via the CaSO₃ and CaSO₃-CaS mechanism (Anthony & Granatstein, 2001; Wieczorek-Ciurowa, 1992). Nonetheless, in the presence of enhanced SO₃ levels, the SO₃ mechanism is also significant. However, the composition of the ash has an effect on the stability of the calcium sulphate formed as alumina, silica and iron oxide accelerate the decomposition of the CaSO₄ that is formed (Stanmore & Gilot, 2005). At 1 atm total pressure and oxygen partial pressure of 0.03 atm the decomposition temperature is above 1100 °C (Fuertes & Fernandez, 1995).

### 2.7 MODELLING

#### 2.7.1. Reaction models

Various models of different complexity have been used to describe and mathematically analyse the calcium-based sorbent sulphation reaction of laboratory and pilot plant generated data. Three classes of models can be used to describe the heterogeneous (gas/solid) reactions that are applicable to sulphur dioxide capture and sulphur self-retention. The models are strongly linked to the assumed structural characteristics of the solid. Depending on the solid structure, the models that can be used include unreacted shrinking core model (Ngeleka, 2005; Grubor et al., 2003; Borgwardt et al., 1987; Szekely & Evans, 1970), grain models (Szekely & Evans 1970; Ramachandran, 1983) and pore models (Bhatia and Perlmutter, 1980; Kocaeva et al., 1987). Most models consider product layer diffusion to be the process limiting the sulphation rate (Borgwardt & Bruce, 1986; Borgwardt et al., 1987; Milne et al., 1990).
2.7.2 Unreacted shrinking core models

This model assumes that particles are all spherical and that this assumed form is maintained during chemical reaction. It also assumes that the reaction occurs at the product layer/unreacted core interface. The reaction gas diffuses into and through the product layer until it reaches the interface where the reaction occurs (Mukondiwa, 2007; Ngeleka, 2005; Rahmani & Sohrabi, 2006; Szekely & Evans, 1970). As the reaction proceeds, the interface progresses towards the centre of the particle, whilst maintaining its form. The porosity of the particle and the number of pores does not change during the reaction; hence the only change will be the expansion or contraction of the particle (Ngeleka, 2005). The model does not take into account the sorbent particle structure or structural changes that occur during the reaction and is mainly applied to non-porous solid reactions (Wang & Bjerle, 1998).

The limitation of the unreacted shrinking core model is that it does not account for the difference in the conversion of chemically similar but physically different sorbents. This can only be successfully described by an unreacted shrinking core model with variable effective diffusivity (USC-VED) (Mukondiwa, 2007; Rahmani & Sohrabi, 2006; Zevenhoven et al., 1998). The model has been successfully used to model data obtained under both atmospheric and pressurised conditions.

2.7.3 The changing grain size model

A grain model takes the sorbent as a collection of non-porous grains surrounded by inter-granular voids. The original grain model assumes the porous solid to be a semi-infinite solid of macroscopically unidirectional movement of the reaction zone, which implies that the structure of the particle remains the same during and after chemical reaction (Mukondiwa, 2007; Szekely & Evans, 1970).

There are three factors that are believed to be critical in the reaction mechanisms involved. These are: diffusion through the product layer; diffusion through the voids; and the reaction at the product layer/unreacted core surface (Mukondiwa, 2007). The changing grain size model developed by Hartmann and Coughlin (1976) accounts for
the reduction in porosity due to the larger molar volume of the product (Manovic et al., 2006; Mukondiwa, 2007).

2.7.4 Pore models

Pore models consider sorbents to be a substance consisting of intersecting pores. A number of pore models defining the sulphation process do not consider the pore size distribution inside the sorbent and assumes cylindrical pore geometry (disregarding the plate-like geometry) to define the pore structure of the sorbents (Adánez et al., 2000; Mai, 1987; Newton, 1987).

Ramachandran and Smith (1977) proposed a single pore model that deals with the pore closure phenomenon due to chemical reaction. A simplified model bearing few independent parameters is produced from an approximate method of mono-dispersed average pore radius. This method neither considers the intersection of pores nor pore size distribution (Mukondiwa, 2007).

The tree like model which considers each pore of the particle to reach the surface of the particle like the trunk of a tree, the branches and the leaves, was proposed by Simon and Garman (1986) and Simon et al (1987). The model involves a progression of a pore from maximum to minimum radius. A simplified mathematical function (requiring no empirical fitting parameters) is employed to model the pore size distribution (Mukondiwa, 2007).

Petersen (1957) proposed a model consisting of randomly intersecting cylindrical pores of uniform size for calculating the surface area and porosity. Bhatia and Perlmutter, (1980) and Gavalas (1980) independently derived a more advanced model on the basis of the assumption that the volume enclosed by the moving pore and reaction surfaces is randomly distributed in the particle.

Bhatia and Perlmutter (1980) used a theory derived by Avrami (1940) for the nucleation of crystals, while Gavalas (1980) assumed a random distribution of the
non-overlapped volume in accordance with a Poisson process. These models incorporate both pore growth and coalescence during the reaction (Kaitano, 2008).

2.7.5 Models for sulphation

The most used models for sulphation chemical reaction are the unreacted shrinking core models (Mukondiwa, 2007; Rahmani & Sohrabi, 2006; Zevenhoven et al., 1998). The motivation for the researchers’ selection includes that the model accounts for the reaction and effective diffusion (in pore and product layer) and that it can be easily solved numerically to determine different mechanisms under different reaction conditions. In addition to that, other model parameters can be easily determined via simple characterisation tests. Above all, the models have been successfully employed by other researchers to model sulphation data (Mukondiwa, 2007; Rahmani & Sohrabi, 2006; Zevenhoven et al., 1998). The usefulness of the models for engineering purposes is dependent on the accuracy of the estimation of the product layer diffusion coefficient (Adánez et al., 2000).
“Observation is a passive science, experimentation an active science.”

Claude Bernard
3 EXPERIMENTAL

3.1 INTRODUCTION

In this chapter, brief descriptions are given of the various experimental apparatus and the methods used for the coal and ash characterisation; for the sulphur self-retention; and for the sulphur dioxide capture experimental work. Section 3.2 gives an overview of the sample selection and preparation. Coal and ash analyses are presented in Section 3.3, with the focus on chemical (proximate, ultimate and sulphur analysis) and petrographic analysis. Section 3.4 covers mineral analysis based on QEMSCAN, and Section 3.5 presents the physical structural analysis. Finally, the sulphur self-retention and capture experimental apparatus, operating procedures and conditions are given in Section 3.6 and 3.7 respectively.

3.2 SAMPLE SELECTION AND PREPARATION

Six typical low grade coal samples originating from different coal deposits in South Africa were used for this study (A2, C3, D1, E1, E3 and F1). These deposits were identified by Eskom for future electrical power generation and are currently being evaluated using fluidised bed technology at pilot plant scale (at the Eskom Research Centre). The particle size of received samples ranged from 3 mm to fine powders. The samples for sulphur self-retention experiments were prepared by screening out particles between 212 µm to 300 µm, inclusive. Insufficient (±40 g) quantities per sample were obtained through screening, and samples thus had to be milled and screened repeatedly until sufficient amounts (± 250 g) were obtained. The milling was
done in 15 min intervals (at the revolutions of 600 rpm). The Fritsh P-14 rotary mill with ceramic macro crusher (Model No. 46-126) and ceramic balls was used in order to avoid contamination. The same procedure was followed in preparing coal samples (1 mm) for sulphur dioxide capture experimentation.

3.3 CHEMICAL AND PETROGRAPHIC ANALYSES

3.3.1 Proximate and ultimate analyses

The chemical analysis, consisting of proximate, ultimate, total sulphur and calorific value analysis was carried out by Advanced Coal Technology (ACT) laboratories in Pretoria. The analyses were carried out in accordance with the analytical methods and standards given in Table 3.1.

Table 3.1: Analytical methods used

<table>
<thead>
<tr>
<th>Item</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample preparation</td>
<td>SABS 0135: Part 1 &amp; 2 - 1997</td>
</tr>
<tr>
<td>Inherent moisture content</td>
<td>SABS Method 925</td>
</tr>
<tr>
<td>Ash content</td>
<td>SABS ISO 1171:1997</td>
</tr>
<tr>
<td>Volatile matter content</td>
<td>SABS ISO 562:1998</td>
</tr>
<tr>
<td>Total sulphur via IR spectroscopy</td>
<td>ISO 19759</td>
</tr>
<tr>
<td>Gross calorific value</td>
<td>SABS ISO 1928:1995</td>
</tr>
<tr>
<td>Ultimate analysis</td>
<td>ISO 12902</td>
</tr>
</tbody>
</table>

3.3.2 Sulphur analysis

The total sulphur in coal was determined according to the method presented in Section 3.3.1 (Total sulphur via IR spectroscopy, ISO 19759). Total sulphur analysis of the ashes was done at the SABS Minerals Laboratory in Richards Bay (using the high-temperature tube furnace and infrared detection). Prior to the onset of the analysis, samples were conditioned at a relative humidity of 45% (+/- 3%) and at a temperature of 23 ºC. The method employed was the ASTM D 5016.
3.3.3 Petrographic analysis

Coal samples milled to a particle size of -3 mm were prepared in petrographic blocks and polished. This was carried out in accordance to the method set out in the ISO Standard 7404 - 2, 1985. The polished blocks were then examined under a microscope at Petrographics SA Laboratory (du Cann, 2008).

Vitrinite random reflectance measurements were done in accordance with the ISO Standard 7404 - 5, 1994 (100 readings on vitrinites in each coal sample) to establish coal rank. The group macerals were quantified by a 500 point-count technique in accordance with the ISO Standard 7404 - 3, 1994. A total maceral reflectance scan was also undertaken on each coal sample representative. 250 random reflectance readings were taken on all macerals over the polished surface of each petrographic block (du Cann, 2008).

Maceral, microlithotype, carbominerite and minerite analyses (to determine the organic/inorganic associations) were carried out in accordance with the ISO Standard 7404 – 4, 1988. Analysis to identify the active macerals was carried out as well (du Cann, 2008). This was done according to the method established by Smith et al. (1983) for South African coals.

3.4 MINERAL ANALYSIS

3.4.1 QEMSCAN

QEMSCAN is an automated electron beam image analysis technique applied in the minerals industry. The technique has the potential to provide quantitative mineralogical and textural data for assessing coal behaviour during preparation, in power generation, in coking and steel production, in gasification, and in the management and utilisation of coal by-products and wastes. The technique was originally developed by CSIRO, Australia. QEMSCAN analysis can provide unique, phase-specific, information not obtainable from other analytical techniques. This is of
relevance to the coal producing and coal utilisation industries. The methods of data acquisition offer advantages over other SEM based techniques in that measurements are made at the individual pixel level rather than averaging over an area. Also, greater use is made of the chemical composition for phase identification rather than relying upon back scattered electron intensity (French et al., 2009; Liu et al., 2005).

The QEMSCAN analysis of coal and the ash samples produced in this study was done at the Eskom Research and Innovation Centre, South Africa (Van Alphen, 2009a & 2009b). The Eskom apparatus is able to acquire 450 000 points in an hour. Mineral identification is based on a 1000 count energy dispersive spectrum. It is mainly used for analysing coal, clinkers, fouling deposits and fly ash.

Sample preparation is done by mixing pulverised fuel with molten carnauba wax and ash with epoxy resin. This is done in 30 mm moulds. The molten wax is allowed to set, whereas the epoxy resin is allowed to cure. The solid wax and cured epoxy resin sections are polished to a 1 µm final finish, thus exposing individual particles in cross-section. The prepared sample is exposed to the scanning electron microscope electron beam positioned at predefined points across a particle. At each point a 7 millisecond 1000 count X-ray spectrum is acquired. The elemental proportions are used to identify the mineral/amorphous phase at each point (Van Alphen, 2009a & 2009b).

The Eskom/VAC fly ash mineral/phase standards (Van Alphen, 2009a & 2009b) were used to classify the ash phases. This standard includes typical minerals in ash samples and the different glass phases. The QEMSCAN output includes area-% mineral proportions, calcium mineral deportment and colour particle images.

Other widely used techniques (discussed in Section 2.4.1), including X-ray florescence (XRF), X-ray diffraction (XRD), Inductively Coupled Plasma (ICP) and Computer Controlled Scanning Electron Microscope (CCSEM), were not used in this study. ICP and XRF present content of the sample in elemental or oxide form. Important mineral phases such as CaCO$_3$, CaMg (CO$_3$)$_2$, FeS and CaSO$_4$ can therefore not be quantified. Similarly, measurements by X-ray diffraction (XRD) are based on
the effect of the crystalline structure of minerals on X-rays. CCSEM measures discrete mineral grains (> 0.5 µm), omitting organically associated inorganic elements and thus reports a significant amount of minerals (<10%) as unknown (Liu et al., 2005 & 2007b). The QEMSCAN technique was selected because it could quantify both the crystalline and amorphous mineral phases in coals and corresponding ashes. Excluded mineral (discrete grains/composite) and included minerals (associated by organic matter in a range of proportions) can also be measured by QEMSCAN (Liu et al., 2005 & 2007b).

3.5 PHYSICAL STRUCTURAL ANALYSIS

3.5.1 Micro-pore surface area and micro-pore volume measurements

The surface area and pore volume measurements of the coals and their corresponding ashes were performed at the North-West University (Potchefstroom Campus), School of Chemical and Mineral Engineering Laboratory. The equipment used was the Micromeritics ASAP 2010, accurate to within 0.15% for the pressure reading and ±0.02 ºC for temperature. The degas system has an accuracy of deviation of less than ±10 ºC for the thermocouple set point (Micromeritics, 2006).

For the carbon dioxide adsorption experiments, a sample of about 0.20 g was first degassed and evacuated to 10 µmHg at a temperature of 380 ºC (25 ºC for parent coals to avoid release of volatiles). The evacuated sample was analysed at 0ºC (ice bath).

A number of gas adsorption interpretation models can be used to determine pore volume and surface area from experimental data. The widely accepted interpretation models are the Dubinin-Radushkevich (D-R) and Langmuir equations (Gürdal & Yalçın, 2001). The Dubinin-Radushkevich (D-R) method was used to calculate the surface area and pore volume (Micromeritics, 2006). The D-R equation takes into account the degree of choking of the micropores and the fact that the molecules of the adsorbate may be apportioned by several surfaces (Gürdal & Yalçın, 2001; Sobolik et
whereas the Langmuir model supposes that adsorption occurs in the form of a single layer of molecules and that the utmost quantity of adsorbate is defined by the monolayer capacity material (Gürdal & Yalçın, 2001; Gregg & Sing, 1982; Sing et al., 1985).

### 3.5.2 Skeletal density measurement

Measurement of the skeletal density of coals and their corresponding ashes were also performed at the North-West University (Potchefstroom Campus), School of Chemical and Mineral Engineering Laboratory. The equipment used was the manually-operated Quantachrome Helium Pycnometer (Stereopycnometer), with accuracy better than 0.2% when properly prepared; when thermally equilibrated; and when the sample occupies greater than 75% of the nominal sample cell volume (Quantachrome, 2009). This Pycnometer measures the volume of the solid discrete particles and their inaccessible pores (coal and corresponding ash); hence density is estimated from the ratio of the mass of discrete solid particles (and inaccessible pores) to the volume of discrete solid particles (and inaccessible pores). Approximately 7 g of sample was used in the small cell (20 cm$^3$). The gas medium used is helium, due, first, to its small molecular volume and its ability to penetrate small pores and, second, to the fact that the van der Waals forces are weak enough that the adsorption of helium on the coal surface can be neglected (Saha et al., 2007). Analyses were performed by pressurizing the sample to 17 psig (1.16 atm) (Webb, 2001; Quantachrome, 2009).

### 3.6 SULPHUR SELF-RETENTION EXPERIMENTATION

The sulphur self-retention experiments were carried out on the six coal samples described in Section 3.2. The experiments were carried out in a Packed Bed Balance Reactor (Figure 3.1). The process can be classified as a dry process (according to classification given in Section 2.2).
The apparatus consists of a Lenton® TSV 15/50/180 vertical tube furnace (equipped with a Eurotherm 808 programmable temperature controller and a Eurotherm 92 over-temperature protection device) mounted on steel guide rails, and a vertical tubular reactor (25 mm diameter, equipped with a K-type thermocouple) mounted directly above a Sartorius® ED4202S mass balance with the accuracy of ±0.01g.

The reactor was heated by the Lenton® furnace and the heating rate and temperature profiles were controlled by the Eurotherm controllers. The mass balance and the thermocouple were connected to an Adam 4521 and Adam 4011 converter modules, respectively. The respective modules converted the voltage signal (from the thermocouple) and the mass balance signal to a RS232 signal, which was converted into a USB signal via the Adam 4561 converter module. The Visidag software package was employed to interpret the data as temperature (in °C) and mass (in mg) on the computer. Coal samples (212-300µm diameter) were combusted for 12 h in dry air, at atmospheric pressure, with a loading of ±60 g and an air flow rate of
800ml/min. The air flow was controlled by a calibrated Kronhe rota meter. The attainment of a constant mass indicated complete combustion. The experiments consisted of an initial non-isothermal heating of 20 °C/min (45 min) followed by an isothermal period at a temperature of 900 °C (675 min).

3.7 SULPHUR DIOXIDE CAPTURE EXPERIMENTATION

The sulphur dioxide capture experiments were carried out with a Cahn Thermax 700 TGA (supplied by Thermo Fisher Scientific), with the accuracy of 1 µg. The coal samples described in Section 3.2 were used. The process can be classified as dry process (according to classification given in Section 2.2). A photograph of the apparatus is shown in Figure 3.2 with features given in Table 3.2.

Table 3.2: Cahn Thermax 700 Thermogravimetric analyser important features

<table>
<thead>
<tr>
<th>Part/feature</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>100 g</td>
</tr>
<tr>
<td>Weighing Range</td>
<td>± 10 g</td>
</tr>
<tr>
<td>Readability</td>
<td>1 µg</td>
</tr>
<tr>
<td>Maximum Temperature</td>
<td>1700 °C</td>
</tr>
<tr>
<td>Heating Rate</td>
<td>1-100 °C/min</td>
</tr>
<tr>
<td>Temperature Repeatability</td>
<td>± 3 °C</td>
</tr>
<tr>
<td>Sample volume</td>
<td>29 cm³</td>
</tr>
<tr>
<td>Reactor Tube Volume</td>
<td>350 cm³</td>
</tr>
</tbody>
</table>

The furnace can be operated isothermally or non-isothermally with an accuracy of ±3 °C. The reaction and purge gases are controlled by an on-off switching sequence as specified by the user. Time, weight and temperature are measured and logged with a coupled computer. The experiments were conducted at atmospheric pressure (0.875 bar) with 1 mm diameter particles at 750 °C and 900 °C. A total mass of 500 mg of the coal sample was loaded into the basket of the TGA and a gas flow rate equal to 800 ml/min was used.
The procedure consisted of a pre-combustion stage using air (ash preparation) with an initial non-isothermal heating period (20 °C/min) followed by an isothermal period (750 °C and 900 °C) (16 h), after which a sulphur dioxide containing gas was introduced (3000 ppm SO$_2$, 8.0% CO$_2$, 8.0% O$_2$, 83.7% N$_2$) for the determination of the desulphurisation properties of the ashes.

![Figure 3.2: Cahn Thermax 700 Thermogravimetric Analyser](image)

The methods employed by other researchers to determine the kinetics of desulphurisation include SO$_2$ concentration measurement and thermogravimetry. The thermogravimetry approach, as previously successfully used by Ar & Balci (2002); Cheng et al. (2004b); Han et al. (2005); Li et al. (2007); Mukondiwa (2007), Ngeleka
(2005), Rahmani & Sohrabi (2006) and Zhang et al. (2003) was employed to
determine the sulphur dioxide capture kinetics of coal ashes in this study. The mass
increase versus time data was employed to evaluate the conversion of active calcium
to calcium sulphate. Experiments were repeated to confirm reproducibility (Appendix
B, Figures B1 – B6).
“If you can't explain it simply, you don't understand it well enough.”

Albert Einstein
RESULTS AND DISCUSSION: SULPHUR SELF-RETENTION

4.1 INTRODUCTION

Sulphur self-retention results are presented and discussed in this chapter. Coal analysis results are presented in Section 4.2. The focus is confined to chemical properties, petrographic properties, mineral analysis and physical structural properties. Section 4.3 presents coal ashes analysis results with the focus on mineral analyses and physical structural analysis. The presentation of sulphur analysis results, calcium analysis results, calcium/sulphur ratio results and retention efficiency discussion is given in Section 4.4.

4.2 COAL ANALYSIS

The following properties are presented, chemical (proximate and ultimate), petrographic, mineral analysis and structural properties for the six samples. The analyses were carried out according to procedures and standards discussed in Section 3.3 and 3.5.

4.2.1 Proximate and ultimate analysis

The proximate analysis results of the coal samples are shown in Table 4.1. The low grade coals studied have high ash contents (ranging from 37.0 wt % to 47.9 wt %,
d.b). Everson et al. (2006) observed similar ash contents on typical Highveld South African coals (37.3 wt % to 54.3 wt %). The ash content values observed by Wagner (2007 and 2008) on coals from Witbank-Highveld – Ermelo coal fields in Mpumalanga Province (South Africa) ranged from 18.4 wt % to 52.6 wt %. Van Dyk et al. (2009) observed 25.8 wt % on coal from coal mines in the Mpumalanga area (South Africa). The ash content provides an indication of the quantity of inorganic material in the coal and incorporates mineral matter in situ in the coal structure, as well as out-of-seam inorganic contamination (Van Dyk et al., 2009). Rajaram, (1999) reported that Indian coals have high ash content (> 45 wt %), hence they are comparable to coals used in this study. Ash can contain alkaline oxides with the potential to react with sulphur dioxide thereby decreasing the required amount of added sorbent (Manovic et al., 2002; 2006 & Grubor et al., 2003).

Table 4:1: Proximate analysis of selected coal sample

<table>
<thead>
<tr>
<th>Sample Identity (Coal)</th>
<th>Inherent moisture</th>
<th>Volatile matter</th>
<th>Ash</th>
<th>Fixed carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>1.7</td>
<td>20.3</td>
<td>47.9</td>
<td>30.1</td>
</tr>
<tr>
<td>C3</td>
<td>3.2</td>
<td>22.9</td>
<td>37.0</td>
<td>36.9</td>
</tr>
<tr>
<td>D1</td>
<td>5.6</td>
<td>19.5</td>
<td>39.3</td>
<td>35.6</td>
</tr>
<tr>
<td>E1</td>
<td>1.9</td>
<td>20.1</td>
<td>38.9</td>
<td>39.1</td>
</tr>
<tr>
<td>E3</td>
<td>3.3</td>
<td>19.3</td>
<td>37.3</td>
<td>40.1</td>
</tr>
<tr>
<td>F1</td>
<td>1.5</td>
<td>19.3</td>
<td>46.4</td>
<td>32.8</td>
</tr>
</tbody>
</table>

The ultimate analysis of the selected coal samples is given in Table 4.2, showing relatively high levels of sulphur (ranging from 0.6 wt % to 1.9 wt %). This is a characteristic of South African low grade coals.

The observed total sulphur values are consistent with published results on South African coals (Van Niekerk et al., 2010) i.e. 1.13 wt % for Waterberg coal and 1.99 wt % for Highveld coal. The sulphur content observed by Everson et al. (2006) on South African coals was 1.7 wt % to 3.1 wt % for the coals examined. Wagner (2007 and 2008) observed total sulphur values that ranged from 1.59 wt % to 1.93 wt %.
4.2.2 Petrographic properties

Microscopic examination using petrographic methods provided valuable information regarding organic composition, maturity and the associations of the organic matter and minerals that occur in coal (du Cann, 2008).

*Rank (degree of maturity) – Reflectance of vitrinite in the coal*

The mean random reflectance of the coal samples ranged from 0.58 to 0.78 (Table 4.3). The samples can be characterised as bituminous Rank C to D coals (du Cann, 2008). The results are typical of single seam, non-blend coals (terminology of the Economic Commission for Europe of the United Nations (ECE-UN) International Codification System for Medium and High Rank coals).

These reflectance values are consistent with previously published values on South African coals i.e. Rr% of 0.69 and 0.64 for Waterberg coal and Highveld coal respectively (Van Niekerk et al., 2010). There is also consistency with random reflectance ranging from 0.63 to 1.71 reported by Fabian’ska and Kruszewska (2003) on fifteen South African coals from the Waterberg, Soutpansberg (Limpopo Province) and Main Karoo (Mpumalanga and KwaZulu-Natal Provinces). The results are comparable to published values on international coals. Alonso et al. (2001), reported...
random reflectance of 0.62, 0.66 and 1.77 for Cerrejon Colombian coal (coal CER),
Australian coal (coal BB2) and Taff Merthyr UK coal (coal TAF) respectively.

Table 4.3: Coal vitrinite random reflectance

<table>
<thead>
<tr>
<th>Sample Identity (Coal)</th>
<th>Vitrinite Random Reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(^a\text{Rr} %)</td>
</tr>
<tr>
<td>A2</td>
<td>0.72</td>
</tr>
<tr>
<td>C3</td>
<td>0.66</td>
</tr>
<tr>
<td>D1</td>
<td>0.58</td>
</tr>
<tr>
<td>E1</td>
<td>0.78</td>
</tr>
<tr>
<td>E3</td>
<td>0.68</td>
</tr>
<tr>
<td>F1</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Nomenclature

\(^a\text{Rr} %\) Random reflectance of vitrinite, oil immersion
\(^b\sigma\) Standard deviation

Maceral, microlithotypes, carbominerites and minerites

A complete analysis of the macerals, microlithotypes, carbominerites and minerites
(vol. %) is shown in Tables 4.4-4.6. All samples have a high concentration of
minerites in accordance with the proximate analysis. The visible minerals values
observed (23 vol. % to 45 vol.%) were higher than that of the South African coal
studied by Van Dyk et al. (2009), who reported visible minerals ranging from 15 mass
% to 19 mass % (i.e. approximately 11.5 vol. % to 14.6 vol. %, assuming the average
coal density (Perry & Green, 1997) of 1.3 g/cm\(^3\)).
Table 4.4: Maceral analysis of coal samples

<table>
<thead>
<tr>
<th>Sample Identity (Coal)</th>
<th>Maceral analysis (percent by volume)</th>
<th>Visible minerals</th>
<th>Total reactives %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vitrinite</td>
<td>Liptinite</td>
<td>Inertinite</td>
</tr>
<tr>
<td></td>
<td>aVIT %  bPV %  cTV %  dS/R/C %  eALG %  fTOTL %</td>
<td>gRSF %  hISF %  iF/SEC %  jMIC %  kINT %</td>
<td>lR INT %  mI INT %  nTOT I %</td>
</tr>
<tr>
<td>A2</td>
<td>26 2 28 2 9 2 1 2 9 2 5 45 34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>26 0 26 4 0 4 6 10 3 1 5 14 39 31 41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>10 0 10 3 0 3 11 17 1 2 9 18 58 29 33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E1</td>
<td>14 0 14 3 0 3 8 12 2 1 10 20 53 30 35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E3</td>
<td>7 1 8 3 0 3 9 11 2 1 18 25 66 23 38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F1</td>
<td>8 0 8 2 0 2 11 17 1 1 10 15 55 35 31</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Nomenclature

- aTotal Reactives = Vitrinite + Liptinite + Reactive Semifusinite + Reactive Inertodetrinite
- bVIT = Vitrinite
- bPV = Pseudovitrinite
- bS/R/C = Sporinite/resinite/cutinite
- bTOT L = Total liptinite (formerly referred to as exinite)
- bRSF = Reactive semifusinite
- bMIC = Micrinite
- aI INT = Inert inertodetrinite
- bTV = Total vitrinite
- bALG = Alginite
- bF/SEC = Fusinite/secretinite
- bR INT = Reactive inertodetrinite
- bTOT I = Total inertinite
Table 4.5: Results of microlithotype, carbominerite and minerite analyses

<table>
<thead>
<tr>
<th>Sample Identity (Coal)</th>
<th>Microlithotype analysis (percent by volume)</th>
<th>Carbominerite maceral/mineral (%)</th>
<th>Minerite mineral-rich (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mono-macerals (%)</td>
<td>Intermediate maceral/maceral mixtures (%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>aVitrite bInertite cClarite dDurite eVitrinertite fTrimacerite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>19 7</td>
<td>3 0 4 7 33 27</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>16 18</td>
<td>3 4 8 9 13 29</td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>7 27</td>
<td>1 8 5 3 31 18</td>
<td></td>
</tr>
<tr>
<td>E1</td>
<td>6 36</td>
<td>1 6 7 4 18 22</td>
<td></td>
</tr>
<tr>
<td>E3</td>
<td>7 43</td>
<td>1 5 5 2 26 11</td>
<td></td>
</tr>
<tr>
<td>F1</td>
<td>4 24</td>
<td>0 3 4 4 27 34</td>
<td></td>
</tr>
</tbody>
</table>

Nomenclature

aVitrite: vitrinite >95 %
bInertite: inertinite > 95 %
cClarite: vitrinite + liptinite > 95 %
dDurite: inertinite + liptinite > 95 %
eVitrinertite: vitrinite + inertinite > 95 %
fTrimacerite: vitrinite, inertinite, liptinite > 5 %

Carbominerite: total inorganic/organic microlithotypes
Minerite: > 60 vol. % minerals
Table 4.6: Carbominerite analysis of coal samples

<table>
<thead>
<tr>
<th>Sample Identity (Coal)</th>
<th>Maceral/mineral associations</th>
<th>Mineral-rich particles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>aCarbargilite and Carbosilicite %</td>
<td>cCarbopyrite %</td>
</tr>
<tr>
<td>A2</td>
<td>27</td>
<td>3</td>
</tr>
<tr>
<td>C3</td>
<td>10</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>D1</td>
<td>26</td>
<td>1</td>
</tr>
<tr>
<td>E1</td>
<td>12</td>
<td>2</td>
</tr>
<tr>
<td>E3</td>
<td>19</td>
<td>1</td>
</tr>
<tr>
<td>F1</td>
<td>21</td>
<td>1</td>
</tr>
</tbody>
</table>

Nomenclature

aCARBARGILITE: Coal + 20 to 60 vol. % clay minerals

bCARBOSILICITE: Coal + 20 to 60 vol. % quartz

cCARBOPYRITE: Coal + 5 to 20 vol. % sulphides

dCARBANKERITE: Coal + 20 to 60 vol. % carbonates

eCARBOMINERITE: Total inorganic/organic microlithotypes
The total carbominerites values are generally higher (13 vol. % to 33 vol. %) when compared to previously published values on South African coals. Wagner (2007 and 2008) reported values ranging from 4.1 vol. % to 26.1 vol. %. The carbominerites fraction consists of carbargilite (coal + 20 vol. % to 60 vol. % clay minerals), carbosilicite (coal + 20 vol. % to 60 vol. % quartz), carbopyrite (coal + 5 vol. % to 20 vol. % sulphides) and carbankerite (coal + 20 vol. % to 60 vol. % carbonates). Calcium bearing carbominerite (e.g. carbankerite), minerates and sulphur bearing carbopyrites can participate in sulphur self-retention and desulphurisation. The argillaceous, carbonates and sulphides observed were comparable with those reported by Singh et al. (2010) on coal from the Lati Formation, Tarakan basin, East Kalimantan, Indonesia.

4.2.3 Mineral analysis

The overall results of wt % phase and mineral proportions in the coal samples are presented in Table 4.7. The analysis was carried out according to methodology and standards discussed in Section 3.4 and in Van Alphen (2009b). The major phases are aluminosilicate (kaolinite) and, to a lesser extent, quartz. This is expected as kaolinite and quartz are the major minerals in South African coals (Maphala, 2008; Matjie et al., 2006; Skhonde, 2009; Van Dyk et al., 2009). Coal A2 had the highest aluminosilicate (kaolinite), whereas coal E1 had the lowest. The lowest quartz mass percentage was observed for coal C3 (Van Alphen, 2009b).

The major calcium bearing phases are calcite (accounting for 1.47 wt % to 6.80 wt %), dolomite (ranging from 0.64 wt % to 4.39 wt %), calcium bearing sulphates (with 0.10 wt % to 0.62 wt %), and apatite (ranging from 0.05 wt % to 0.55 wt %). Of all these phases, only calcite and dolomite are active during sulphur dioxide capture (Conn et al., 1993; Grubor & Manovic, 2002). Sulphur is distributed amongst inorganic sulphate (accounting for 0.10 wt % to 0.62 wt %), pyritic minerals (ranging from 0.73 wt % to 8.79 wt %) and organically bound sulphurs (ranging from 4.72 wt % to 23.2 wt %) in coals. The elemental sulphur (bound in these coal organic structures) was not quantified.
The QEMSCAN results were comparable with the results for Australian coal sample CRC272 observed by Liu et al. (2005). The researchers observed 10.5 wt %, 1.11 wt %, 0.04 wt % and 1.54 wt % for calcite, dolomite, gypsum and pyrite, respectively, at the CCSD (Cooperative Research Centre for Coal in Sustainable Development).

The coal mineral matter analyses were consistent with the previously published results by Van Dyk et al. (2009) for South African Highveld coals. Van Dyk et al. (2009) reported 2.3 wt %, 3.9 wt % and 4.3 wt % on calcite, dolomite and pyrite, respectively. The minerals in coal occur in various phases with the mode of occurrence

Table 4.7: Coal mineral analysis

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Composition</th>
<th>Sample Identity (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A2</td>
</tr>
<tr>
<td>Sulphate/Gypsum</td>
<td>Ca- and Al-bearing sulphates</td>
<td>0.13</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>5.56</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO₃</td>
<td>1.03</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>2.19</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
<td>0.64</td>
</tr>
<tr>
<td>Apatite</td>
<td>Ca₅(PO₄)₃(OH,F,Cl)</td>
<td>0.33</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al₂Si₂O₅(OH)₄(clay)</td>
<td>39.5</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂(sand)</td>
<td>6.29</td>
</tr>
<tr>
<td>Illite/Hydromusc</td>
<td>K₂Al₆Si₆O₂₀(OH)₄</td>
<td>0.66</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₅Si₇O₂₀(OH)₄</td>
<td>1.02</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₂(AlSi₃O₁₀)(F,OH)₂</td>
<td>0.28</td>
</tr>
<tr>
<td>Microcline</td>
<td>(K,Na)AlSi₃O₈</td>
<td>0.43</td>
</tr>
<tr>
<td>Rutile</td>
<td>TiO₂</td>
<td>6.42</td>
</tr>
<tr>
<td>Coal-organic</td>
<td></td>
<td>35.1</td>
</tr>
<tr>
<td>Coal</td>
<td>C,H,O,N</td>
<td>0.45</td>
</tr>
<tr>
<td>Other</td>
<td>Unidentified Phases</td>
<td>100</td>
</tr>
</tbody>
</table>
depending on the conditions to which the coal was subjected. Most minerals are predominantly favoured by phases occurring during the mining state, but may also occur after coal is treated (Vassileva & Vassilev, 2006). For example, dolomite and unaltered calcite are mostly of detrital occurrence and originate from the coarse-grained carbonate rocks of the source areas (Vassileva & Vassilev, 1996). Pyrite occurs as euhedral and massive cell-filling form, mainly from the bacterial reduction of sulphate-rich waters permeating through the peat bed. Included and excluded pyrite will behave differently upon oxidation e.g. excluded grains of pyrite fragment and oxidise to form magnetite and hematite (Liu et al., 2005; Ward, 1978; Slater et al., 1995).

4.2.4 Physical structural properties

The results of structural properties of the coal samples are presented in Table 4.8. Measurements done on coal samples were performed according to the method and conditions presented in Section 3.5.1.

The Dubinin-Radushkevich (D-R) equation was applied to the carbon dioxide adsorption data. The reliability of results was checked by the correlation coefficient between the logarithm of volume of adsorbed gas and the logarithm of relative pressure (Gürdal & Yalçın, 2001). The obtained correlation coefficient values were >0.94, indicating acceptable measurements. Coal D1 had the biggest Dubinin-Radushkevich surface area of 93.9 m$^2$/g, and coal A2 had the lowest Dubinin-Radushkevich surface area of 55.5 m$^2$/g. These observed Dubinin-Radushkevich micropore surface area values were comparable with previously published results by Mastalerz et al. (2008), who reported ranges of 68.7 m$^2$/g to 110 m$^2$/g, 75.8 m$^2$/g to 94.8 m$^2$/g and 74.3 m$^2$/g to 106 m$^2$/g for coal samples from Sullivan County, Knox County and Gibson County, respectively.

Pores in coal can be categorised into three classes according to diameter. These are: micropores (<2 nm); mesopores (2-50 nm); and macropores (>50 nm), (IUPAC, 1982; Ngeleka, 2005; Gürdal & Yalçın, 2001). Micropore volume and surface area were determined in this study.
The density measurements were carried out according to the method presented in Section 3.5.2. The observed skeletal densities (ranging from 1.61 to 1.71 g/cm$^3$), were comparable to densities of coals reported by other researchers.

Alvarez & Borrego (2005) reported helium skeletal densities ranging from 1.279 g/cm$^3$ to 1.776 g/cm$^3$ on coals from Prairie (Canada), Anna (Germany), Ebony (Indonesia), Brunner (New Zealand), Victoria (Peru) and Buller (New Zealand). Victoria coal (with the lowest hydrogen content of 1.2 wt % daf) had the highest density (1.77 g/cm$^3$) whereas the Buller coal (with the highest hydrogen content of 5.8 wt % daf) had the lowest density of 1.279 g/cm$^3$. Saha et al. (2007) employed both Helium Pycnometer and Nitrogen Pycnometer techniques to determine the skeletal densities of 44 coals of Indian origin. The same authors reported densities ranging from 1.20 to 1.57 g/cm$^3$ on Indian coals.

Table 4.8: Physical structural properties of coal samples

<table>
<thead>
<tr>
<th>Sample Identity (coal)</th>
<th>aSkeletal density (g/cm$^3$)</th>
<th>bDubinin-Radushkevich surface area (m$^2$/g)</th>
<th>bDubinin-Radushkevich micropore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>1.71</td>
<td>55.5</td>
<td>0.022</td>
</tr>
<tr>
<td>C3</td>
<td>1.68</td>
<td>78.2</td>
<td>0.031</td>
</tr>
<tr>
<td>D1</td>
<td>1.71</td>
<td>93.9</td>
<td>0.038</td>
</tr>
<tr>
<td>E1</td>
<td>1.65</td>
<td>66.0</td>
<td>0.026</td>
</tr>
<tr>
<td>E3</td>
<td>1.66</td>
<td>56.9</td>
<td>0.022</td>
</tr>
<tr>
<td>F1</td>
<td>1.61</td>
<td>66.9</td>
<td>0.027</td>
</tr>
</tbody>
</table>

**Equipment**

a – Measured using Quantachrome Helium Pycnometer
b – Measured using Micromeritics ASAP 2010

Dubinin-Radushkevich micropore volume and surface area were observed to decrease with the increase in coal rank (Figures 4.1 and 4.2). This trend can be attributed to the blocking of pore space by bitumen generated during the coalification process (Gürdal & Yalçin, 2001; Levine, 1993; Mann et al., 1995). Similar trends were observed by Gürdal and Yalçin, (2001) for carboniferous bituminous coals from the Zonguldak
basin in north-western Turkey, and by Mukhopadhayay et al. (1995) for coals from Stellarton basin, Nova Scotia, Canada.

Figure 4.1: Relationship between coal rank and micropore surface area of coals

Figure 4.2: Relationship between coal rank and micropore volume of coals
4.3 ASH ANALYSIS

The results of ash analysis are presented and discussed in this section. The main focus was on mineral analyses (Section 4.3.1) and physical structural analyses (Section 4.3.2).

4.3.1 Mineral analyses

The overall results of wt % mineral phases in coal ash samples are presented in Table 4.9. The ashes were produced by combusting coal according to the method presented in Section 3.6. The mineral analyses were carried out according to methodology and standards discussed in Section 3.4 and in Van Alphen (2009a). The results show that the major phases are aluminosilicate and to a lesser extent quartz (Van Alphen, 2009a).

The major calcium bearing phases are calcium oxide (ranging from 0.9 wt % to 5.2 wt %), calcium magnesium oxide (ranging from 0.4 wt % to 0.8 wt %), Ca-sulphate (ranging from 2.20 wt % to 13.3 wt %), CaMg-sulphate (ranging from 1.1 wt % to 5.7 wt %), CaFe-aluminosilicates glass (ranging from 0.1 wt % to 1.4 wt %) and calcium aluminosilicates glass (ranging from 1.4 wt % to 4.5 wt %). Anhydrite (CaSO₄), gypsum (CaSO₄·2H₂O) and bassanite (CaSO₄·0.5H₂O) are the common calcium sulphates formed when a coal sample is combusted (Van Alphen, 2009a). The form of calcium sulphate is dependent on the environment (humidity and temperature) (Van Alphen, 2009a, Henke et al., 2007; Bezou et al., 1995). Calcium sulphate and calcium magnesium sulphate were not observed in the mineral analysis of coal samples (Table 4.7), whereas the mineral analysis of ashes (Table 4.9) presented calcium sulphates ranging from 2.2 wt % to 13.3 wt % and calcium magnesium sulphate ranging from 1.1 wt % to 5.7 wt %. This observation can be attributed to sulphation of calcium oxide and calcium magnesium oxide during coal combustion (SSR). CaFe-aluminosilicates glass and calcium aluminosilicates glass were also not observed in the coal mineral analysis. The presence of these glass calcium phases (in the ash)
could be attributed to the transformation of original calcium phases (e.g. calcite, dolomite and apatite) in the parent coal.

Table 4.9: Mineral analysis of coal ashes

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Coal Mineral Source</th>
<th>Sample Identity (wt %)</th>
<th>A2</th>
<th>C3</th>
<th>D1</th>
<th>E1</th>
<th>E3</th>
<th>F1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Oxide</td>
<td>Pyrite cleats</td>
<td></td>
<td>1.4</td>
<td>2.3</td>
<td>1.6</td>
<td>5.7</td>
<td>2.7</td>
<td>5.5</td>
</tr>
<tr>
<td>Ca-sulphate</td>
<td>Calcite/sulphur</td>
<td></td>
<td>2.2</td>
<td>4.7</td>
<td>3.2</td>
<td>13.3</td>
<td>2.2</td>
<td>6.8</td>
</tr>
<tr>
<td>CaMg-sulphate</td>
<td>Dolomite/sulphur</td>
<td></td>
<td>1.6</td>
<td>2.9</td>
<td>1.1</td>
<td>4.5</td>
<td>3.3</td>
<td>5.7</td>
</tr>
<tr>
<td>Ca-Oxide(lime)</td>
<td>Calcite cleats</td>
<td></td>
<td>1.0</td>
<td>2.1</td>
<td>1.3</td>
<td>5.2</td>
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<tr>
<td>Ca-P-oxide</td>
<td>Apatite</td>
<td></td>
<td>0.2</td>
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<td>0.0</td>
<td>0.2</td>
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<tr>
<td>CaMg-Oxide</td>
<td>Dolomite cleats</td>
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<td>0.4</td>
<td>0.7</td>
<td>0.6</td>
<td>0.8</td>
<td>0.6</td>
<td>0.7</td>
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<tr>
<td>Quartz</td>
<td>Quartz (sand)</td>
<td></td>
<td>16.9</td>
<td>6.1</td>
<td>26.4</td>
<td>20.5</td>
<td>12.9</td>
<td>16.9</td>
</tr>
<tr>
<td>Aluminosilicate</td>
<td>Kaolinite (clay)</td>
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<td>69.8</td>
<td>75.5</td>
<td>54.9</td>
<td>38.9</td>
<td>72.4</td>
<td>48.0</td>
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<tr>
<td>K-aluminosilicate (microcline)</td>
<td>Microcline</td>
<td></td>
<td>0.8</td>
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<td>1.1</td>
<td>2.0</td>
<td>0.5</td>
<td>3.2</td>
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<tr>
<td>K-aluminosilicate (Muscovite/Illite)</td>
<td>Muscovite/Illite</td>
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<td>0.4</td>
<td>1.2</td>
<td>1.7</td>
<td>0.1</td>
<td>1.4</td>
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<td>Rutile</td>
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<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Anorthite</td>
<td>Crystallised from glass</td>
<td></td>
<td>0.1</td>
<td>0.4</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Diopside</td>
<td>Crystallised from glass</td>
<td></td>
<td>N.D</td>
<td>N.D</td>
<td>N.D</td>
<td>N.D</td>
<td>N.D</td>
<td>N.D</td>
</tr>
<tr>
<td>Ca-aluminosilicate glass</td>
<td>Carbonate/kaolinite coalescence</td>
<td></td>
<td>1.8</td>
<td>2.3</td>
<td>4.5</td>
<td>1.8</td>
<td>1.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Fe-Aluminosilicate glass</td>
<td>Pyrite/kaolinite coalescence</td>
<td></td>
<td>0.9</td>
<td>0.4</td>
<td>1.4</td>
<td>1.2</td>
<td>0.3</td>
<td>2.1</td>
</tr>
<tr>
<td>CaFe-Aluminosilicate glass</td>
<td>Carbonate/pyrite/kaolinite coalescence</td>
<td></td>
<td>0.2</td>
<td>0.1</td>
<td>0.4</td>
<td>0.8</td>
<td>0.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Silica-rich glass</td>
<td>Quartz/carbonate and pyrite coalescence</td>
<td></td>
<td>0.3</td>
<td>0.2</td>
<td>1.1</td>
<td>0.6</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Other</td>
<td>Undefined</td>
<td></td>
<td>1.3</td>
<td>1.5</td>
<td>0.8</td>
<td>2.1</td>
<td>1.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

ND – not detected
Calcite (1.47 wt % to 4.98 wt %) and dolomite (2.16 wt % to 4.39 wt %) are only observed in coal mineral analysis and not in the ash mineral analysis. Similarly calcium oxide, calcium magnesium oxide, calcium sulphate, calcium magnesium sulphate, CaP-oxide, CaFe-aluminosilicate and Ca-aluminosilicate were only observed in ash mineral analysis and not in the coal mineral analysis. This can be attributed to the high temperature transformation of calcite and dolomite. The evaluation of mineral transformation could be extensive and was considered to be beyond the scope of this investigation (Matjie et al., 2006; Van Alphen, 2007; Matjie & Van Alphen, 2008).

Higher pyrite concentrations were observed in coal mineral analysis (up to 7.2mg/100 mg coal) than the pyrite/haematite/magnetite in the ash mineral analysis (maximum 2.2 mg/100 mg coal). This can be attributed to the reaction of pyritic sulphur with calcium oxide and calcium magnesium oxide to form calcium sulphate (anhydrite) and calcium magnesium sulphate. Only inorganic sulphaurs were observed in ashes, distributed amongst Ca-sulphate (ranging from 2.20 wt % to 13.3 wt %), CaMg-sulphate (ranging from 1.10 wt % to 5.70 wt %) and pyrite/hematite/magnetite (ranging from 1.40 wt % to 5.70 wt %). The observed mineral transformations were consistent with the previously published results by Matjie et al. (2006) for South African coals.

X-ray florescence (XRF) and X-ray diffraction (XRD) analyses were not conducted in this study (reason given in Section 3.4.1). QEMSCAN results can be verified (qualitatively) by XRD and XRF results in literature e.g. Loubser & Verryn, 2008; Silva et al., 2010; Akinyemi et al., 2012; Silva et al., 2012 etc.

### 4.3.2 Physical structural analysis

The skeletal densities of coal ash samples are presented in Table 4.10. The measurements were carried out according to the method presented in Section 3.5.2. Ash particles with mullite and quartz inclusions can be expected to have skeletal densities range of 2 g/cm³ to 2.5 g/cm³ (Hemmings & Edwin, 1985). Ash particles with high-Ca glass can be expected to have skeletal density close or lower than 2.5
g/cm³. Ash particles with free oxides such as lime, magnetite, haematite and/or calcium salts such as anhydrite, can be expected to have skeletal density >2.6 g/cm³ (Moreno et al., 2005). The observed skeletal densities ranged from 2.3 to 2.53 g/cm³. These results are to be expected and can be ascribed to the mineralogical composition of the respective coal ashes, considering that the coal ashes in this study are dominated by aluminosilicate and quartz.

Similar observation was made by Moreno et al. (2005) on twenty three coal ashes from European pulverised coal-fired power plants (from Spain, The Netherlands, Italy and Greece).

The same authors observed skeletal densities ranging from 1.3 g/cm³ to 2.7 g/cm³ (i.e. for CCB ash and La Robla ash respectively). Ashes with the highest magnetite content had skeletal densities of 2.5 g/cm³ and 2.7 g/cm³ (i.e. for Ternel ash and La Robla ash respectively). Ash with high lime and anhydrite contents (Lignite ash) had a skeletal density of 2.6 g/cm³.

Young and Cotton (1994) reported skeletal densities of 2.5 to 2.9 g/cm³ and 2.7 to 2.8 g/cm³ for bottom and fly ashes (respectively) tested at Ahlstrom Pyroflow. The corresponding bulk densities were 1.3 to 1.8 g/cm³ and 1.0 to 1.6 g/cm³ for bottom and fly ashes respectively.

Table 4.10: Physical structural properties of coal ashes

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Skeletal density (g/cm³)</td>
<td>2.37</td>
<td>2.30</td>
<td>2.52</td>
<td>2.40</td>
<td>2.53</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Equipment
a – Measured using Quantachrome Helium Pycnometer

4.4 SULPHUR AND CALCIUM ANALYSES
The sulphur analysis of coal was conducted according to the method and standard presented in Section 3.3.2, while the sulphur analysis of their corresponding ashes was conducted according to method and standard presented in Section 3.3.3.

### 4.4.1 Sulphur analysis

The sulphur analysis of coal was presented (Table 4.2) and discussed in Section 4.2.1. The sulphur analysis of ashes is presented in Table 4.11. Ash F1 was observed to have the highest content (2.74 wt %) and ash A2 the lowest (0.76 wt %). This can be attributed to different potential abilities of the respective coal ashes to retain and/or release sulphur during coal combustion. The observed sulphur contents are in agreement with the values (0.39 - 2.21 wt %) reported by Skhonde, (2009) for ash derived from rank C, bituminous coal, from a Highveld mine in South Africa. Matjie and Van Alphen (2008) reported sulphur content ranging from 0.1 - 0.5 wt % on dry screened ash fractions (produced as a by-product of coal gasification at the Sasol gasifier) from Highveld, South African coals.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur (wt %)</td>
<td>0.76</td>
<td>1.05</td>
<td>0.96</td>
<td>2.38</td>
<td>1.52</td>
<td>2.74</td>
</tr>
</tbody>
</table>

**Equipment**

a – High-temperature tube furnace and infrared detection

Comparison of sulphur analysis results of the parent coal and corresponding ash samples are presented in Figure 4.3. Coals were observed to contain higher amount of sulphur ($S_{Coal}$, evaluated in mg/100 mg coal) than their corresponding ashes ($S_{Ash}$, also evaluated in mg/100 mg coal). This can be attributed to the release of sulphur in the form of sulphur dioxide and sulphur trioxide during coal combustion. Coal A2 released the highest amount, whilst coal F1 released the lowest.
The proportions of sulphur forms observed in the South African coals are comparable with those reported by Demirbas (1999) for Turkish Eastern Black Sea Region coals. Demirbas (1999) observed organic sulphur ranging from 0.34 wt % to 2.08 wt %; pyritic sulphur of 0.15 wt % to 5.27 wt %; and sulphate sulphur of 0.02 wt % to 0.52 wt %. Similar results were reported by Shah et al. (2002) for Chinese Beisu and Dizong coals. Only inorganic sulphur was observed in the selected coal ashes.

### 4.4.2 Active calcium oxide evaluation

The basis on which active calcium and active calcium oxide (defined in Glossary) were quantified/evaluated is similar to that employed by Conn et al. (1993) and Grubor and Manovic (2002). Active calcium oxide is considered to be formed as the product of decomposition of calcite and/or dolomite during coal combustion (Li et al., 2008; Fleig et al., 2011). The evaluation of active calcium phases in carbominerite and sulphur in carbopyrites could be extensive and was considered to be beyond the scope of this investigation. Further investigation would be necessary. Calcium present in clays and silicates is considered not to transform into active calcium oxide during
coal combustion (Conn et al., 1993). Active calcium oxide can be evaluated using Equation 4.1. Active calcium was evaluated by calculating the amount of calcium in active calcium oxide.

\[
\text{Active calcium oxide in coal (CaO}_{\text{Active,Coal}}) = \text{CaO}_{\text{calcite}} + \text{CaO}_{\text{dolomite}} \quad (4.1)
\]

\[
\text{Active calcium oxide in ash (CaO}_{\text{Active,Ash}}) = \text{CaO} + \text{CaO}_{\text{CaOMgO}} \quad (4.2)
\]

All phases of calcium oxide in Equations 4.1 and 4.2, (CaO in calcite, dolomite, from decomposition of calcite and from decomposition of dolomite) were calculated from QEMSCAN results. The details of the calculations, based on QEMSCAN (Tables 4.7 and 4.9), are presented in Appendix A.

Calculated active Ca-bearing phases (equivalent CaO) in the coal samples were between 1.22 mg/100mg coal and 4.92 mg/100mg coal. The equivalent active calcium oxide in the ashes ranged between 0.47 mg/100mg coal and 2.2 mg/100mg coal (Figure 4.4).

This can be attributed to the transformation of some of the active calcium oxide (e.g. calcite and dolomite) into inactive calcium bearing phases (e.g. Ca-sulphate, CaMg-sulphate, Ca-aluminosilicate glass and CaFe-Aluminosilicate glass) during coal combustion (see Section 4.3.1).

Conn et al. (1993) studied the reactivity of different calcium forms in low grade coals and stated that the calcium present in clays and silicates cannot react with SO2 under FBC conditions. Cheng et al. (2004a) reported that the active calcium content (CaCO3 and CaO) in Shennu coal ash prepared at 800 °C was 22.4 wt %. The active calcium content of the corresponding sulphation product (CaSO4) was 17.8 wt %.
The results of active calcium to sulphur ratio are presented in Figure 4.5. The details of the calculations, based on QEMSCAN (Tables 4.7 and 4.9), ultimate analysis (Table 4.2) and sulphur analysis of ashes (Table 4.11), are presented in Appendix A. It was observed that the active Ca/S ratios of the parent coals ranged from 0.64 to 3.20, whilst, active Ca/S ratios of their corresponding ashes range between 0.55 and 1.71.

The observed Ca/S ratios are comparable with previously reported values by Cheng et al. (2004a) and Grubor et al. (2003) who reported Ca/S ratios of 1.07 (initial) and a range of 0.34 to 3.17, respectively. A summary of sulphur and calcium analysis results is given in Table 4.12.
The details of the calculations, based on QEMSCAN (Tables 4.7 and 4.9), ultimate analysis (Table 4.2) and sulphur analysis of ashes (Table 4.11), are presented in Appendix A. The basis of mg/100 mg coal was chosen for better comparison of active calcium oxide; active calcium; sulphur; active calcium oxide/sulphur ratio; and active calcium/sulphur ratio for the coals and their corresponding ashes.

Figure 4.5: Active calcium to sulphur ratio
Table 4.12: Sulphur and Calcium analysis

<table>
<thead>
<tr>
<th>COAL</th>
<th>Method</th>
<th>Standard</th>
<th>Equation</th>
<th>Reference</th>
<th>A2</th>
<th>C3</th>
<th>D1</th>
<th>E1</th>
<th>E3</th>
<th>F1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Total Sulphur (mg/100 mg coal)</td>
<td>IR Spectroscopy</td>
<td>ISO 19759</td>
<td></td>
<td>Table 4.2</td>
<td>1.60</td>
<td>0.70</td>
<td>0.60</td>
<td>1.60</td>
<td>1.10</td>
<td>1.90</td>
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<tr>
<td>2. Calcium analysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 Active CaO (mg/100 mg coal)</td>
<td>QEMSCAN</td>
<td>Eskom/VAC</td>
<td></td>
<td>A1</td>
<td>1.42</td>
<td>1.48</td>
<td>1.22</td>
<td>3.14</td>
<td>4.92</td>
<td>4.13</td>
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<tr>
<td>3. Calcium/Sulphur ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>3.1 Ca (Active) /S</td>
<td></td>
<td></td>
<td></td>
<td>A7</td>
<td>0.64</td>
<td>1.51</td>
<td>1.45</td>
<td>1.40</td>
<td>3.20</td>
<td>1.55</td>
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<table>
<thead>
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<th>Method</th>
<th>Standard</th>
<th>Equation</th>
<th>Reference</th>
<th>A2</th>
<th>C3</th>
<th>D1</th>
<th>E1</th>
<th>E3</th>
<th>F1</th>
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<tbody>
<tr>
<td>1. Percentage ash remaining (wt %)</td>
<td></td>
<td>SABS ISO 1171:1997</td>
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<td>Table 4.1</td>
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<td>37.00</td>
<td>39.30</td>
<td>38.90</td>
<td>37.30</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 Active CaO (mg/100 mg ash)</td>
<td>QEMSCAN</td>
<td>Eskom/VAC</td>
<td></td>
<td>A2</td>
<td>0.59</td>
<td>0.93</td>
<td>0.65</td>
<td>2.20</td>
<td>0.47</td>
<td>0.98</td>
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<td>3. Sulphur Analysis</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3.1 Total S (mg/100 mg ash)</td>
<td>HTTFIR</td>
<td>ASTM D 5016</td>
<td></td>
<td>Table 4.11</td>
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<td>0.39</td>
<td>0.38</td>
<td>0.93</td>
<td>0.57</td>
<td>1.27</td>
</tr>
<tr>
<td>3.2 Sulphur self retention (wt %)</td>
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<td></td>
<td></td>
<td>A9</td>
<td>22.9</td>
<td>55.3</td>
<td>63.0</td>
<td>57.8</td>
<td>51.5</td>
<td>66.9</td>
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<tr>
<td>4. Calcium/Sulphur ratio</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.2 Ca (Active)/Sulphur</td>
<td></td>
<td></td>
<td></td>
<td>A8</td>
<td>1.15</td>
<td>1.71</td>
<td>1.23</td>
<td>1.70</td>
<td>0.59</td>
<td>0.55</td>
</tr>
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a: Quantitative Evaluation of Mineralogy by Scanning Electron Microscopy
b: Infrared spectroscopy
c: High-temperature tube furnace and infrared detection
d: Eskom/VAC fly ash mineral/phase standards
4.4.4 Sulphur self-retention

Sulphur self-retention was calculated from the ratio of sulphur retained in coal ash after the coal was combusted (Table 4.11), to the total sulphur in the raw coal (Table 4.2 and 4.11). Details of the calculations are presented in Appendix A. The sulphur self-retention results in this study are shown in Figure 4.6. Combustion of coals in this study resulted in self retention ranging from 22.9 to 66.9 wt %.

Cheng et al. (2004a) reported that 64% of the sulphur is retained in the coal ash during the combustion of Chinese Shenmu (Shanxi Province) coal in a furnace at 800 °C. This can be attributed to the fact that organic sulphur decomposes rapidly at around 400 °C to be liberated as SO₂, while it is difficult for CaCO₃ to directly undergo sulphation at this low temperature. Also, higher temperatures are required for CaCO₃ to decompose into CaO and CO₂ (Cheng et al., 2004a). The results are comparable with previously published results by Puff et al. (1983) who reported that approximately 60% of sulphur is retained due to sulphur self-retention (SSR), while values around 90% were observed with fly ash recirculation. Coal ash is expected to
give much higher sulphur-retention efficiency in a fluidised bed combustor due to the low furnace temperature and long residence times (Sheng et al., 2000; Cheng et al., 2004a).

Combustion conditions (temperature, pressure, excess air ratio, coal ash residence time, combustor design etc) and coal characteristics (coal rank, Ca/S ratio, content of sulphur forms, particle size etc) have been reported to influence sulphur self-retention efficiency (Grubor et al., 1999; Sheng et al., 2000; Manovic et al., 2002; Li et al., 2008). The effect of the active Ca/S ratio on sulphur self-retention is presented in Figure 4.7. The sulphur self-retention percentage was observed to increase with an increase in active Ca/S (with coal E3 being an aberration). High active Ca/S would imply high amount of active CaO to react with SO$_2$ released during coal combustion, according to Equation 5.1.

Some of the sulphates (e.g. calcium sulphate) are expected to be stable during coal combustion (Borgwardt & Harvey, 1972). Pyrite is expected to release around 30% of its sulphur (to become pyrrhotite/troilite) during devolatilisation at temperatures around 550 – 600 °C, according to Equation 2.1 (such that only FeS is left at around 1000 °C) (Gryglewicz, 1995). Different kinds of organic sulphurs are expected to be released (at different temperatures) during devolatilisation. Aliphatic thiols are
expected to decompose at 200-300 °C, sulphides and disulphides at around 350-400 °C, cyclic and aromatic sulphides at 700-800 °C and thiophenes at above 800 °C (Section 2.3) (Telfer & Zhang, 1998).

The effect of active random reflectance on sulphur self-retention is presented in Figure 4.8. The sulphur self-retention percentage was observed to increase with a decrease in random reflectance percentage (with coal E1 and F1 being offsets). The deviations of coals E1 and F1 could be attributed to the degree of the influence of other factors on sulphur self-retention (e.g. distribution of active calcium, forms of sulphur, distribution of different sulphur forms).

Figure 4.8: Effect of random reflectance on SSR%

Coal rank has been reported to be one of the factors influencing the efficiency of sulphur self-retention (Grubor et al., 1999; Sheng et al., 2000). Sulphur self-retention can be expected to increase with a decrease in coal rank, if the dominant active calcium is the calcium associated within the coal matrix as exchangeable ions. This can be attributed to the fact that low-rank coals are considered to contain more highly active calcium associated to the coal matrix as exchangeable ions (Grubor & Manovic, 2002; Sheng et al., 2000). Sulphur self-retention can, however, conversely be expected to increase with an increase in coal rank, if the retention is dependent on
the distribution of the sulphur forms. This can be attributed to the fact that high-rank coals are considered to contain more stable sulphur compounds (Grubor & Manovic, 2002).

Organically associated Ca and S in the coal macerals interact with each other at lower temperatures to form bassanite (CaSO$_4$·0.5H$_2$O). This mineral transforms further at 400 ºC to form anhydrite (CaSO$_4$). Anhydrite starts to decompose at elevated temperatures (>1150 ºC) to form CaO and SO$_2$ (Pinetown & Boer, 2006; Matjie et al., 2006; Skhonde, 2009; Matjie, 2008; Matjie et al., 2008).

A trend in which sulphur self-retention increased with a decrease in coal skeletal density (Figure 4.9) was observed in this study (with coals C3 and D1 being the deviations). The deviations of coals C3 and D1 can be attributed to the content and distribution of active calcium as well as to the influence of other factors on sulphur self-retention.

![Figure 4.9: Relationship between SSR% and skeletal density of coal](image-url)
The sulphur self-retention efficiency of low rank coals can be expected to increase with the decrease in coal density. This can be ascribed to the high organic matter content in less dense coal, under conditions in which the high organic matter will contain high organically associated active calcium (Fleig et al., 2011; Grubor and Manovic, 2002). Grubor and Manovic (2002) reported that coals with less dense particles had high sulphur self-retention efficiency during combustion of Kolubara coals.
“Research is to see what everybody else has seen, and to think what nobody else has thought.”

Albert Szent-Gyorgyi
5 RESULTS AND DISCUSSION: SULPHUR DIOXIDE CAPTURE

5.1 INTRODUCTION

In this chapter the results and discussion of sulphur dioxide capture are presented. Only two coals (C3 and E1) were investigated in this section. The two coal samples were selected on the basis of highest active calcium content in their respective ashes (2.51 wt % and 5.67 wt % respectively, Table A1). In Section 5.2, the ash preparation results are presented. The results of sulphur dioxide capture are presented and discussed in Section 5.3. Attention was paid to the effect of temperature on ash properties. Section 5.4 presents the results of conversion of active calcium oxide. Adsorption capacity results are presented in Section 5.5. In Section 5.6, the modelling of the sulphur dioxide capture results is given, where the shrinking core model was used.

5.2 ASH PREPARATION

The coal combustion profiles (up to 60 min) are presented in Figure 5.1. Reproducibility results for coal C3 combustion are shown in Figures B1 and B2. Preparation of the ashes was accomplished under conditions specified in Section 3.7. The ash preparation followed the typical coal combustion temperature profile (Crelling et al., 1992). The profile for coal C3 flattened at 43 min for the experimental run at 750 ºC, whereas the profile of coal E1 flattened at 45 min. The combustion profiles of coals C3 and E1 at 900 ºC both flattened at 40 min (Figure 5.1).
Combustion at 900 °C occurred over slightly shorter periods of time when compared to combustion at 750 °C. Full combustion profiles of coals C3 and E1 are presented in Figure 5.2.

Figure 5.1: Coal C3 and E1 combustion

Figure 5.2: Coals C3 and E1 combustion
Table 5.1 compares the ash content from coal combustion with the proximate analysis. The ash contents observed during ash preparation were higher than the ash content values from the (SABS ISO 1171:1997) proximate analysis (presented in Table 4.1), with coal E1 (750 °C) being the exception.

This can be attributed to the non-representativeness of the samples used, considering that 1 mm particles (mass of 500mg) were used in the TGA experiments. Relatively long coal combustion durations (960-1000 min) were employed in order to ensure complete combustion (Figure 5.2). No significant change in mass was observed for times greater than 600 min.

<table>
<thead>
<tr>
<th>Sample Identity (Coal)</th>
<th>Temperature (°C)</th>
<th>Coal mass (mg)</th>
<th>Ash mass (mg)</th>
<th>Ash content (wt %) [TGA]</th>
<th>Ash content (wt %) [Proximate analyses]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3</td>
<td>750</td>
<td>505</td>
<td>227</td>
<td>45.0</td>
<td>37.0</td>
</tr>
<tr>
<td>C3</td>
<td>900</td>
<td>510</td>
<td>240</td>
<td>47.1</td>
<td>37.0</td>
</tr>
<tr>
<td>E1</td>
<td>750</td>
<td>507</td>
<td>200</td>
<td>39.3</td>
<td>38.9</td>
</tr>
<tr>
<td>E1</td>
<td>900</td>
<td>508</td>
<td>209</td>
<td>41.2</td>
<td>38.9</td>
</tr>
</tbody>
</table>

5.3 SULPHUR DIOXIDE CAPTURE

The normalised results of the ash mass increase in the presence of SO\(_2\) as time progresses are presented in Figure 5.3. Reproducibility results for the sulphur dioxide capture by coal ash C3 are presented in Figures B3 and B4. Sulphur dioxide capture experiments were executed according to the conditions and procedure given in Section 3.7. The increase in ash mass as time progresses is considered to be sulphur dioxide capture (defined in Glossary).

Sulphur dioxide capture is considered to occur according to Equation 5.1 (conditions favouring the maintenance of calcium oxide).

\[
\text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4
\]  

(5.1)
The parameters influencing the sulphur dioxide capture capability of a sorbent include: combustion conditions (e.g. temperature, pressure, residence time); physical properties of the sorbent (e.g. porosity, morphology, surface area); combustor design (e.g. fluidised bed combustor, pulverised coal-fired boiler); and so forth (Celentano et al., 1987; Cheng et al., 2004a&b). Above all, the parameters considered to have influenced the sulphur capturing capabilities of ashes C3 and E1, active calcium content are observed to have the greatest influence (active calcium contents of ashes C3 and E1 are presented and discussed in Table 4.12 and Section 4.4.2, respectively). A similar observation was made by Cheng et al. (2004a). The same authors reported that coal ash with high active calcium content (Shenmu coal ash consisting of 22.4% active calcium) had the highest CaSO$_4$ content (17.79%) in the sulphation product, when compared to Huangling coal ash (bearing 4.48% active calcium) which produced a sulphation product consisting of 4.92% CaSO$_4$. Experiments conducted at 900 °C were observed to result in higher sulphur dioxide capture than those conducted at 750 °C for both ashes C3 and E1 respectively.
5.4 CONVERSION OF ACTIVE CALCIUM OXIDE

The results of the mass increase as time progresses (Section 5.3) were employed to evaluate the increase in moles of CaSO₄ or decrease in moles of active CaO as time progresses. The decrease in moles of active CaO (and SO₂ + ½ O₂) as the moles of CaSO₄ increase is considered to be the conversion of active calcium oxide. The equipment and method employed to determine the rate of change in mass are presented and discussed in Section 3.7. The reproducibility results of conversion of active CaO (equivalent) are presented in Figures B5 and B6. Mass increase is considered to be as a result of the chemical reaction of sulphur dioxide with active CaO in the presence of oxygen (Equation 5.1). For easier calculations, mass increase is attributed to SO₃ (SO₂ + ½ O₂) moles gained (Dennis and Hayhurst, 1990).

The same approach was employed to evaluate the conversion of calcium oxide to calcium sulphate by: Ar & Balci (2002); Cheng et al (2004b); Han et al (2005); Li et al (2007); Mukondiwa (2007); and Ngeleka (2005). Generally, the conversion of active calcium oxide to calcium sulphate can be evaluated by calculations based on the increase in moles of CaSO₄/ moles of active CaO, using equation 5.2a or by integrating through the conversion curve on the basis of change in SO₂ concentration, using equation 5.2b (Cheng et al., 2004b). The mathematical equation used, in this study, to calculate conversion is Equation 5.2a, since the thermogravimetric analysis method was employed (Section 3.7).

\[ X_{CaO} = \frac{\text{Moles of CaSO}_4 \text{ formed}}{\text{Moles of active CaO in sample}} \]

\[ = \frac{(W_t - W_0)M(SO_3)}{(X_{CaO} W_0)M(CaO)} \]  \hspace{1cm} (5.2a)

\[ X_{CaO} = \frac{M(CaO)n_{SO_2}}{W_0} \left[ \int_0^t \left( 1 - \frac{C_{SO_2 \text{ in}}}{C_{SO_2 \text{ out}}} \right) dt \right] \]  \hspace{1cm} (5.2b)
The time taken to convert 50% of active calcium oxide (in the coal ash) to CaSO₄ was employed as a yard stick to determine the active calcium oxide conversion efficiency of coal ashes C3 and E1 at 750 °C and 900 °C temperatures. Some of the parameters considered to influence the active calcium oxide conversion efficiency of coal ashes C3 and E1 (namely, temperature and Ca/S ratio) are presented in Table 5.2.

Table 5.2: Parameters influencing active calcium oxide conversion

<table>
<thead>
<tr>
<th>Sample Identity (Ash)</th>
<th>Temperature (°C)</th>
<th>( t_{0.5} ) (min)</th>
<th>(^b) Active Ca/S ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3 750</td>
<td>215</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>C3 900</td>
<td>165</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>E1 750</td>
<td>430</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>E1 900</td>
<td>200</td>
<td>1.70</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) – time taken to convert 50% of the active calcium oxide (in coal ash) to CaSO₄

\( b \) – Table A1

5.4.1 Effect of temperature on conversion of active calcium oxide

It was observed that the conversion increased with the temperature, i.e. experiments conducted at higher temperatures had higher conversion of active calcium oxide than did experiments conducted at lower temperatures (Figures 5.4 and 5.5). This expected phenomenon is in agreement with observations made by other researchers (Han et al., 2005; Cheng et al., 2004b; Mukondiwa, 2007).

The sulphur dioxide capture experiments were allowed to proceed for longer periods (500 min) in order to optimise the utilisation of active calcium. Conversion of active calcium oxide in coal ash C3 goes up to 80% at 900 °C, whereas it only reaches 75% at 750 °C. Similarly, for coal ash E1, conversion of up to 70% was observed at 900 °C and 55% at 750 °C.
For shorter time periods (90 min), the conversion of active calcium in coal ash C3 goes up to 40% at 900 °C, whereas it only reaches approximately 30% at 750 °C. Similarly, for coal ash E1, conversion of up to 35% was observed at 900 °C and 25% at 750 °C.
Figure 5.6 presents the rate of active calcium oxide conversion versus time. The plot is for the rate of conversion from time, \( t_0 \) to \( t_{0.5} \), \( \frac{dX}{dt} \).

A similar approach was employed by Li et al. (2007). The same authors differentiated calcium oxide conversion from time, \( t = 0 \) min to time, \( t = 20 \) min, and plotted \( \frac{dX}{dt} \) against time. Li et al. (2007) stipulated that the rate of conversion integrates the effect of chemical reaction rate and gas diffusion during sulphation.

The temperature was observed to have a greater influence than active Ca/S on the conversion rate of active CaO. The Ca/S ratio did not vary much for both ash C3 and E1 (1.71 and 1.70 respectively), yet the rate of conversion varied at the same temperature.

This can be ascribed to the forms of sulphur in ash, e.g. non-reactive calcium sulphate and calcium magnesium sulphate, which does not influence sulphur dioxide capture. Li et al. (2007) made a similar observation (i.e. CaO conversion rate increasing with temperature) for the conversion rate of calcium oxide in CaO/fly ash sorbent at temperatures ranging from 400 °C to 800 °C (under atmospheric pressure). These
observations were consistent with results reported by other researchers. Cheng et al. (2004a) and Sheng et al. (2000) reported that coal ash gives higher sulphur dioxide capture efficiency in a fluidised bed combustor at temperatures ranging from 800 – 900 °C with long residence times. The travelling grate furnace has been reported to give low sulphur capturing efficiency (10%) on Chinese coal ash due to instability of CaSO₄ at 1200 °C to 1500 °C and poor gas-solid contact conditions (Zhou et al., 2001). Cheng et al. (2003) reported that Chinese Shikantai coal ashes with high Ca/S ratio gave lower sulphur capturing efficiency (>28%) in the pulverised coal-fired boiler, due to high flame temperature (1300 °C to 1600 °C) and short residence time.

5.4.2 Effect of ash properties on conversion of active calcium

A comparison of active calcium conversion of coal ashes C3 and E1 is presented in Figure 5.7 and 5.8. Coal ash E1 had higher active calcium content (5.20 wt % and 0.80 wt % CaO and CaMgO respectively) when compared to active calcium content of coal ash C3 (with 2.10 wt % and 0.70 wt % CaO and CaMgO respectively). Also, coal ashes C3 and E1 showed similar Ca/S ratios (1.71 and 1.70 respectively).

Larger conversions were obtained with coal ash sample C3, which did not correlate with the calcium to sulphur ratio given in Figure 4.5, Table 4.12 and Table A1. An understanding of the difference was, however, obtained by means of the reaction rate modelling described in the modelling section. The distribution of the active calcium phases (low concentration) in a predominantly high ash solid structure appears to affect (dominate) the overall performance of the sulphation process. The distribution of active calcium phases (segregation and liberation) in coal ashes requires further investigation. However, the process could be extensive and was thus considered to be beyond the scope of this investigation.
Figure 5.7: Active CaO conversion to CaSO$_4$ at 750 ºC – Ashes C3 and E1

Figure 5.8: Active CaO conversion to CaSO$_4$ at 900 ºC – Ashes C3 and E1
5.5 ADSORPTION CAPACITIES

The adsorption capacities (after 90 min) of coal ashes C3 and E1 at 750 ºC and 900 ºC, respectively, are shown in Table 5.2. A period of 90 min was chosen for comparison with published work by Li et al. (2007) and Mukondiwa (2007). Mukondiwa (2007) evaluated the adsorption capacity of ash, dolomite and limestone over periods of 180 min. Equation 5.3 was used to calculate the adsorption capacity of these ashes per kg. The same equation was used by Mukondiwa (2007).

Adsorption capacity = weight of sulphur dioxide adsorbed/ total weight of ash

\[ \text{Adsorption capacity} = \frac{(W_t - W_0)(M(SO_2))}{W_0(M(SO_3))} \]  

(5.3)

Table 5.2: Adsorption capacities after 90 min

<table>
<thead>
<tr>
<th>Sample identity (Ash)</th>
<th>Temperature (ºC)</th>
<th>SO₂ adsorption (g/kg Ash)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3</td>
<td>750</td>
<td>17.9</td>
</tr>
<tr>
<td>C3</td>
<td>900</td>
<td>21.3</td>
</tr>
<tr>
<td>E1</td>
<td>750</td>
<td>24.4</td>
</tr>
<tr>
<td>E1</td>
<td>900</td>
<td>38.1</td>
</tr>
</tbody>
</table>

Since the increase in mass is considered to result from the sulphation of coal ash with \( SO_3 \) (\( SO_2 + \frac{1}{2} O_2 \)), the molecular weight ratio of \( SO_2 \) to \( SO_3 \) was used in calculating the mass of \( SO_2 \) captured.

Coal ash E1 was observed to have a higher adsorption capacity (at 90 min sulphation time) when compared to ash C3, at both 750 ºC and 900 ºC. This can be attributed to the relatively higher amount of active calcium in ash E1 (2.20 mg/100mg coal). The adsorption capacities of both samples were higher at 900 ºC than at 750 ºC respectively. A similar observation was reported by Mukondiwa (2007) for the adsorption capacity of a South African coal ash. Lee et al. (2005) reported desulphurisation activity ranging from 53.6 to 244.7 mg \( SO_2/g \) CaO on sorbent synthesised from fly ash, CaO and CaSO₄.
There are few publications on the adsorption of coal ash available in the literature. A lot has been published on sulphur dioxide adsorption of fly ash derived zeolites for temperatures and pressures ranging from 25 °C to >800 °C and 1 to 21.4 atm (Srinivasan and Grutzeck, 1999; Chriswell and Gollakota, 1987; Gollakota and Chriswell, 1988; Davini, 1996; Suchecki et al., 2004; Querol et al., 2002; Ogenga et al., 2010). The silicates in ashes C3 and E1 could have played a role in the absorption of SO₂ in this study.

In most cases, adsorption breakthrough curves (plots of change in concentration of SO₂ against time) are used to evaluate the adsorbed SO₂ (in terms of mg SO₂/g sample). Gollakota and Chriswell (1988) presented adsorption capacities ranging from 7.6 – 37.9 mg SO₂/g of sample at 25-800 °C and 1 – 21.4 atm. Srinivasan and Grutzeck (1999) reported adsorption of 6-7 mg SO₂/g of sample on zeolites prepared by mixing and heating 5 g fly ash, 12.5 g (3M) NaOH and 1 g NaCl at 150 °C over 7 days. An adsorption capacity of up to 38 mg SO₂/g of sample was observed by Suchecki et al. (2004). Querol et al. (2002) reported adsorption of up to 20 mg SO₂/g of sample.

5.6 MODELLING OF OVERALL REACTION RATE

5.6.1 Introduction

In this section the modelling of the sulphation reaction rate (active CaO conversion) is presented for two ash samples (C3 and E1) in order to generate meaningful results (considering the accuracy of thermogravimetric analyser). A number of models e.g. unreacted shrinking core models, grain models and pore models, can be employed to describe and to mathematically analyse the calcium-based sorbent sulphation reaction of laboratory and pilot plant generated data as discussed in Section 2.7 (Ngeleka, 2005; Grubor et al., 2003; Borgwardt et al., 1987; Szekely & Evans, 1970; Ramachandran, 1983; Bhatia and Perlmutter, 1980; Kocaefe et al., 1987; Borgwardt & Bruce, 1986; Borgwardt et al., 1987; Milne et al., 1990). The most commonly used models for sulphation chemical reaction are the unreacted shrinking core models.
(Mukondiwa, 2007; Rahmani & Sohrabi, 2006; Zevenhoven et al., 1998). The motivation is discussed in Section 2.7.5.

5.6.2 Ash properties

The coal ashes used have been shown in Section 4.3 to be very complex mixtures of many minerals that can be expected to have an influence on the overall chemical and physical properties. These properties are very different to those of dolomites normally used for desulphurisation and must be considered when choosing the overall reaction rate model. The major differences with corresponding effects are the following:

(1) The presence of a large quantity of inert minerals such as aluminosilicates and quartz, (Table 4.9) with low concentrations of calcium minerals (active material) dispersed throughout ash particles to create a medium in which diffusion of gas could become important.

(2) The element calcium in the particle is distributed between active and inactive mineral phases which need to be quantified for reliable reaction rate kinetics. This does not occur with dolomites with a high concentration of calcium oxide or carbonate (Zevenhoven et al., 1998).

Many researchers (e.g. Mukondiwa, 2007; Ngeleka, 2005; Rahmani & Sohrabi (2006); Szekely & Evans, 1970; Zevenhoven et al., 1998) used the shrinking core model for desulphurisation with dolomites and mixtures of dolomites and coal ashes. Under these circumstances a sharp interface between reacted and unreacted zones exists where chemical reaction takes place. This model was also chosen for this study with the assumption that the fine calcium oxide particles, that react (surface reaction) with the sulphur dioxide, are dispersed at the interface, and that a product layer is formed and offers resistance to mass transfer.
5.6.3 Shrinking core model

The shrinking core model was selected based on the characteristics of the ash samples. The evaluation was confined to product layer diffusion and reaction only, with negligible film diffusion resistance which was deliberately minimised experimentally by using high gas flow rates. A regression procedure involving the comparison of experimental results with model predictions and treating parameters such as reaction constants and diffusion coefficients as unknowns (regressed parameters within groups) was carried out.

The samples used in this study have very low concentrations of calcium oxide. It was thus assumed that no pore blocking occurred. As a result, physical structural changes were assumed to be negligible after the conversion of CaO to CaSO$_4$. In contrast to carbonaceous matter, characterised by growing and collapsing pores, the overall physical structure (pores sizes) of the particle does not change much. The random pore model incorporates both pore growth and coalescence during the reaction (Kaitano, 2008). On this basis, the random pore model accounting for pore size changes would not be applicable for ashes such as those examined in this study.

The shrinking core model incorporating diffusion through the ash layer and chemical reaction on the surface was evaluated according to Equations (5.4) to (5.8) (Han et al., 2005; Li et al., 2007; Zevenhoven et al., 1998). The overall reaction time (total) is given by Equation (5.4), which consists of a linear relationship involving diffusion and chemical resistances (additive). Equations (5.5) and (5.6) are the respective parameters describing diffusional and chemical steps. Equations (5.7) and (5.8) account for the size reduction of the inner core that, according to the shrinking core model, results from the conversion that produces the surrounding outer layer. The effective diffusivity and particle diameter were assumed to be constant. The evaluation consisted of fitting the model, Equation (5.4), to experimental results using a regression procedure with $t_{kin}$ and $t_{dif}$ as unknowns. Various combinations of the terms in Equation (5.4) were examined. This consisted of overall reactions controlled by either chemical reaction or diffusion or by a combination of chemical reaction and diffusion.
\[ t = t_{\text{kin}} A(X) + t_{\text{diff}} B(X) \]  

(5.4)

with

\[ t_{\text{kin}} = \frac{\rho_{\text{mol,CaO}} R_p}{bk_j C_{\text{SO}_2}} \]  

(5.5)

and

\[ t_{\text{diff}} = \frac{\rho_{\text{mol,CaO}} R_p^2}{6b D_{\text{eff}} C_{\text{SO}_2}} \]  

(5.6)

\[ A(X) = 1 - (1 - X)^{1/3} \]  

(5.7)

\[ B(X) = 1 - 3(1 - X)^{2/3} + 2(1 - X) \]  

(5.8)

Zevenhoven’s unreacted shrinking core model with a variable effective diffusivity had been successfully used to model sulphation by investigators such as Mukondiwa, (2007); Ngeleka, (2005); Rahmani & Sohrabi, (2006); and Zevenhoven et al. (1998). The USC-VED is a variant model of the unreacted shrinking core model, but differs from the ordinary unreacted shrinking core model in the sense that it accounts for the changes in form or structure that occur during the chemical reaction of the adsorbent particles. The structural changes are accounted for by a diffusion resistance that depends on conversion, initial porosity, average pore diameter, and pore and product layer diffusivity. These changes lead to alteration of the reaction kinetics to diffusion rate ratio and a variation of the Thiele modulus (Ngeleka, 2005). Zevenhoven’s unreacted shrinking core model with a variable effective diffusivity was also used in this investigation, and it was found that the experimental results were not satisfactorily fitting the model.
5.6.4 Results and Discussion

The experimental results reported under Sections 5.3 – 5.4 for ash samples C3 and E1 were used (at atmospheric pressure). The conversion of active calcium occurring in the calcite and dolomite were used for all the calculations. Model validation and the determination of parameters were carried out for results over long (<500 min) reaction times.

It was found that very good results were obtained with the model (SCM) controlled by diffusion only, when compared to the experimental results for all cases examined as shown in Figures 5.9 to 5.11. A result, based on the model with chemical reaction only, which is clearly not valid, is shown in Figure 5.9.

![Comparison of experimental and SCM model results. Diffusion controlled and reaction controlled Ash C3](image-url)
The results from the regression analysis, the effective diffusion coefficients (at 900 °C) and the parameters required for the calculations are shown in Table 5.3.
It should be noted that the lumped parameter $t_{\text{dif}}$ decreases with temperature. These results also confirmed the presence of an invariant diffusion coefficient during the sulphation period, which is a result of the presence of predominately inert minerals such as aluminosilicates and quartz with very little active calcium minerals. The value of the effective diffusivity (order of $10^{-8} \text{ m}^2/\text{s}$) is relatively small compared to values that can be expected if diffusion within the pores in a porous structure is rate limiting. The presence of another resistance to diffusion is apparent. This resistance may lie in the matrix of the ash, and not in the porous structure of the ash particles. Evidence of this is the fast initial sulphation, when calcium is still available at the walls of the pores, followed by a slower reaction which may be attributed to diffusion of SO$_2$ within the solid matrix of the ash. Error analyses were not conducted in this study due to a limited number of reproducibility experiments (two repeats per experiment). The comparison and averages of respective experiments’ characteristic experimental data parameters are presented in Table B1. The parameters involved are diffusion constant ($D_{\text{eff}}$) and diffusion time scale ($t_{\text{dif}}$).

Table 5.3: Regressed parameters and calculated effective diffusion coefficients

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coal Ash C3</th>
<th>Coal Ash E1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T , (^\circ \text{C})$</td>
<td>750</td>
<td>900</td>
</tr>
<tr>
<td>$T , (\text{K})$</td>
<td>1023</td>
<td>1173</td>
</tr>
<tr>
<td>$t_{\text{dif}} \times 10^3$</td>
<td>1.82</td>
<td>1.26</td>
</tr>
<tr>
<td>Average deviation %</td>
<td>7.50</td>
<td>3.80</td>
</tr>
<tr>
<td>$C_{\text{SO}_2} , (\text{mol/m}^3)$</td>
<td>0.031</td>
<td>0.027</td>
</tr>
<tr>
<td>$\rho_{\text{ash}} , (\text{kg/m}^3)$</td>
<td>2303</td>
<td>2303</td>
</tr>
<tr>
<td>$x_{\text{CaO}} , (\text{wt} %)$</td>
<td>2.52</td>
<td>2.52</td>
</tr>
<tr>
<td>$\rho_{\text{CaO}mol} \times 10^3$</td>
<td>1.04</td>
<td>1.04</td>
</tr>
<tr>
<td>$D_{\text{eff}} \times 10^{-8}$</td>
<td>1.28</td>
<td>2.10</td>
</tr>
</tbody>
</table>

Average deviation% – Average deviation between experimental and model %
“Reasoning draws a conclusion, but does not make the conclusion certain, unless the mind discovers it by the path of experience.”

Roger Bacon
CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The conclusions drawn from this study on characterisation, sulphur self-retention, sulphur dioxide capture and modelling are as follows:

1) The South African low grade coals studied have high ash content (maximum of 47.9 wt %), consisting mainly of kaolinite and quartz and low concentrations of calcium minerals. The major calcium bearing phases in coals were found to be calcite (accounting for 1.47 wt % to 6.80 wt %); dolomite (ranging from 0.64 wt % to 4.39 wt %); calcium/aluminium bearing sulphate (with 0.10 wt % to 0.62 wt %); and apatite (ranging from 0.05 wt % to 0.55 wt %). Of all these phases, only calcite and dolomite are active during sulphur self-retention. The major calcium bearing phases on corresponding ashes were calcium oxide (ranging from 0.9 wt % to 5.2 wt %); calcium magnesium oxide (ranging from 0.40 wt % to 0.80 wt %); Ca-sulphate (ranging from 2.2 wt % to 13.3 wt %); CaMg-sulphate (ranging from 1.1 wt % to 5.7 wt %); CaFe-aluminosilicates glass (ranging from 0.10 wt % to 1.40 wt %); and calcium aluminosilicates glass (ranging from 1.40 wt % to 4.80 wt %). Calcium oxide and calcium magnesium oxide are the only active phases during sulphur dioxide capture.

2) Sulphur in the coal (ranging from 0.6 wt % to 1.9 wt %) is distributed among inorganic sulphate/gibbsite (accounting for 0.10 wt % to 0.62 wt %); pyritic
minerals (ranging from 0.73 wt % to 8.79 wt %); and sulphur bearing organic
structure (ranging from 4.72 wt % to 23.2 wt %). However, only inorganic
sulphurs were observed in ashes, distributed amongst Ca-sulphate (ranging
from 2.2 wt % to 13.3 wt %); CaMg-sulphate (ranging from 1.1 wt % to 5.7 wt
%); and pyrite/haematite/magnetite (ranging from 1.4 wt % to 5.7 wt %).

3) From a petrographic analysis (carbominerite) the presence of carbopyrite (coal
+ 5 to 20 vol. % sulphides) and carbankerite (coal + 20 to 60 vol. %
carbonates) was detected. This may account for some organic sulphur and
calcium/organic minerals. The Ca/S (active calcium) ratio of coals ranged
from 0.64 to 3.20, whilst the Ca/S ratios of ashes ranged from 0.55 to 1.71.
The combustion of coals at 900 °C resulted in sulphur self-retention ranging
from 22.9 wt % to 66.91 wt %. Preparation of the ashes prior to the
desulphurisation experiments (in situ in a thermogrametric analyser) required
very long time periods (up to 1000 min) to ensure a constant mass. This was
attributed to minor mineral transformation and residual carbon burn-off.

4) The calculation of the calcium conversion rates was based on active calcium
oxide (equivalent) present as calcium oxide (lime) and the dolomite.
Increasing conversion results (no plateau) were obtained indicating, as has
been observed for limestones and dolomites (Zevenhoven et al., 1998), that no
pore blocking occurred. This was a result of the very low concentration of
active sorbent in an alumosilicate-rich ash particle. Conversions in the order of
40% of the active calcium oxide were obtained at 900 °C after 90 min of
reaction time.

5) The shrinking core model with diffusion through the product layer as the
determining mechanism was found to describe the overall reaction rate very
well. The different conversions obtained for the two different samples
examined are attributed to the presence of different product layers. The
effective diffusion co-efficient (of the order of 10 \(-8\) m\(^2\) / s) for one of the
samples was found to be small compared to values expected for pore
diffusion, which indicates that diffusion through the solid matrix could be
present.
6.2 CONTRIBUTIONS TO THE KNOWLEDGE BASE OF COAL SCIENCE AND TECHNOLOGY

The following results derived from this study are considered important contributions to the knowledge base of coal science and technology:

1) The use of detailed mineral analyses of coals and ashes for sulphur removal studies using QEMSCAN for assessing the transformation of active calcium minerals during combustion is considered to be very important. This occurs with mineral-rich coals consisting of mainly kaolinite and quartz that form amorphous calcium containing minerals during combustion but are inactive with respect to reacting with sulphur dioxide.

2) The behaviour of calcium containing minerals in coal ashes is very different to calcium containing minerals in dolomite and limestone due to the presence of inactive calcium containing minerals.

3) The use of the ratio of active calcium to sulphur as a parameter for assessing retention is more correct and applicable to mineral-rich coals and ashes.

4) The modelling of sulphation with coal ashes must consider the active calcium oxide involved for correct results.

5) Due to the low concentration of active calcium containing minerals in coal ashes, the effect of a variable diffusivity as a result of structural changes as observed with dolomite and limestone sorbents is not significant.

6.3 RECOMMENDATIONS FOR FUTURE RESEARCH

This study was confined to investigating sulphur self-retention and sulphur dioxide capture of typical low grade South African coal and corresponding ashes using limited operating conditions and ranges and should be expanded in order to get a better
understanding and to acquire more quantitative information for application in fluidised bed combustion and gasification. It is recommended that the following be undertaken:

1) An in-depth study involving the effects of particle size; surface area; pore size distribution (porosity); and detailed morphology of the coal ash on sulphur retention and captive properties.

2) More experimentation concerning mineralogy and transformation during combustion at different temperatures and pressures. Optimisation (temperature and reaction time) of final sulphur retention and capture with respect to mineral composition and transformation.

3) The development of a reaction rate model for retention involving diffusion, thermal gradients and mineral transformation.

4) Sulphur retention experimentation with a fluidised bed involving simultaneous retention and capture.

5) Mineral analyses of coal ash before and after sulphur dioxide capture experiments, in order to track the increase in CaSO$_4$ content.

6) The evaluation of active calcium phases in carbominerite (e.g. carbankerite) and sulphur in carbopyrites.

7) The contribution of organically associated calcium and sulphur towards sulphur self-retention; sulphur dioxide capture; transformation; and the reaction kinetics thereof needs to be investigated.
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APPENDIX A: SULPHUR SELF-RETENTION CALCULATIONS

EQUATIONS

1. Calcium oxide

Active CaO in coal = $\text{CaO}_{\text{Active,Coal}}$

$$\text{Active CaO in coal} = \frac{\text{M(CaO)}}{\text{M(CaCO}_3)} \times \text{CaCO}_3 + \frac{\text{M(CaO)}}{\text{M(CaCO}_3\text{MgCO}_3)} \times \text{CaCO}_3\text{MgCO}_3$$ (A1)

Active CaO in ash = $\text{CaO}_{\text{Active,Ash}} = \frac{\text{M(CaO)}}{\text{M(CaOMgO)}} \times \text{CaOMgO}$ (A2)

Active CaO/S ratio (in coal) = $\frac{\text{CaO}_{\text{Active,Coal}}}{\text{S}_{\text{Coal}}}$ (A3)

Active CaO/S ratio (in ash) = $\frac{\text{CaO}_{\text{Active,Ash}}}{\text{S}_{\text{Ash}}}$ (A4)

2. Calcium

Active Ca in coal = $\text{Ca}_{\text{Active,Coal}} = \frac{\text{M(Ca)}}{\text{M(CaO)}} \times \text{CaO}_{\text{Active,Coal}}$ (A5)

Active Ca in ash = $\text{Ca}_{\text{Active,Ash}} = \frac{\text{M(Ca)}}{\text{M(CaO)}} \times \text{CaO}_{\text{Active,Ash}}$ (A6)

Active Ca/S ratio (in coal) = $\frac{\text{Ca}_{\text{Active,Coal}}}{\text{S}_{\text{Coal}}}$ (A7)
Active Ca/S ratio (in ash) = \frac{\text{Ca}_{\text{Active,Ash}}}{\text{S}_{\text{Ash}}} \quad (A8)

3. Sulphur

Sulphur self-retention = SSR\% = \frac{\text{Sulphur in ash (mg/100 mg coal)}}{\text{Sulphur in coal (mg/100 mg coal)}} \times 100\%

= \frac{\text{S}_{\text{Ash}}}{\text{S}_{\text{Coal}}} \times 100\% \quad (A9)
## Table A1: Sulphur self-retention calculation (mg/100 mg coal and wt %)

<table>
<thead>
<tr>
<th>Analysis/parameter</th>
<th>Method</th>
<th>Standard</th>
<th>Equation</th>
<th>Reference</th>
<th>A2</th>
<th>C3</th>
<th>D1</th>
<th>E1</th>
<th>E3</th>
<th>F1</th>
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<td>100</td>
<td>100</td>
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<td>2. <strong>Calcium oxide</strong></td>
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<td>Eskom/VAC</td>
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**Notes:**
- a - Quantitative Evaluation of Mineralogy by Scanning Electron Microscopy
- b - Infrared spectroscopy
- c - High-temperature tube furnace and infrared detection
- d - Eskom/VAC fly ash mineral/phase standards
APPENDIX B: REPRODUCIBILITY

Figures B1 and B2 presents the normalised reproducibility results of coal C3 combustion at 750 °C and 900 °C respectively (with the accuracy of the Cahn Thermax 700 TGA balance being 1µm and that of the furnace being ±3 °C, Section 3.7). Combustion at both temperatures is observed to be reproducible.

Figure B1: Coal C3 combustion at 750 °C

Figure B2: Coal C3 combustion at 900 °C
Normalised reproducibility results of sulphur dioxide capture of coal ash C3 at 750 °C and 900 °C are presented in Figures B3 and B4, respectively. Cahn Thermax 700 was employed to conduct these experiments, Section 3.7.

Figure B3: Coal ash C3 Sulphur dioxide capture at 750 °C

Figure B4: Coal ash C3 Sulphur dioxide capture at 900 °C
Conversion of active CaO (equivalent) in coal ash C3 at 750 °C and 900 °C was observed to be reproducible (Figures B5 and B6, respectively).

Figure B5: Conversion of active CaO (equivalent) to CaSO$_4$ at 750 °C (C3)

Figure B6: Conversion of active CaO (equivalent) to CaSO$_4$ at 900 °C (C3)
Effective diffusivity ($D_{eff}$) and diffusion time scale of respective experiments (C3 at 900 °C) are compared in Table B1. Full error analysis was not conducted, since only two experiments are compared.

Table B1: Characteristic experimental data of sulphation (C3 at 900 °C)

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<td>(min)</td>
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