# CHAPTER 3

# EXPERIMENTAL PROCEDURES

## 3.1 Introduction

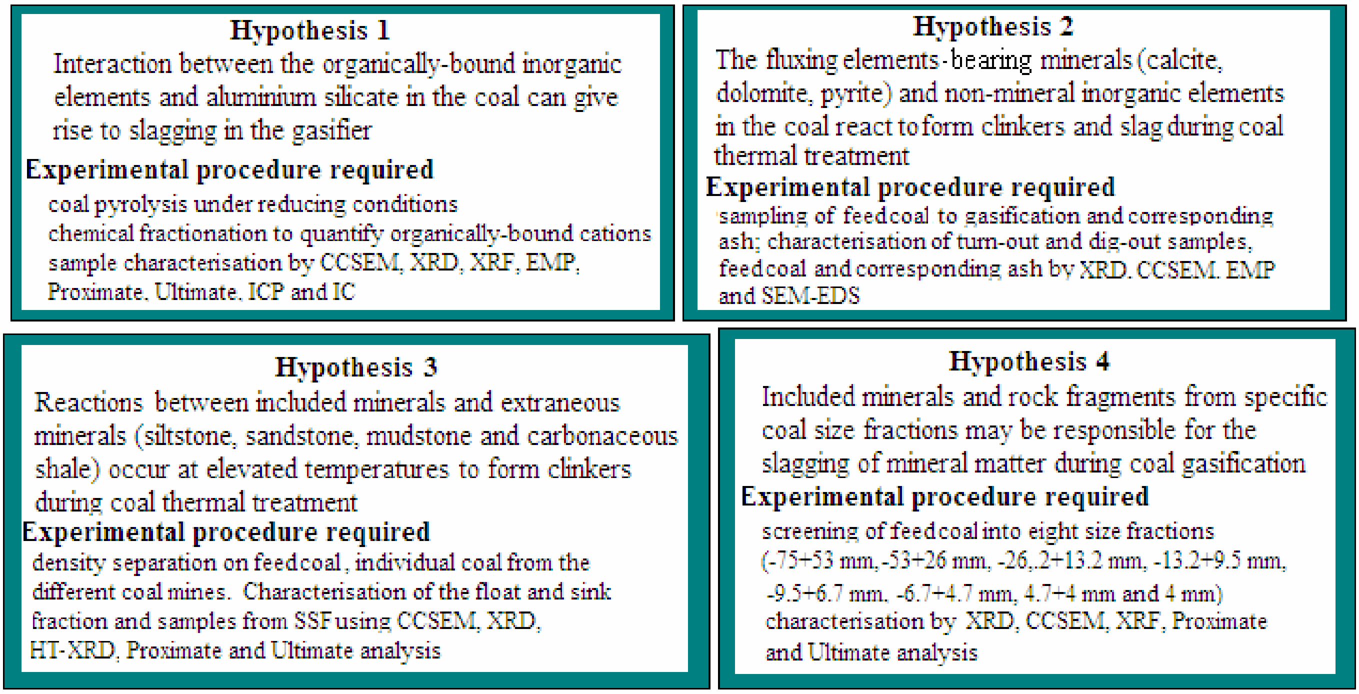
Various experimental methods were used to test the hypotheses that were formulated in Chapter 1, regarding actions and interactions of and between minerals and non-mineral inorganic elements in coal. These are expected to transform or interact with each other at elevated temperatures and pressures to form sintered particles or melt. The experimental procedures used in this study are given in this chapter.

The Run of Mine (ROM) coal samples from six different mines situated in the Mpumalanga province in South Africa contained rock fragments (sandstone, siltstone, mudstone and carbonaceous shale) in addition to the coal itself. These ROM samples were characterised using several analytical techniques to determine fluxing elements that are expected to be responsible for the sintering and slagging of mineral matter (refer to Figure 3.1 for an overview). A blend sample of coarse coal particles (>4-120mm coal fraction; suitable for the gasification process) from the various coal sources was firstly characterised to better understand the chemical and mineralogical characteristics. Subsequently, each sample from the individual mine was tested in a high temperature and pressure autoclave under reducing conditions to better understand transformation of minerals and the organically-bound inorganic elements to new minerals or sintered ash particles.

Samples of "turn-out" test material were taken from a Sasol-Lurgi Fixed Bed Dry Bottom (FBDB) gasifier, using the sampling procedure developed by Bunt (2006). A number of different clinker particles, heated rock fragments and partially burned carbonaceous shale fragments were selected from the gasification ash on the basis of their texture, colour and size. The approach taken here to hand-pick coal and ash particles for characterisation was not used for sampling of these gasifiers in the past. Homogenised coal and gasification ash samples, as was done in the past, were also characterised.

Since the turn-out was done by extracting the gasifier contents from the bottom of the gasifier, only variations along the vertical axis could be determined. Gasifier dig-out is a method that can provide axially as well as radially resolved information.

A simple diagram of the hypotheses tested in this study as well as the experimental procedures followed is shown in Figure 3.1. The experimental procedures are described in detail in this chapter.



**Hypothesis 1**

Interaction between the organically-bound inorganic elements and aluminium silicate in the coal can give rise to slagging in the gasifier

**Experimental procedure required**

coal pyrolysis under reducing conditions
chemical fractionation to quantify organically-bound cations
sample characterisation by CCSEM, XRD, XRF, EMP, Proximate, Ultimate, ICP and IC

**Hypothesis 2**

The fluxing elements-bearing minerals (calcite, dolomite, pyrite) and non-mineral inorganic elements in the coal react to form clinkers and slag during coal thermal treatment

**Experimental procedure required**

sampling of feedcoal to gasification and corresponding ash; characterisation of turn-out and dig-out samples, feedcoal and corresponding ash by XRD, CCSEM, EMP and SEM-EDS

**Hypothesis 3**

Reactions between included minerals and extraneous minerals (siltstone, sandstone, mudstone and carbonaceous shale) occur at elevated temperatures to form clinkers during coal thermal treatment

**Experimental procedure required**

density separation on feedcoal, individual coal from the different coal mines. Characterisation of the float and sink fraction and samples from SSF using CCSEM, XRD, HT-XRD, Proximate and Ultimate analysis

**Hypothesis 4**

Included minerals and rock fragments from specific coal size fractions may be responsible for the slagging of mineral matter during coal gasification

**Experimental procedure required**

screening of feedcoal into eight size fractions (-75+53 mm, -53+26 mm, -26,.2+13.2 mm, -13.2+9.5 mm, -9.5+6.7 mm, -6.7+4.7 mm, 4.7+4 mm and 4 mm)
characterisation by XRD, CCSEM, XRF, Proximate and Ultimate analysis

**Figure 3.1:** Hypotheses tested and experimental procedures used in this study.

## 3.2 Mineralogical analysis across the screened coal fractions

Based on the results reported by Matjie et al. (2006), coarse ash from the gasification process contains Ca-Fe-Ti-K aluminosilicate glass, anorthite and mullite crystals that could be derived from the included minerals in the carbon matrix and from rock fragments. To evaluate the compositions of included minerals and rock fragments from the different size fractions, the representative feed coal stock to the gasification process (a blend from the different mines) was screened into eight size fractions ranging from <75+53mm to <4mm as shown in Figure 3.2. The screened size fractions were crushed to 100% passing 1 mm for the mineralogical investigations. The mineralogy of each screened coal fraction was determined using CCSEM, XRD and chemical analyses (proximate, ultimate and XRF ash elemental). The calculated mass-% size distribution (mass retained) is illustrated in Figure 3.2. A high proportion (>55 mass-%) of the coal feedstock is concentrated in the <53+13.2mm size fractions (Figure 3.2).

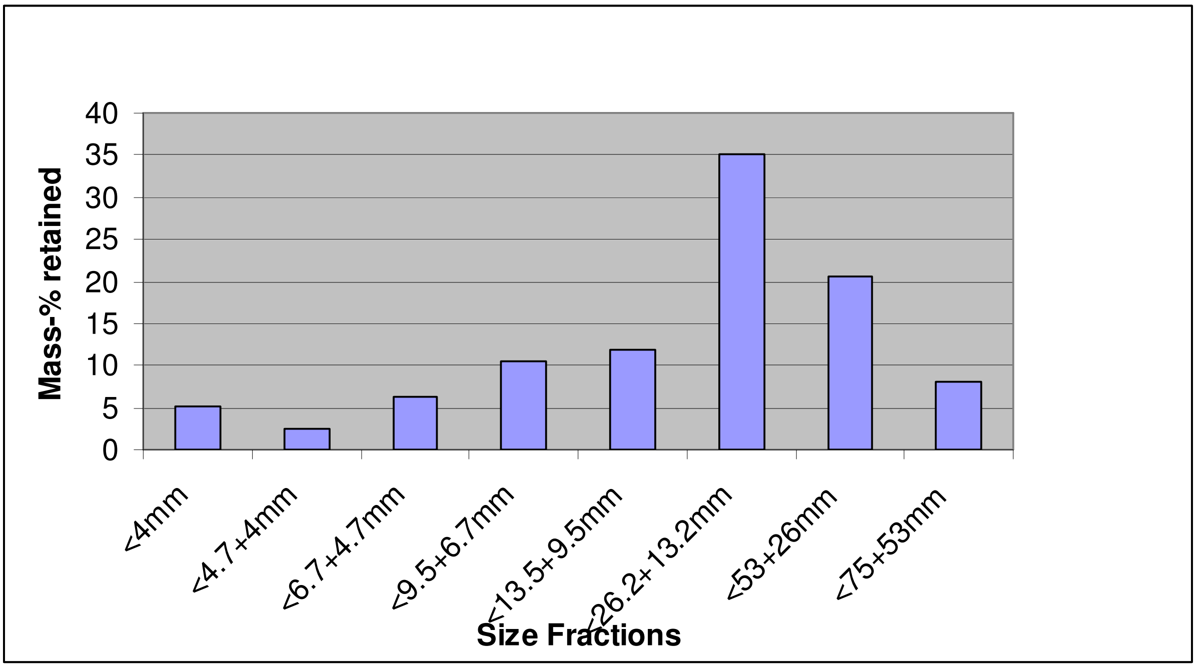


**Figure 3.2:** Mass-% size distribution (mass-% retained).

## 3.3 Density separation of Sasol coals

### 3.3.1 Density separation on the feed coal to the coal-conversion process

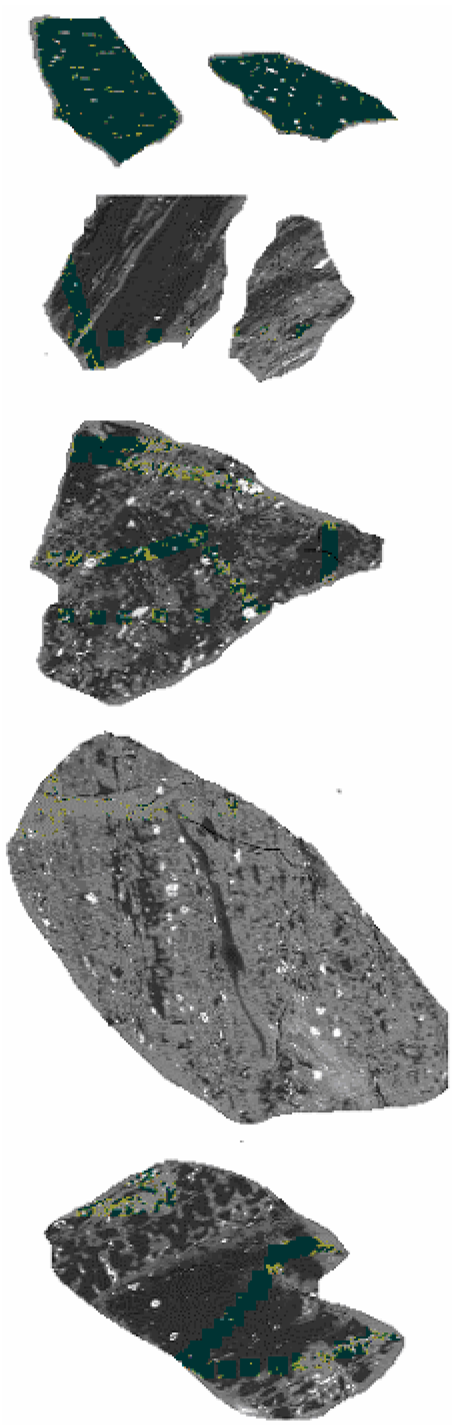
The feed coal to the coal-conversion process is a blend of coals from the different Highveld coal mines, with a wide particle size distribution (PSD) and containing extraneous rock ("stone") fragments. A representative sample of the bulk feed coal taken from a commercial gasifier was crushed and pulverised to obtain 100% passing 1 mm material. The pulverised coal sample was separated into three density fractions (Table 3.1) using mixtures of toluene and bromoform (see Figures 3.3 and 3.4 for examples of higher-density and lower-density materials).

Representative samples of the three density fractions produced from the sink-float techniques were submitted to van Alphen Consultancy for CCSEM analysis, to Sasol Syngas and Coal Research for petrography analysis, to Set Point Laboratories for ash elemental analysis and to Coal and Mineral Technologies (CMT) (Pty) Ltd for proximate, ash fusion temperature and ultimate analyses. Additionally, 25mm polished sections were prepared for electron microprobe analysis at the University of Johannesburg (UJ). Electron microprobe analysis was used to accurately determine the elemental proportions of selected minerals.

In parallel, the -1mm particles of the crushed feed coal were screened by 0.25mm sieve to produce fine coal fractions (100% <0.25mm particles) as well as coarse coal fractions (100% >0.2mm particles). Each fraction was separated by float-sink techniques into a low-density ("floats") fraction and a high-density or "sinks" fraction. The density of the separation medium used in this study was 1.56g/cm$^3$. The mineral matter in the individual size and density fractions was isolated using low-temperature oxygen-plasma ashing; the resulting LTA residues subjected to Rietveld-based X-ray diffraction analysis using procedures described by Ward et al. (2001) and also by the high-temperature XRD using procedure described by French et al. (2001).

**Table 3.1:** Mass (g) and mass-% distribution for the density fractions of Sasol Coal Supplier (SCS) blend

| Density Fraction | Mass (g) | Mass-% |
|---|---|---|
| <1.5g/cm$^3$ | 296.8 | 32.5 |
| >1.5 to <1.8g/cm$^3$ | 458.83 | 50.2 |
| >1.8g/cm$^3$ | 158.14 | 17.3 |
| Total | 913.77 | 100.0 |



Black coal - predominantly black "coal" with minor mineral inclusions (white). Assumed to be vitrinite and/or liptinite

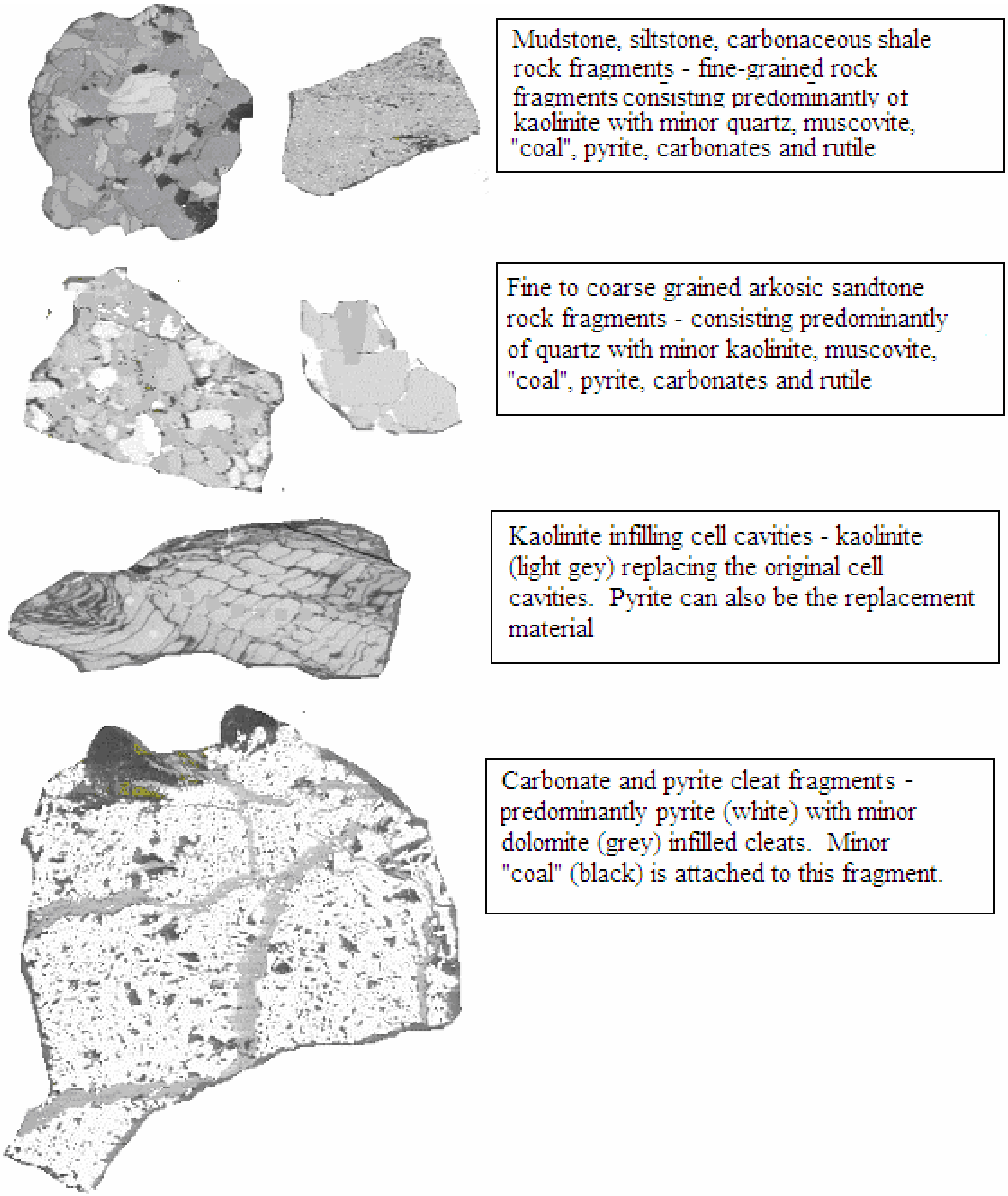
Layered coal - alternating layers of "black" and grey coal. It is assumed that the "grey" coal is predominantly inertinite

Patchy coal particles - particles with "patchy" texture. It is perceived that this could represent inertodetrinite. Minerals are present as white inclusions

Grey coal particles - predominantly "grey" coal particles. Minor "black" coal lenses and white mineral inclusions are present. It is assumed that inertinite is the dominant maceral

Mixed layered and patchy - alternating layers of "black" and "grey" coal. One or more layers have a patchy texture

**Figure 3.3:** Optical images of float coal particles hand-picked from the float fractions (<1.5g/cm$^3$ to <1.8g/cm$^3$). The average width of the images is 6.7mm.



Mudstone, siltstone, carbonaceous shale rock fragments - fine-grained rock fragments consisting predominantly of kaolinite with minor quartz, muscovite, "coal", pyrite, carbonates and rutile

Fine to coarse grained arkosic sandtone rock fragments - consisting predominantly of quartz with minor kaolinite, muscovite, "coal", pyrite, carbonates and rutile

Kaolinite infilling cell cavities - kaolinite (light gey) replacing the original cell cavities. Pyrite can also be the replacement material

Carbonate and pyrite cleat fragments - predominantly pyrite (white) with minor dolomite (grey) infilled cleats. Minor "coal" (black) is attached to this fragment.

**Figure 3.4:** Optical images of rock fragments or stone taken from the sink fractions (>1.8g/cm$^3$). The average width of the samples shown in the images is 6.7mm.

### 3.3.2 Density separation on coal from the individual mines

As was stated in the previous section the coal feedstock contains minerals that are associated with the carbon matrix and also with the extraneous rock fragments. The proportions of fluxing elements-bearing minerals and organically-bound inorganic elements (that are expected to cause the slagging process during gasification) could significantly depend on particle size, mode occurrence of mineral matter in the coal and the density of the coal.

To test these effects for coals from different mines, coal samples were taken from the coal belt of each coal mine using the procedure developed by the operators from the mine. In the experimental procedure 50kg coal sample was taken from the coal belt every 15min. Approximately 100kg coal sample was separated using a mixture of tetra-bromo ethane and benzene at a density of 1.8g/cm$^3$ to produce float and sink fractions.

The sink and float fractions produced in this manner were separately crushed and pulverised to obtain 100% passing 1mm. The prepared samples of the composites from the different mines, float and sink fractions were subsequently submitted for proximate, ultimate, elemental analyses and ash fusion analyses. The proximate, ultimate and elemental analyses of the original sample, float and sink fractions were used in van Alphen Consultancy Coal Quality Predictor (CQP) model to predict the mineral proportions of the composite feed coal, calculated feed coal based on float and sink fractions, float and sink fractions. The model is also based on the elemental analysis of the mineral matter present in the coal. The composite samples were measured by CCSEM.

## 3.4 Pyrolysis of coal samples from Highveld coal mines

Pyrolysis experiments were conducted on six coarse coal samples mined from different collieries situated in the Mpumalanga province in South Africa. The coal samples were tested in a high pressure and temperature autoclave using the following procedure:
Coarse coal particles from the different coal mine (i.e. mines 1 to 6), as well as the blended feed coal (termed "Feed 32") for the coal-conversion process, were tested. Due to the confidentiality issues related to the real names of some South African coal mines, coal samples taken from these mines are termed coal samples 1 to 6. For each test, 1.2kg of coarse coal was pyrolysed at a maximum temperature of 600°C and pressure of 26bars under nitrogen gas for one hour. The flow-rate of nitrogen gas used in this study was 40ml/min (at room temperature and 26bars pressure). The experimental setup is shown in Figures 3.5 and 3.6.

The volatile matter produced during the pyrolysis experiment was condensed in a round bottom flask and the excess gas bubbled through a series of scrubbing solutions, each containing 700ml of distilled water (as shown in Figure 3.6). The first scrubbing solution was removed after the pyrolyser had reached 200°C. The second, third and fourth scrubbing solutions were removed after the coal sample had reached 300°C, 400°C and 600°C respectively. The coal and corresponding char samples were subsequently pulverised to 100% passing 212µm and these samples were submitted for chemical and mineralogical analyses. All scrubbing solutions, the gas liquor (condensed volatile matter) as well as the blank solution (distilled water) were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Ions that are contained in these liquid samples were determined by ion chromatography (IC).

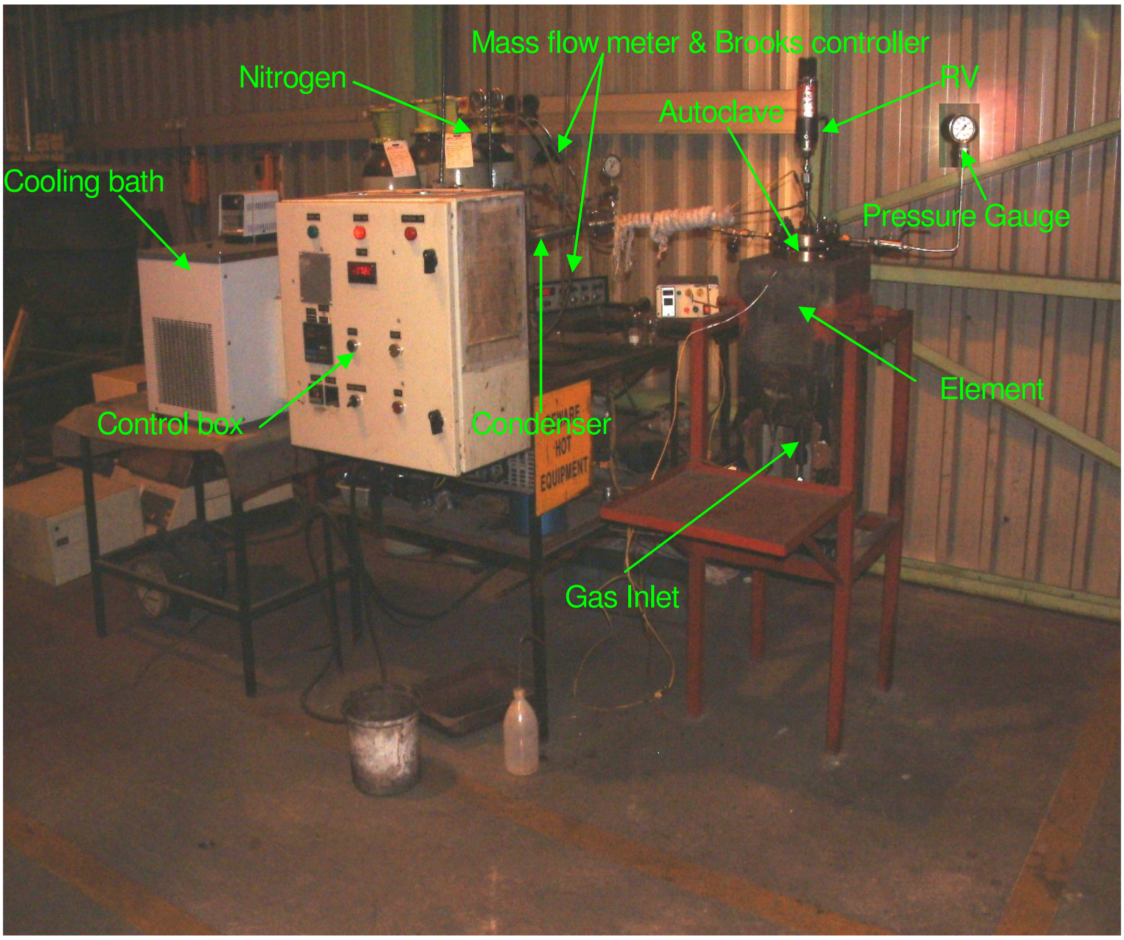


**Figure 3.5:** Photograph showing the high temperature autoclave for pyrolysing coal.

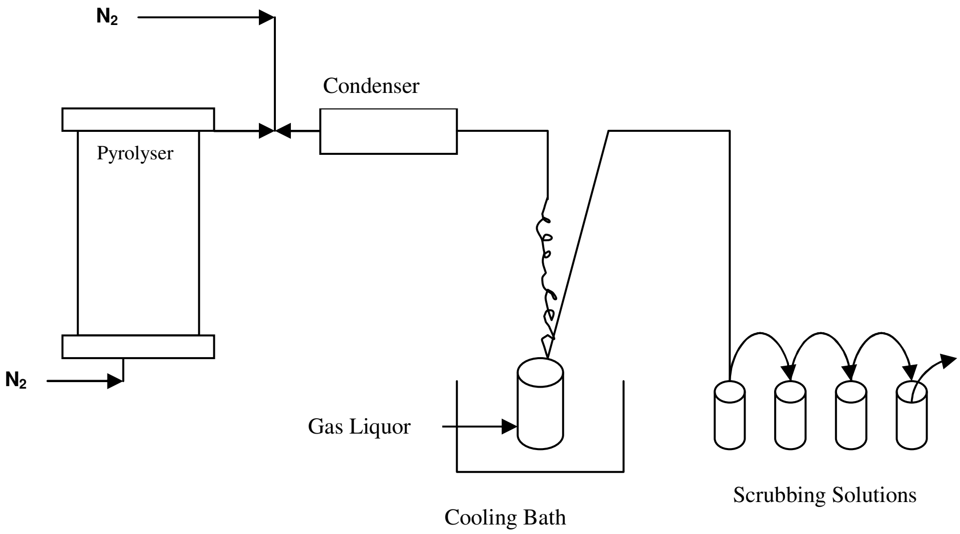


**Figure 3.6:** Schematic showing the experimental setup for the pyrolysis tests with four water scrubbers.

## 3.5 Coal and ash sampling methodology - gasifier

In order to evaluate the chemical, mineralogical and physical properties of coal as well as mineral characteristics of the minerals, glasses and elements present in the coarse gasification ash, representative coal and ash samples from a gasifier were required in this study.

A sampling plan was developed to prepare representative coal and ash samples for this investigation from a commercial gasifier. This gasifier was constructed like the other gasifiers that are being used in the gasification process, but it was assigned to the gasifier tests. In this procedure, the wet coarse coal entering the top of the gasifier was sampled from the conveyor belt on an hourly basis over a 24h period. Approximately 20kg of the coal was acquired for each sample taken. A 50kg sample of corresponding gasification ash was collected from the bottom of the gasifier every three hours for an equivalent 24h period. At the end of the 24h period, the entire composite samples (approximately 480kg coarse coal and 400kg coarse gasification ash) were separately crushed and ground to obtain 100% passing 1mm. Before crushing, the coarse ash fraction, clinker particles were hand-picked from this sample, based on their visual appearance.

Representative fractions of the crushed coal feedstock and coarse ash (100% <1mm particles) were submitted to Sasol Technology Research and Development (Materials Characterisation Group) for (1) qualitative and quantitative XRD analyses and to (2) van Alphen Consultancy for CCSEM analysis (van Alphen, 2000). Proximate, ultimate and XRF ash elemental analyses were also undertaken to support the XRD and CCSEM analysis.

### 3.5.1 Sampling methodology of composite turn-out samples, coarse coal and ash particles taken from the coal-conversion process facility

In order to understand coal mineral matter that gives rise to the slagging and clinker formation within Sasol gasifiers, it was necessary to take coal and ash samples at different levels along the (height) of the gasifier. Since the gasifiers operate under high pressure, it is not feasible to obtain samples while the gasifier is operating. Fortunately, in 2005 a gasifier was shut-down, enabling samples to be acquired from different depths from within the gasifier. Thirty two samples of "turn-out" test material were taken from another gasifier (Figure 3.7), using the sampling procedure developed by Bunt (2006). This gasifier typically contains c.a. 100 tons of material, thus if the ash grate was rotated at its lowest speed and every increment sampled every 0.5h, then 32 x 3m$^3$ samples would be obtained in total. This implied that each sample taken represented a composite of the material in every 0.26m x 4m (height x diameter) slice of the gasifier, given that the gasifier is c.a. 9m high. From the 32 samples taken from the gasifier, 4 gasifier "ash"samples and the original coal (Table 3.2) were selected and analysed by CCSEM and XRD to determine the mass-% variation in mineral and phase proportions formed at the different temperatures.

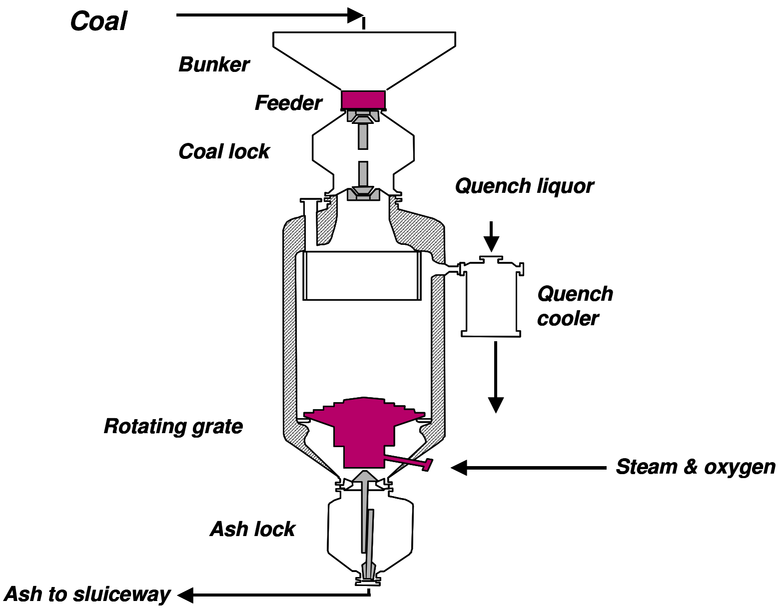


**Figure 3.7:** Schematic showing the Sasol-Lurgi Fixed Bed Dry Bottom (FBDB) gasifier.

**Table 3.2:** Table showing sample number, zones of the gasifier and approximate temperature of the sample

| **Samples number** | **Zones of the gasifier** | **Approximate temperature of sample (°C)** |
|---|---|---|
| 32T | Top of gasifier | 25 |
| 24T | Drying zone | 400 |
| 16T | Pyrolysis | 700-900 |
| 8T | Gasification | 1000-1350 |
| 1T | Bottom of gasifier | 1100-1350 |

**Note**: T: turn-out

The author of this thesis selected a number of different clinker particles, heated rock fragments and partially burned carbonaceous shale fragments from the selected turn-out samples based on their colour, texture and size (Figure 3.8). For each group, individual specimens were selected and regions of interest were identified and cut into 20mm sections (Figure 3.9). The sections were placed in a 30mm mould. Epoxy resin was added and allowed to cure for 12h. The hardened sections were ground and polished, exposing a cross-section surface for analysis. To ensure good sample conductivity and image quality (under the SEM), the polished sections were carbon-coated. Thin sections, polished sections and polished thin sections were prepared from these particles for optical and electron microscope studies.

Selected polished thin sections were further analysed in a Cameca SX-50 electron microprobe, using procedures described by Patterson et al. (1994).

On a hand-specimen scale, many of the samples could be seen to contain partially burnt carbonaceous shale and other rock fragments, set in a fine-grained glassy matrix (Figures 3.10a and 3.10b). The fragments commonly showed reaction rims around the contact with the matrix; these rims presumably developed as they became incorporated into the clinker while moving through the gasifier. Under the microscope some fragments still displayed their original sedimentary texture, with granular silt- and sand-sized particles surrounded by partly fused matrix material (Figure 3.10b). The matrix containing these fragments was seen (under the microscope) to consist mainly of elongated feldspar crystals, set in a very fine grained, essentially glassy vesicular groundmass (Figures 3.10c and 3.10d).

The off-cuts from the sections, representing duplicates of the clinker and ash particles studied under the microscope, were pulverised, and analysed by XRD using a Philips X'pert diffractometer system. The percentages of the individual crystalline phases (minerals) in each sample were determined using the Rietveld-based Siroquant software system (Taylor, 1991), with XRD data for a poorly crystalline metakaolin component incorporated in each task to evaluate the proportion of non-crystalline (amorphous) or glassy components (Ward and French, 2006). The results obtained from this approach were checked by separate tests involving the addition of a weighed-in ZnO spike to some ash samples (Ward and French, 2006), which confirmed that the metakaolin provided a consistent basis for evaluation of the amorphous content.

The chemical composition of each powdered sample was also determined by XRF spectrometry, based on the sample preparation procedures of Norrish and Chappell (1977). The abundance of the individual crystalline phases as indicated by the XRD analysis, combined with their respective stoichiometric compositions, was used to estimate the overall chemical composition of the crystalline components. The overall composition of the glassy (amorphous) phase in each case, was then estimated by subtracting the proportion and inferred composition of the crystalline phases from the bulk ash composition, following procedures described by Ward and French (2006).

**Figure: 3.8:** Photographs of ash clinkers, heated rock fragments, partially burned carbon and coal particles (selected from the turn-out samples) based on their size and colour.
Top row: small and medium heterogeneous clinkers with black and white colours taken from the gasification ash exiting the gasifier.
Second row: small, medium and large heterogeneous clinkers with black and white colours taken from the gasification ash exiting the gasifier.
Third row: large heterogeneous clinkers with black and white colours and partially burnt carbonaceous siltstone taken from the gasification ash exiting the gasifier.
Fourth row: partially burnt carbonaceous siltstone, partially burnt carbonaceous shale and coal particles taken from the gasification ash exiting the gasifier and coal feedstock.
Fifth row: coal particles taken from the coal feedstock.

**Figure 3.9:** Photographs of the polished sections of the selected clinkers, coal, partially burned carbon, and heated rock fragment particles from the turn-out samples.

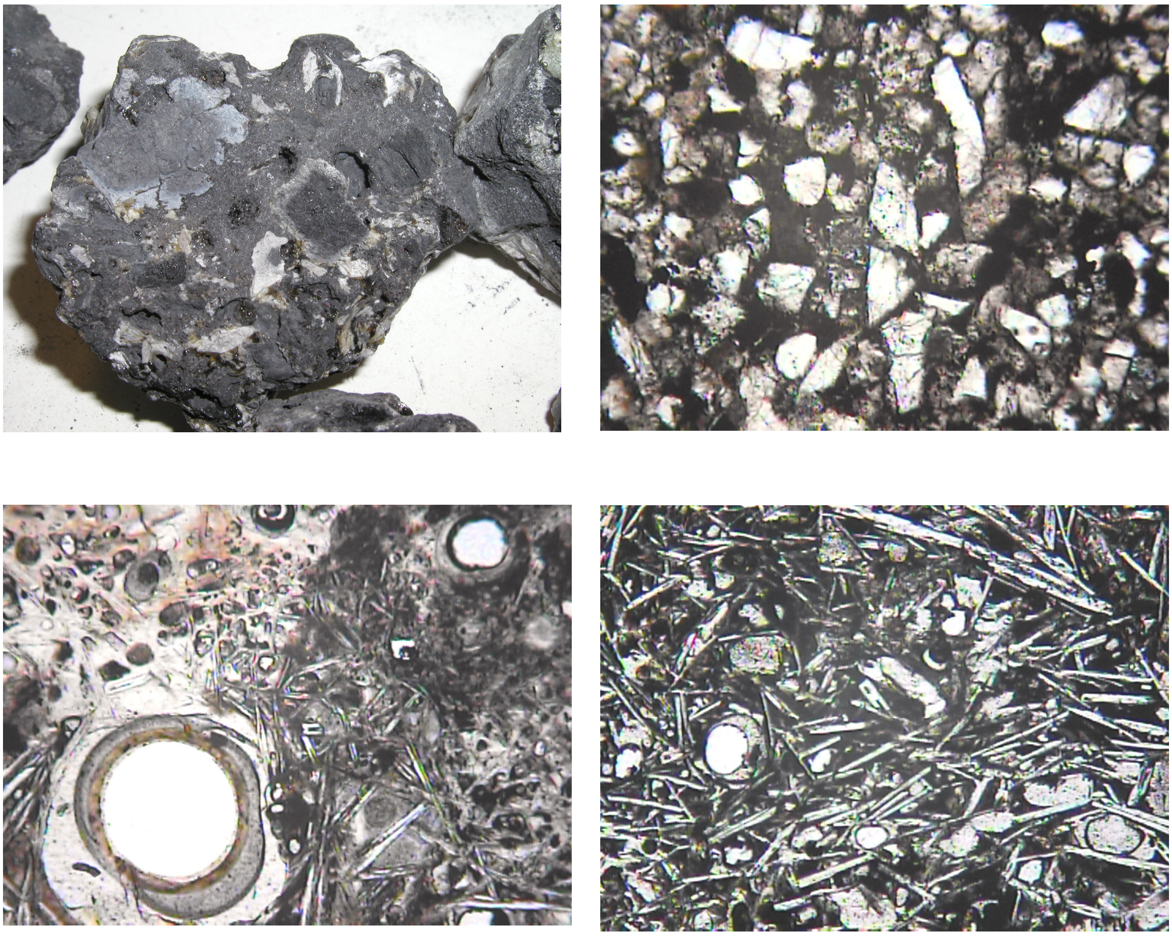


**Figure 3.10:** Textures of clinker materials (optical images). Top left (Figure3.10a): Clinker fragment from gasifier (width approximately 7cm), showing partly burnt carbonaceous shale particles with light-coloured reaction rims set in a fine sintered to glassy matrix. Other images: Thin-section photomicrographs (open polars, field width 1.4mm) of detrital quartz grains in fused siltstone fragment Figure 3.10b (top right), and vesicles (gas cavities) and elongate feldspar crystals in fine glassy groundmass Figures 3.10 c and d (lower left and right.)

### 3.5.2 Sampling methodology of dig-out samples, coarse coal and ash particles taken from the coal-conversion process facility

One of Sasol gasifiers used in a coal gasification process to produce syngas and ash as a by-product was shut down in 2007 due to normal maintenance of the gasification process facility. The opportunity was used to dig out the gasifier to obtain samples. Before the commencement of sampling of coal and ash particles as well as the removal of coal lock from the gasifier, water quenching of the burning coal inside the gasifier was used to cool the gasifier. Water was allowed to pass through the coal-bed and ash-bed in the gasifier until it exited the ash lock at the bottom of the gasifier. The water quenching was repeated several times until it was safe to dig out the gasifier.

The gasifier was dug out by mining it from the top, loading the coal into a drum which was lifted out of the gasifier using cranes. Samples of coal and ash particles (Table 3.3) were taken from the water cooled gasifier at 1m vertical intervals. The procedure as described in Paragraph 3.5.1 was followed to select a number of different clinker particles, heated rock fragments and partially burned carbonaceous shale fragment and coal lumps, for SEM-EDS analyses. Representative sub-samples of all thirteen samples dug out from the gasifier were ground to obtain 100% passing 212µm. The ground coal and ash samples were submitted for proximate, ultimate, XRF and XRD analyses.

**Table 3.3:** Table showing sample number, zones of the gasifier and approximate temperature of the samples taken from the gasifier during the dig-out tests

| **Samples number** | **Zones of the gasifier** | **Approximate temperature of sample ($^{o}C$)** |
|---|---|---|
| 1D | Drying (Top of skirt) | 25 |
| 3D | Drying | 350 |
| 5D | Pyrolysis | 400-900 |
| 6D | Pyrolysis | 400-900 |
| 7D | Pyrolysis | 400-900 |
| 9D | Gasification | 900-1000 |
| 11D | Combustion (Bottom of gasifier) | 1350 |

**Note**: D: dig-out

## 3.6 Methods and instrumentation

Since the objective of this study was not to develop analytical characterisation methodologies for all samples generated from the pyrolysis experiment, ROM samples, turn-out and dig-out samples from the coal-conversion process, but rather to use the "standard" analytical techniques, no detailed preamble will be provided. However, the reader is referred to Sections, 2.5.2-2.6, 2.7.1and 2.7.2 in Chapter 2 in which a detailed review of the coal and ash analyses employed in this study is given. From a study structure perspective, the characterisation methodologies used will be discussed in four general categories, based on the chemical, mineralogical, petrographical and physical properties which impact on slagging and sintering of mineral matter during coal-conversion processes.

In this study, the chemical analysis of coal and ash samples involving proximate analysis (as described in Section 2.5.4), ultimate analysis (as described in Section 2.7.1) and ash analysis (as described in 2.5.5), were used to qualify and quantify inorganic elements present in these samples. The mineralogical analysis (as described in Sections 2.5.6-2.5.7) of coal and ash sample was used to identify and quantify crystalline phases present in the coal and ash samples analysed in this study. A low temperature oxygen-plasma ashing technique developed by a number of authors (Glukoter, 1965; Miller et al., 1979; Ward, 1986, 1999, 2002; Ward and French, 2004 and Foscolos et al., 1989) to oxidise organic matter present in coals at low temperature, without altering the coal minerals was also used in this study. A standard petrographic technique was applied to determine types and concentrations of maceral in the coal samples tested in this study. The laboratory instruments as well as methods followed in this study are briefly described in this section.

### 3.6.1 Chemical fractionation method

The chemical fractionation analysis which was described in Section 2.5.3 was followed to determine: (1) the concentration of non-mineral inorganic elements within macerals, (2) inorganic elements dissolved in the pore waters and (3) the dissolved inorganic salts in the coals.

The procedure involved the three sequential leaching procedures performed on a coal sample that was pulverised to -200mesh. Chemical fractionation is used to selectively extract elements from the coal based on solubility, which reflects their association in the coal. Briefly, the technique involves: (1) treating the coal with water to remove water-soluble elements such as sodium in sodium sulphate or those elements that were most likely associated with the groundwater in the coal (Benson and Holm, 1985). This is followed by (2) an extraction with ammonium acetate (1M concentration, 70°C) to remove elements such as sodium, calcium, and magnesium that may be bound as salts of organic acids. The residue of the ammonium acetate extraction is then extracted (3) with hydrochloric acid (1M concentration, 70°C) to remove acid-soluble species such as iron and calcium that may be in the form of hydroxides, oxides, carbonates, and organically-coordinated species. The components remaining in the residue after all three extractions are assumed to be associated with the insoluble mineral species such as clays, quartz and pyrite. The leach liquor samples, leached coal residues from the chemical fractionation analysis, as well as the feed coal samples from the different coal mines were submitted for chemical and mineralogical analyses.

### 3.6.2 Proximate analysis

The proximate analysis uses standard methods to measure the percentage of moisture (SABS 924, ISO 589), ash content (ISO 1171) and volatile matter (ISO 562). The difference between these three percentages and the dry mass of the original sample (100%) is referred to as the fixed carbon.

### 3.6.3 Ultimate analysis

The A.S.T.M. D5373 procedure for ultimate analysis was used to determine the proportion of carbon, hydrogen and nitrogen present in the coal. The sulphur content in the coal is determined by A.S.T.M. D4239 and the oxygen content is calculated by the difference.

### 3.6.4 Ash analysis by XRF

An XRF spectrometer (ARL9800XP SIM-SEQ) was used to determine the elemental compositions. For quantification, the intensity of characteristic lines of the element to be analysed was measured. Coal ash contains typically Fe, Al, Mg, Mn, V, Ti, Si, Ca, Na, K, P, S and Cr, which are reported as oxides by default ($Fe_2O_3$, $Al_2O_3$, MgO, MnO, $V_2O_3$, $TiO_2$, $SiO_2$, CaO, $Na_2O$, $K_2O$, $P_2O_5$, $SO_3$ and $Cr_2O_3$).

For XRF analysis, each coarse solid sample (coal and ash particles) was initially ground to 100% passing 212 µm. The powdered sample was then calcined at 850°C in air for 4h in order to remove all organic compounds and water originally contained in the sample. The calcined sample was then converted into a solid solution by fusion with lithium tetraborate ($Li_2B_4O_7$).

The prepared solid solution and standard (NIMN from Mintek) were placed in the sample holders. The sample holder was then placed in the sample compartment of an XRF spectrometer. The intensity of a characteristic line of element to be determined was measured and concentration of the element in the sample was calculated from the intensity measured (Matjie, 1997).

### 3.6.5 Elemental analysis by ICP-AES

A Vista AZ CCD simultaneous Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) instrument was used to determine concentrations of elements present in the gas liquor samples. The sample was shaken or stirred well before and an aliquot was weighed into a clean borosilicate glass beaker. The sample was spot-treated with 30 vol. $H_2O_2$. The beaker was then placed on a sand bath at 100°C. The sample was not completely dried. It was removed from the sand bath and 10ml of 56% $HNO_3$ and 2ml of 10% Br in $HC_2H_3O_2$ were added to the heated sample. The mixture was subsequently placed on the sand bath at 100°C and taken to incipient dryness. To the dried sample, 5ml of 56% $HNO_3$ was added and again taken to incipient dryness. This step was repeated twice more. Finally 5ml of 32% HCl was added to the resulting solution and warmed. The sides of the beaker were washed down; after cooling, it was diluted to the desired volume. Subsequently, the concentration of the element present in the liquid sample was determined using the ICP-AES instrument.

A method number, 010-002 AICP-aqua-Regia 010-002, is briefly prescribed as follows:
Five standards with appropriate concentrations, using a ratio 1:1 of the mixture 32% HCl and 56% $HNO_3$ as diluents, were prepared.

The ICP-AES spectrometer was allowed to warm up for 20min and a wavelength calibration was performed at the beginning of the session. A wavelength resloping procedure was performed at every 50th sample of each analytical condition, as previously determined. A calibration for every element to be determined, using the prepared standards, was performed and the calibration curve of each element was checked. Finally the samples were analysed and the concentrations of the elements present in these samples were reported as ppm, g/l or %.

### 3.6.6 Electron microprobe analysis

For determination of the chemical composition of amorphous material and crystalline phases, the electron microprobe technique as described earlier in Section 2.5.9 was used. In addition, the author of this thesis suggests that this equipment could be used to determine the proportions of the organically-bound inorganic elements in the individual coal macerals. The author also proposes that the proportions of the organically-bound inorganic elements (magnesium, potassium, titanium) in the coal macerals, that were not determined by the electron microprobe in the past, must be undertaken in this study. Some of these elements could also be responsible for the slagging process during coal-conversion processes.

Polished sections were prepared from six lump coal samples produced by six Highveld coal mines, South Africa. The sections were prepared to embrace the range of coal macerals in each sample, as indicated by the macroscopic appearance (lithotype) of selected particles.

The surfaces of the polished sections, as shown in Figure 3.9, were coated with a thin layer of carbon and loaded into a Cameca SX-50 electron microprobe analyser equipped with the Windows-based SAMx operating system and interface software. The elemental chemistry of the individual macerals in each sample was analysed in this instrument using special light-element techniques, following procedures described more fully by Bustin et al. (1993) and Ward et al. (2005).

Individual points on the various macerals in each coal were analysed under operating conditions described by Ward et al. (2005).

The accelerating voltage for the electron beam was 10kV and the filament current 20nA, with a magnification of 20,000x giving a beam spot size on the sample of around 5 to 10µm in diameter. As discussed by Bustin et al. (1993), an independently analysed anthracite sample was used as the standard for carbon in the analysis process.

A range of mineral standards was used for the other elements. The detection limit of nitrogen in the coal, determined by Mastalerz and Gurba (2001) using accelerating voltage of 10kV, beam current of 20nA and counting time of 20s during electron microprobe analysis, was found to be 0.5%. However, the detection limits of other inorganic elements present in the coal macerals were not reported.

The percentages of carbon, oxygen, nitrogen, sulphur, silicon, aluminium, calcium, magnesium, potassium, titanium and iron were measured for each point, with a note on the type of maceral represented in each case. The results of the individual analyses were tabulated in spreadsheet format. Although care was taken to analyse only "clean" macerals and avoid areas where visible minerals were also present, the area analysed for some points unavoidably included significant proportions of mineral components (e.g. quartz, clay, and pyrite) as well as the organic matter. Points that apparently included mineral contaminants (e.g. points with high [> 0.5%]) Si or points with particularly high percentages of both Fe and S) were excluded from consideration; so, too, were points that included some of the mounting epoxy resin (e.g. epoxy filling empty cell structures), indicated by unusual oxygen and high nitrogen contents.

As mentioned in Section 3.6, a number of different clinker particles and partially burned carbonaceous shale fragments were selected from the gasification ash on the basis of their colour and size. Thin sections, polished sections and polished thin sections were prepared from these particles for optical and electron microscope studies (as shown in Figure 3.9). The same prepared sections of the selected clinkers and heated rock fragments were analysed by electron microprobe to determine the chemical composition and relative abundance of the amorphous or glassy material, as well as the crystalline phases present in coarse gasification ash. Minerals such as diopside ($CaMgSi_2O_6$), pyrite ($FeS_2$), apatite ($Ca_5F(PO_4)_3$), hematite ($Fe_2O_3$), rutile ($TiO_2$) and sanidine ($KAlSi_3O_8$) supplied with the electron microprobe were used as standards for silicon, calcium, magnesium, sulphur, iron, phosphorus, titanium, potassium and aluminium during the electron microprobe analysis of the selected clinkers and heated rock fragments.

### 3.6.7 Determination of mineral matter in the coal by low temperature asher

Representative portions of coal samples from the six coal mines were finely powdered. A representative portion of each powder was subjected to low-temperature oxygen-plasma ashing using an IPC 4-chamber asher, as outlined in Australian Standard 1038, Part 22. The mass percentage of low-temperature ash representing the proportion of mineral matter in the coal was determined in each case.

### 3.6.8 XRD analysis

Coarse samples (coal, char and ash) to be analysed were initially ground using a ball mill in order to obtain -212μm particles. The powdered sample was transferred to a suitable sample holder (preferably made of aluminium) and the sample in the holder was tamped gently, but thoroughly, with the edge of a glass slide. It was important to fill the sample holder; thereafter the surplus sample was sliced off with a glass slide (approximately 50x70mm and 5mm thick), whilst simultaneously compressing the sample in the holder. The above procedure was repeated until a suitable surface (a smooth surface of even texture) was obtained. The pulverised coal and char samples prepared in this way were analysed by XRD using an X'Pert PRO PANalytical (Philips) – Unit 2 diffractometer system.

The XRD system: X'Pert PRO PANalytical (Philips) – Unit 2 was used to analyse the samples. The experimental parameters were as follows:

Goniometer: PW3050/60 ($\Theta$ / $\Theta$ configuration)
X-ray detector: X'Celerator (Solid State, RTMS)
X-ray tube: Cobalt target, ceramic, LFF-type; $\lambda$ Co K$\alpha$ = 1.7889 Å
Voltage: 40KV
Amperage: 40mA
Prog. Divergence Slit: 1.0° (fixed)
Anti-scatter Slit: 2.0°
Scan from: 5° 2$\Theta$
Scan to: 135° 2$\Theta$
Soller slits: 0.02 Rad
Scanning: Continuous.
Duration of scan for quantitative XRD analysis: 6-14h

The qualitative XRD analysis was carried out using the Graphics & Identification programme. The percentages of the individual crystalline phases (minerals) in each sample were determined using the Rietveld-based Siroquant software system (Taylor, 1991). In order to determine the proportion of amorphous material in the samples, calcium fluoride was used as an internal standard.

In parallel, the mineralogy of low temperature ash from the coal samples and the pulverised ash from the coal-conversion process were analysed by X-ray powder diffraction using a Phillips X'pert diffractometer with copper Kα radiation; the minerals present were identified by reference to the ICDD Powder Diffraction File. Quantitative analyses of mineral phases in the LTA and ash were made using SIROQUANT™, commercial interpretation software written by CSIRO based on the Rietveld XRD analysis technique (Taylor, 1991).

### 3.6.9 High-temperature X-ray diffraction (HT-XRD)

The -1mm particles of the crushed feed coal were screened into fine (100% <0.25mm) and coarse (100% >0.25mm) fractions. Each fraction was separated by float-sink techniques into a low-density ("floats") fraction, and a high-density ("sinks") fraction. The density of the separation medium used in this study was 1.56g/cm$^3$. The mineral matter in the feed coal, as well as the individual size and density fractions, were isolated using low-temperature oxygen-plasma ashing. The resulting LTA residues were subjected to Rietveld-based X-ray diffraction analysis using procedures described by Ward et al. (2001) and also to HT-XRD analysis using procedures described by French et al. (2001).

### 3.6.10 Determination of clay mineral in the coal

The clay fraction (less than 2µm effective diameter) of each sample was isolated by ultrasonic dispersion in sodium hexametaphosphate (Calgon) and subsequent settling. The clay fraction was further investigated by X-ray diffraction of oriented aggregates, using glycol and heat treatment. The relative proportions of the different clay minerals in this fraction for each sample were determined by the method of Griffin (Carver, 1971).

### 3.6.11 Computer controlled scanning electron microscope (CCSEM) (van Alphen, 2005)

CCSEM at Technology Service International (TSI, Eskom), is a SEM configured to automatically and rapidly determine the minerals in coal and phases in fly ash and slag deposits. Samples of pulverised coal or fly ash were mixed with iodinated epoxy resin and allowed to cure. The cured 30mm mount was polished, exposing individual particles in cross-section.

The CCSEM analytical procedure is as follows:

- Appropriate magnification based on particle sizes was selected. The polished section was divided into regularly spaced analytical fields of view or frames.
- The sample was positioned at the first field of view and a back-scattered electron image (BSI) acquired. BSI (Figure 3.11) is based on atomic number contrast and ensures that coal and minerals can be identified by image processing routines.
- The image was processed and the regular grid of analytical points established for each field of view.
- The electron beam was positioned at each analytical point and a 100msec X-ray spectrum acquired (Figure 3.12). The elemental composition of the phase was derived from the X-ray spectrum.
- The sample was positioned at the next field of view and the process repeated until all the fields of view had been analysed.

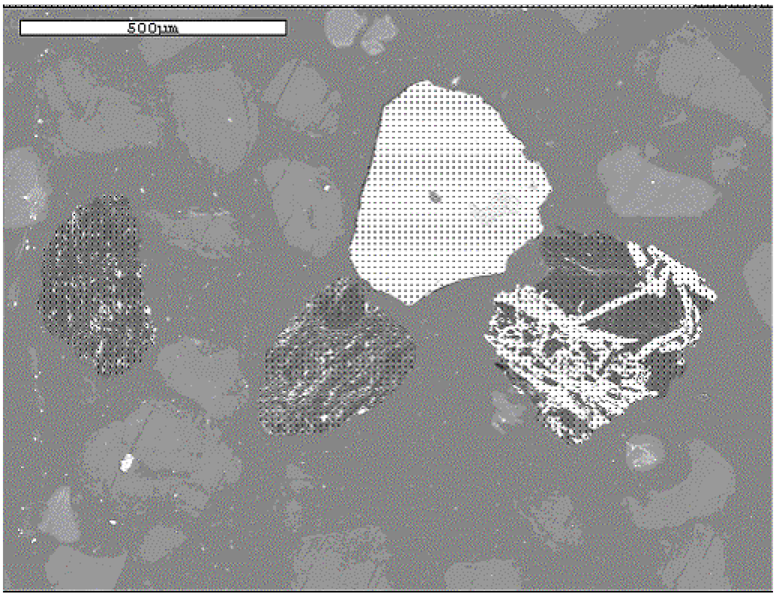


**Figure 3.11**: Processed back-scattered electron image of pulverised coal with the regular grid of analytical points superimposed (black dots).

The scale bar represents 50µm and the estimated point spacing is 11.21µm. In this image the coal is black, the epoxy resin is grey and the mineral matter is white.

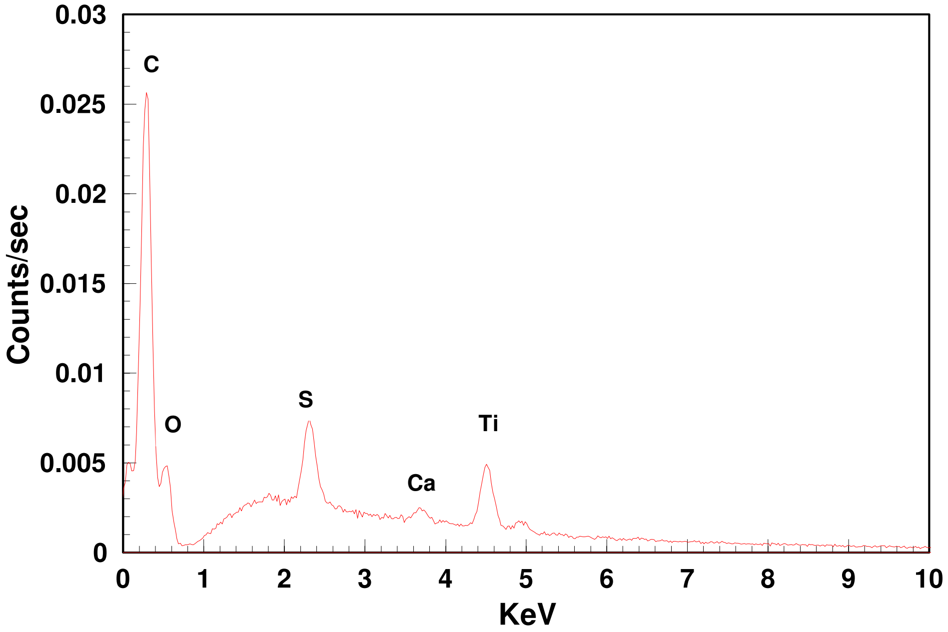


**Figure 3.12:** Typical X-ray spectrum of coal.

The development of mineral identification rules based on the principles of fuzzy logic is crucial for CCSEM analysis. The rules are listed in an ASCII file (*.sui) and are developed by examining the polished section and identifying the minerals present prior to undertaking an automated CCSEM analysis. The file developed is unique and can be used for subsequent CCSEM analysis.

Mineral nomenclature for pulverised fuel is based on the typical minerals found in pulverised fuel (van Alphen, 2005). In context of pulverised fuel, the CCSEM mineral “coal” describes a C-rich phase (Figure 3.11), describing the organic-rich fraction of pulverised coal. Coarse ash and clinker phase identification is based on the elemental composition, while nomenclature is based on the perceived coal mineral source.

The major outputs from CCSEM analyses are:

- Mass-% mineral or phase proportions in pulverised fuel or fly ash, respectively. Mineral proportions (volume-%) are determined by dividing the number of analytical points for each phase by the total number of analysed points. The mass-% can be calculated by multiplying the volume-% by the density of the phase.

- The oxide elemental composition can be calculated from the mass-% mineral proportions.
- Association characteristics of minerals in coal and phases in fly ash.
- Size variation of the different minerals.
- Proportion of included minerals compared to proportion of extraneous minerals. From a slagging perspective, included minerals (within the coal which is undergoing gasification) can be expected to be exposed to higher temperatures and more reducing conditions, compared to extraneous mineral particles. This difference in localised environment may affect mineral transformations.

### 3.6.12 QEMSCAN analysis

As stated earlier in Section 2.5.8, QEMSCAN equipment can be used to determine mineral-mineral associations, particle size, mineral compositions and texture of particles in the coal and ash samples. In this study the polished sections and polished thin sections of coal and ash samples (as shown in Figure 3.9) were placed into the sample compartment of QEMSCAN for characterisation.

As illustrated in Figure 3.13, the electron beam of the QEMSCAN interacts with a sample during scanning, generating secondary X-rays with distinct energy levels that can be interpreted in terms of type and amount of element present. Combinations of elements and relative proportions are interpreted on-line and used to automatically identify a mineral or phase present. Typically 100,000 individual X-ray identifications per hour can be achieved automatically. This procedure is therefore similar to CCSEM, but with a higher degree of automation.

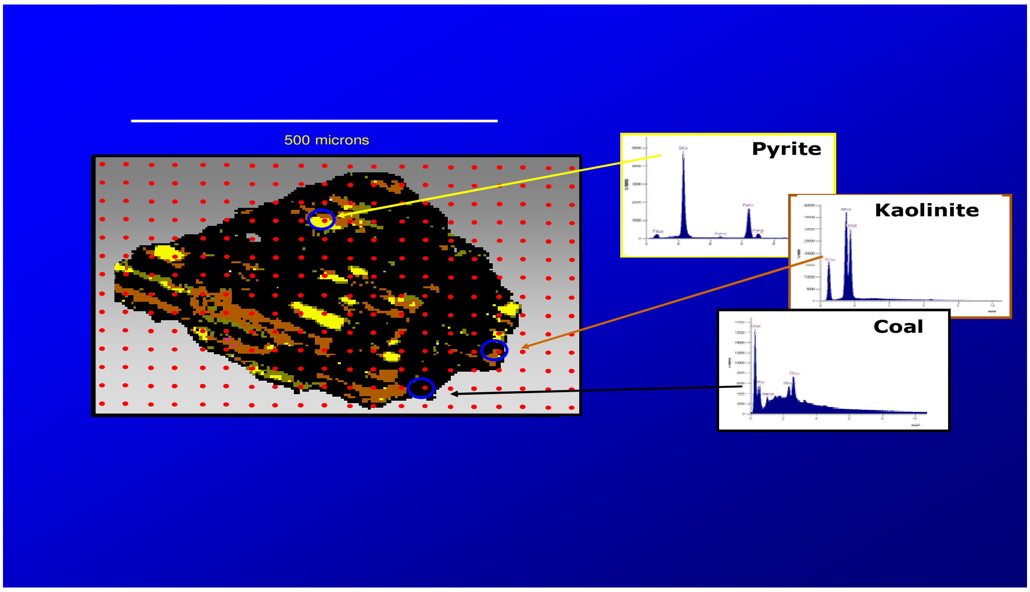


**Figure 3.13:** Identification of minerals in coal particles by QEMSCAN (Butcher, 2006).

### 3.6.13 Petrographic analysis

Coal and ash samples, crushed to -1mm, were prepared as per routine preparation for petrography following ISO standard 7404-2. A maceral group analysis as per ISO 7404-3 was conducted on sample 32T, considered as the gasifier feed coal, as well as on six coal samples from the six different mines.

The samples were obtained and prepared to minimise contamination and 500 sampling points were determined for each sample. The particle falling directly under the cross hair was categorised, applying a 50x50µm field of view. Large particles were classified several times, if meeting the requirements above. All particles -30µm were not counted, due to reduced ability to observe these small particles accurately. As more than 10 categories were required and the point counter only measured up to 10 variables at a time, certain measurements were recorded separately on paper, ensuring that 500 particles were counted per block.

Reflectance analysis was conducted before (or very shortly after), the particle type analysis, in order to limit the potential impact of the oil on reflectance readings. Initially, every second sample was analysed and additional samples were analysed where significant changes in trends were determined.

### 3.6.14 Ash Fusion Temperature analysis

The standard method ISO 540 was used to demonstrate the fusion properties of laboratory prepared coal ash. The ash was heated to 1600°C in an oxidising atmosphere. The results of an AFT analysis consist of four temperatures, namely: (1) initial deformation temperature (DT), (2) softening temperature (ST), (3) hemispherical temperature (HT) and (4) flow temperature (FT).

### 3.6.15 Particle size distribution

The representative coal feedstock to gasification process, prepared by blending coals from the different mines, was screened into eight size fractions using the screen aperture sizes: 75mm, 53mm, 26mm, 13.2mm, 9.5mm, 6.7mm, 4.7mm and 4mm. Each fraction of coal was ground to 100% passing lmm, before submitting the prepared samples for chemical analysis (XRF, proximate and ultimate analyses) and mineralogical analysis (XRD and CCSEM analyses).

### 3.6.16 FactSage modeling

As stated by Matjie et al. (2006), the thermodynamic package was used to predict the equilibrium phases in the lower part of the gasifier (where the temperature decreases from the peak in the coal combustion region towards the grate). The FactSage modeling was undertaken to support XRD, CCSEM and QEMSCAN results for char and ash samples produced in this study. The fluxing elements such as sodium, potassium, calcium, magnesium and iron as ferrous oxide in the coal may possibly react with aluminium silicates in the coal and give rise to the slagging process during coal conversion processes, under either reducing or oxidising conditions. This possibility was examined by calculating the equilibrium speciation of elements between the coal and the solid formed during coal-conversion processes.

For predicted changes during pyrolysis the practical conditions during the pyrolysis experiments were approximated. The equilibrium state was found for a combination of the 1.2kg of coal which was fed to the reactor, with all the nitrogen which entered the reactor in one hour (40ml/min at room temperature and 26bar pressure, giving a total of 2.52mol $N_2$) and a reaction temperature of 600°C, the maximum temperature attained during pyrolysis.

These conditions would give an upper boundary on the extent of sintering of mineral matter which can be expected.

The thermodynamic package FactSage was used for undertaking the calculations, considering species in the gas phase and liquid phase, as well as solid compounds and solid solutions. The products of pyrolysis of the coal macerals were assumed to be limited to char (heated carbon), $CH_4$, $H_2$, $H_2O$, CO and $CO_2$ (which could react further to yield other products, such as $H_2S$, HCl and HF). The assumed chemistry for the pyrolysis calculations was an average of all the coals in this study, given in Table 3.4.

**Table 3.4:** Assumed coal chemistry for equilibrium calculations

| **Species** | **Mass %** | **Mineral** |
|---|---|---|
| $H_2O$ | 3 | |
| S | 1 | |
| O | 8 | |
| C | 55 | |
| H | 3 | |
| $SiO_2$ | 8 | quartz |
| $Al_2Si_2O_5(OH)_4$ | 10 | kaolinite |
| $FeS_2$ | 1 | pyrite |
| $KAl_2(OH)_2AlSi_3O_{10}$ | 4 | muscovite |
| $CaCO_3$ | 2 | calcite |
| $MgCa(CO_3)_2$ | 3 | dolomite |
| NaCl | 0.82 | halite |
| $Ca_5F(PO_4)_3$ | 0.44 | fluoroapatite |