CHAPTER 1

INTRODUCTION

1.1 Background and statement of the problem

The feed to the Sasol-Lurgi Fixed Bed Dry Bottom (FBDB) gasification process principally consists of coarse coal (>6mm) and extraneous rock fragments (“stone”) including siltstone, mudstone, carbonaceous shale and sandstone. These stones, termed roof and floor, are sometimes mined with coal. This low rank bituminous coal is gasified to produce synthesis gas (also referred to as syngas, a mixture of carbon monoxide and hydrogen). Coal ash is a by-product of the gasification process. Coal consists of different types of inorganic constituents (minerals and organically-associated inorganic elements) and organic matter (macerals). The behaviour of the inorganic constituents and organic matter, as well as the operating conditions during gasification of the coal, is important in initiating and controlling clinker formation (Matjie et al., 2006). When the temperature in the combustion zone exceeds the melting point of the ash-forming minerals, the minerals will melt / flow and agglomerate. Due to the counter-current mode of operation, hot ash exchanges heat with the cold incoming agent (steam and oxygen or air), while higher in the gasifier hot raw gas exchanges heat with cold incoming coal. These results in the ash and raw gas leaving the gasifier at relatively low temperatures compared to other types of gasifiers, improving the thermal efficiency and lowering the steam consumption. A schematic representation of a Sasol-Lurgi Fixed Bed Dry Bottom (FBDB) gasifier is shown in Figure 1.1

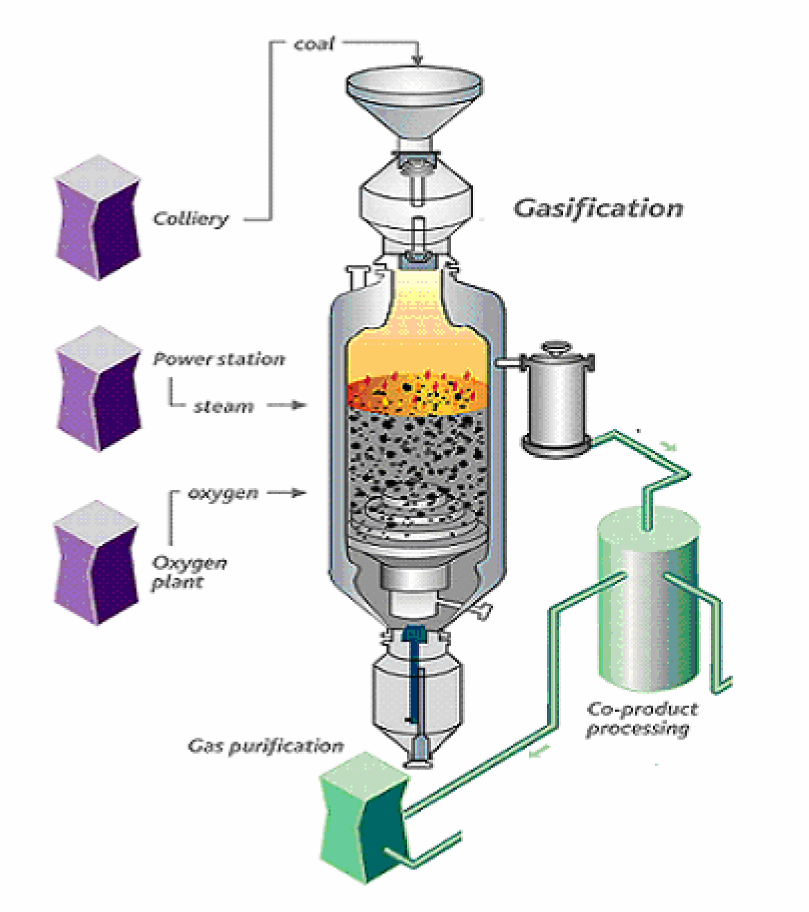

Figure 1.1: Sasol-Lurgi Fixed Bed Dry Bottom (FBDB) gasifier.

In the gasification process, fluxing elements-bearing minerals or non-mineral inorganic elements interact with aluminium silicate present in the coal to lower the melting points of the aluminium silicate and subsequently form the melt (Matjie et al., 2006). Some of the extraneous rock fragments, as well as partially burnt coal, attach themselves to the melt to form a clinker. In most cases, clinker is formed when fluxing elements such as Ca, Fe^{2+} and Mg reduce the ash fusion temperature of aluminium silicates (clays) to form a melt. In some other instances, rock fragments as well as trace amounts of unburnt carbon are encapsulated by the melt (Matjie et al., 2006). In addition, the included minerals that are finely dispersed within the carbon matrix, as well as the organically-bound cations may partially volatilise from the coal gasification process and condense at low temperatures to form a deposit or precipitate. The resultant fouling by the inorganic species and corrosion at the gasification and phenosolvan plants during treatment of gas liquor (quenched water produced during the cooling of syngas) continues to cause significant operational problems (Matjie and Engelbrecht, 2007).

Currently, clinker formation can result in the blockage of gasifiers and also contributes to the loss of carbon (approximately 4 to 6% fixed carbon) which has a negative impact on process efficiencies. Furthermore, the influence of both chemical and physical factors on the sintering (a bonding of particles that may arise from their partial melting during heating) and slagging (melting of the entire mineral matter particle) of coal mineral matter, to control the clinker formation and physical properties of a sintered deposit during gasification, is not properly understood.

Indications of possible behaviour of the inorganic coal constituents are provided by observations relevant to boiler conditions. According to Benson (1987), Jung and Schobert (1991), Ward and French (2004), van Alphen (2005) and Gupta (2005), during the combustion of the pulverised coal particles at elevated temperature, the inorganic constituents are liberated upon burn-out of organic matter to form gas, liquid and solid phases. In most cases, the inorganic constituents subsequently interact with each other to produce fly ash particles, with varying elemental compositions, morphological features (size and shape) and physical characteristics (viscosity and density) (Attalla et al., 2004 and van Alphen, 2005).

At high temperatures, fly ash particles with low melting points adhere to internal boiler surfaces and also form sintered deposits. Molten deposits formed on the internal walls of large furnace cavities are termed a slag.

The inorganic constituents are distributed within the coal matrix in several forms, including: coal-bound (included minerals), coal free (extraneous minerals) and organically-associated inorganic elements. According to Given (1984), low rank coals contain high quantities of the organically-associated cations. The rank of the typical Sasol coals, in terms of vitrinite reflectance, is 0.61 RoV%. Low-rank subbituminous and lignitic coals contain high levels of oxygen that can act as bonding sites for various cations; approximately 25% of oxygen is associated as carboxylic acid groups. Benson and Holm (1985) indicated that carboxylic acid groups can act as ion exchange sites for cations such as sodium, calcium, magnesium, potassium, strontium and barium. Higher-ranked coals do not contain high levels of the organically-associated inorganic elements, because of the lower levels of oxygen.

Extensive research was also conducted on the inorganic matter present in the coal in order to study the sintering temperature and mechanisms of ash deposits in boilers (Raask, 1985; Conn and Austin, 1984; Cumming et al., 1986; Tangsathitkulchai, 1986 and Benson, 1987). During their studies, an ash pellet was prepared and heated slowly, while simultaneously measuring the electrical resistance across the heated pellet. The sinter point that was observed by these researchers is termed the sintering temperature of the fly ash particles and it is expected to be equal to or greater than the electrical sinter point. Cumming et al. (1986) stated that the electrical sinter point is always below the deformation temperature of the ash, determined in the A.S.T.M. ash fusion test. The sintering of the ash is an important part of the overall process of ash deposition on heat transfer surfaces in boilers.

Slagging of fly ash particles in boilers has also been studied extensively. Minerals on the surface of the coal enhance the slagging propensity of the coal particles during pulverised coal combustion. Slagging can cause several problems which reduce the ability to raise steam, lead to increased corrosion and slag dropping into the bottom of the furnace, leading to hopper blockage in boiler operation. For pulverised coal combustion the sintered deposits were found to be rich in anorthite (Unsworth et al., 1987). Most of the researchers argued that anorthite ($CaAl_2Si_2O_8$) is formed by solid-state reactions and not by crystallisation from a homogeneous melt (slag).

It has similarly been proposed that the included minerals, organically-associated inorganic elements, fluxing elements-bearing minerals (pyrite, dolomite, calcite and siderite), fluxing elements (sodium, calcium, iron and magnesium) and sodium- and potassium-bearing aluminium silicates present in Sasol coals as well as operating conditions are most likely responsible for the clinker formation in the gasifiers (Matjie et al., 2006). During coarse coal gasification, the mineral matter present in the coal feedstock could interact to form melt. On cooling, the molten solution could encapsulate the surrounding “stone”, uncombusted char and large extraneous Fe-oxide/Fe-S-oxide and Ca-oxide/CaMg-oxide particles to form clinkers (Matjie et al., 2006). Management of clinkers in the gasifier, by using the optimal sintering parameters in order to enhance carbon efficiency is important to Sasol.

A comprehensive understanding of chemical and physical processes involved in the formation of clinkers in the gasifiers would include: mode of occurrence of the inorganic constituents in the coal, effect of particle size distribution of coal on the clinker formation, reactions of the organically-bound cations with each other or with coal minerals, effect of the mineralogical composition on the clinker formation, effect of stone (extraneous rock fragments) content on the clinker formation, effects of temperature and pressure on the clinker formation, effects of reducing and oxidising atmospheres on the clinker formation and impact of steam on the crystallisation from the slag. Understanding of the individual high temperature mineral transformations or mineral interactions during the gasification of the coarse coal particles at elevated temperatures and pressures is not well developed.

1.2 Scope and objectives of study

The primary objective of this study is to determine which mineral matter is primarily responsible for the sintering behaviour of coal ash, and also to test the hypotheses mentioned below in paragraph 1.3. The secondary objective of this study is to optimise or investigate the existing operating parameters for gasification that are possibly responsible for a clinker formation in the gasifiers. An in-depth characterisation study of composite samples of coals taken from various Sasol sources situated in Mpumalanga province in South Africa, their coal blends (Sasol coal feedstock for gasification process) as well as the gasification ash are also included in this study.

1.2.1 Physical factors: Ash Fusion Temperature (AFT), Particle Size Distribution (PSD)

The AFT of the bulk coal blend entering the gasifier, float and sink fractions of coals from the different mines and the coal size fractions, was determined under reducing or oxidising conditions. The AFT of coal samples and that of the samples retrieved from a commercial gasifier were compared.

1.2.2 Chemical factors:

- Mineralogical composition and attributes (included in the carbon-rich particles or extraneous minerals).

Indications are that the mineralogical composition and attributes play a significant role in controlling slagging and clinker formation in the gasifier. Composite samples of the coarse coal and the gasification ash were taken from a commercial gasifier on the Sasol Synfuels Secunda for an in-depth characterisation study.

- Volatilisation of organically-bound cations and sulphur

The hypotheses that describe the possible mechanisms of volatilisation of the organically-bound cations and organic sulphur present in coal, including the interaction of these cations with each other or with aluminium silicates at elevated temperatures, are given in paragraph 1.3 of this section.

- Mineral reactions at elevated temperatures

When clays such as kaolinite, illite, muscovite and montmorillonite that are originally present in coal are heated at an elevated temperature of around 450°C, they start to lose water of crystallisation during decomposition (Grim, 1962; Bryers, 1986; Unsworth et al., 1987b; Ward and French, 2004 and van Alphen, 2005). In the case of kaolinite, its structure is partially re-arranged to form meta-kaolinite (kaolinite with no water of crystallisation) and it has a lower melting point in comparison with the coal kaolinite. At this elevated temperature cations (sodium, potassium, calcium, iron, magnesium) arising from the metallic salts of carboxylic acids can react with the reactive meta-kaolinite and result in the reduction of the melting point of the aluminium silicates (Tangsathitkulchai, 1986; Benson, 1987).

In this study, a low temperature ashing (LTA), a high temperature X-ray diffraction (HT-XRD) and ambient X-ray diffraction (XRD) were used to better understand the transformation of clays present in coals at elevated temperatures.

The thermodynamic package FactSage 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 information obtained from this study could be used to blend coals from various Sasol coal sources, according to their chemical and physical properties in order to control the proportion of the molten glass phases formed in the gasifier and assist in reducing the incidents of slagging and severe clinkering of mineral matter during the gasification process.

1.3 List of hypotheses that were tested in this study

The hypotheses are listed below with a brief discussion:

- Specific minerals, mineral associations as well as the organically-bound inorganic elements are thought to be primarily responsible for slagging and sintering.
  The mineralogical and elemental compositions and AFT of the coal feed, and coal size fractions, were used for this study.

- The Ca-Fe-Mg-K-Ti aluminosilicate glass present in the gasification ash is thought to be produced directly from the included minerals.

- The extraneous rock fragments may attach to the molten material to form clinkers.

In order to test the above-mentioned hypotheses, chemical fractionation (CHF), QEM*SEM or QEMSCAN (quantitative evaluation of materials by scanning electron microscopy), and electron microprobe (EMP) techniques were utilised to determine the concentrations of both organically-bound inorganic elements and minerals that are less than 20 micron in size, present in the coals. In this study the HT-XRD, XRD and X-ray fluorescence (XRF) were also used. A laboratory autoclave, simulating the pyrolysis of coarse coal in the gasification plant, was utilised to qualify and quantify volatilisation of inorganic constituents from the organometallic species present in the coal.

CHAPTER 2

BACKGROUND INFORMATION AND LITERATURE REVIEW

Three constituents of coal are thought to play important roles in slagging and clinker formation. These are listed below, before continuing with a review of the coal types studied and possible high-temperature reactions of and interactions between the constituents.

- **Included minerals in the coal**

Included minerals occur within the coarse carbon-rich (coal) particles. These minerals (approximately 55% of the inorganic material in the coal) could react with aluminium silicates (mainly kaolinite transformation products) in the pyrolysis and gasification zones to form melts.

- **Organically-bound species**

Attalla et al., (2004) indicated clearly that the organically-associated inorganic elements in coal have a significant effect on ash formation mechanisms during coal combustion. Quann and Sarofim (1986) established that organically-associated Ca and Mg interacted with free aluminium silicates (clays) in lignite coals at elevated temperatures to form a melt that resulted in agglomerate formation. Matjie et al., (2007) found that Sasol feed coal contains less than 0.2% organically-bound inorganic elements (Ca, Mg, Al, Si, Na, K, Ti and Fe). These are thus a minor constituent, but are expected to contribute strongly to volatilisation of compounds of the listed elements.

- **Rock fragments**

Sasol feed coal to the gasification contains approximately 15-20% extraneous rock fragments particles. These rock fragments could attach to the molten solution to form heterogeneous clinkers.

2.1 Selected South African low-rank bituminous coals as a feedstock for the gasification process

The South African low-grade, medium rank C bituminous coals (as considered in this study) are mined from six different collieries situated in the Mpumalanga Province in South Africa.

Coarse coal particles (> 6 mm coal fraction) from the various coal sources are transported to the preparation plant, where they are blended according to their availability to form a mixture that is suitable for the gasification process. The feed coal to gasification typically has a 25 - 28% ash yield. The locations of the mines that supply the coals are shown in Figure 2.1. The shaded areas represent mines that belong to Sasol; producing coals that contain slightly different proportions of carbon-rich particles, included mineral particles and rock fragments (extraneous minerals) for use in gasification and combustion processes.

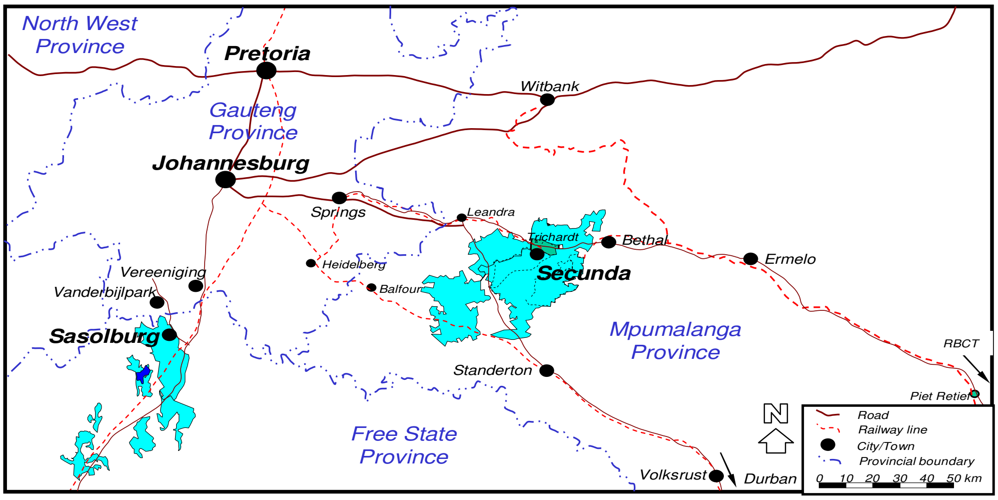

Figure 2.1: Locations of Sasol coal mines (South Africa).

2.2 Nature of mineral matter in coal

Coal contains three fundamentally different types of inorganic constituents, namely:

- Dissolved salts and other inorganic substances in the coal pore water;
- Inorganic elements incorporated within the organic compounds of the macerals;
- Discrete inorganic particles (crystalline or non-crystalline) representing the mineral components (Ward, 1984; Benson, 1987; Ward and French, 2004).

According to Ward and French (2004) the first two types of mineral matter in the list are best described as non-mineral inorganics, substantially contained in the macerals of brown coals, lignite, and subbituminous materials. Low rank coals contain high levels of organically-associated cations (Given, 1984). Such low-rank subbituminous and lignitic coals contain high levels of oxygen that can act as bonding sites for various cations; approximately 25% of the oxygen is associated as carboxylic acid groups. The proportion of organically-associated inorganic elements is much smaller than the discrete inorganic particles (minerals) in both lower-rank and higher-rank coals (Benson, 1987; Given, 1984).

Coals from the different mines contain different classes of minerals depending on their origin:

- Extraneous minerals may be in the form of ultra-fine material on the surface of coal or rock fragment (siltstone or sand stone), originating from contamination of the mined product by roof or floor strata. These minerals can be easily separated from the carbon-rich fraction of coal by physical methods, including density separation or flotation (van Alphen, 2005; Ward, 1984).
- Included (inherent) minerals are associated with macerals. These types of minerals are encapsulated in the coal matrix (Ward and French, 2004; van Alphen, 2005).

The transformation of mineral matter in coal at elevated temperatures during coal gasification is illustrated in Figure 2.2.

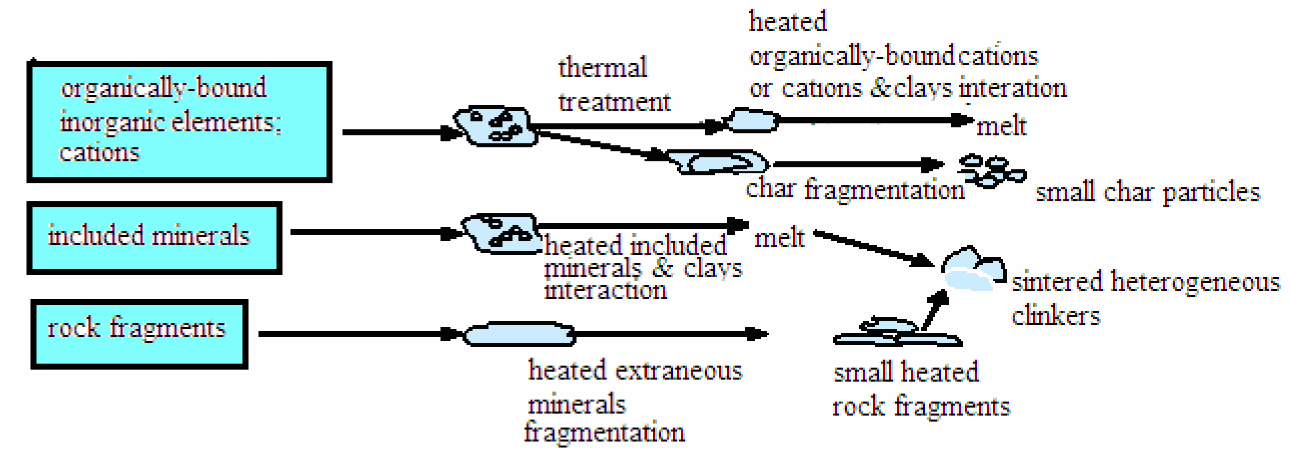

Figure 2.2: Block diagram showing transformation of organically-bound inorganic elements, cations, included minerals as well as rock fragments during coal gasification at elevated temperatures.

A list of minerals found in coals from the different coal mines, as well as in low temperature ash (LTA), was compiled by Ward and French (2004) and is summarised in Tables 2.1, 2.1a and 2.1b.

Table 2. 1: Silicate, clay, interstratified clay, carbonate and sulphate minerals found in coal and LTA samples (compiled from various sources and slightly modified after Ward and French, 2004)

Silicates	
Quartz	SiO_2
Chalcedony	SiO_2
Clay Minerals	
Kaolinite	$Al_2Si_2O_5(OH)_4$
Illite	$K_{1.5}Al_4(Si_{6.5}Al_{1.5})O_{20}(OH)_4$
Smectite	$Na_{0.33}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$
Chlorite	$(MgFeAl)_6(AlSi)_4O_{10}(OH)_8$
Muscovite	$K_2O.3Al_2O_3.6SiO_2.2H_2O$
Montmorillonite	$(1\text{-}x)Al_2O_3.x(MgO, Na_2O).4SiO_2.H_2O$
Interstratified Clay Minerals	
Feldspar	$KAlSi_3O_8$
	$NaAlSi_3O_8$
	$CaAl_2Si_2O_8$
Tourmaline	$Na(MgFeMn)_3Al_6B_3Si_6O_{27}(OH)_4$
Analcime	$NaAlSiO_6.H_2O$
Clinoptilolite	$(NaK)_6(SiAl)_{36}O_{72}.20H_2O$
Carbonates	
Calcite	$CaCO_3$
Aragonite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Ankerite	$(Fe, Ca, Mg)CO_3$
Siderite	$FeCO_3$
Dawsonite	$NaAlCO_3(OH)_2$
Strontianite	$SrCO_3$
Witherite	$BaCO_3$
Alstonite	$BaCa(CO_3)_2$

Table 2.1 (a): Sulphate minerals found in coal and LTA samples (compiled from various sources) and slightly modified after Ward and French, 2004)

Mineral	**Composition**
Coquimbite	$Fe_2(SO_4)_3.9H_2O$
Rozenite	$FeSO_4.4H_2O$
Szomolnokite	$FeSO_4.H_2O$
Natrojarosite	$NaFe_3(SO_4)_2(OH)_6$
Thenardite	Na_2SO_4
Glauberite	$Na_2Ca(SO_4)_2$
Hexahydrite	$MgSO_4.6H_2O$
Tschermigite	$NH_4Al(SO4)2.12H2O$
Gypsum	$CaSO_4.2H_2O$
Bassanite	$CaSO4.1/2H_2O$
Anhydrite	$CaSO_4$
Heulandite	$CaAl_2Si_7O_{18}.6H_2O$
Barite	$BaSO_4$
Jarosite	$KFe_3(SO_4)_2(OH)_2$
Alunite	$KAl_3(SO_4)_2(OH)_6$

Table 2.1 (b): Others, sulphide, phosphate minerals found in coals and LTA samples (compiled from various sources and slightly modified after Ward and French, 2004)

Mineral	Composition
Others	
Anatase	TiO_2
Rutile	TiO_2
Boehmite	Al.O.OH
Goethite	$Fe(OH)_3$
Crocoite	$PbCrO_4$
Chromite	$(Fe, Mg)Cr_2O_4$
Clausthalite	PbSe
Zircon	$ZrSiO_4$
Magnetite	Fe_3O_4
Hematite	Fe_2O_3
Limonite	$Fe_2O_3.H_2O$
Sulphides	
Pyrite	FeS_2
Marcasite	FeS_2
Pyrrhotite	$Fe_{(1-x)}S$
Sphalerite	ZnS
Galena	PbS
Stibnite	SbS
Millerite	NiS
Chalcopyrite	CuFeS
Phosphates	
Apatite	$Ca_5F(PO_4)_3$
Crandallite	$CaAl_3(PO_4)_2(OH)_5.H_2O$
Gorceixite	$BaAl_3(PO_4)_2(OH)_5.H_2O$
Goyazite	$SrAl_3(PO_4)_2(OH)_5.H_2O$
Monazite	$(Ce, La, Th, Nd)PO_4$
Xenotime	$(Y, Er)PO_4$

The list was slightly modified to show minerals commonly found in the coals in this study. Clay minerals (kaolinite, illites or muscovite and smectite) and quartz were the dominant included minerals.

van Alphen (2005) indicated that kaolinite is a common mineral deposited in the cavities in fusinite, dispersed through vitrinite as included sub-micron spherical particles and sub-spherical grains filling the microstructures within the coal. Kaolinite can also occur as an epigenetic cleated mineral intersecting the coal seam.

Illites ($K_{1.5-1.0}Al_4[Si_{6.5-7.0}Al_{1.5-1.0}O_{20}](OH)_4$) are characterised by high silica content and low potassium content, physically having clay size (<2µm) particles (Velde, 1985; Chamely, 1989; Deer et al., 1992). Illites contain potassium ions without hydration shells that are more stable in the interlayer sites than the hydrated sodium ions of smectites. When illites are exposed to heat, the grain size of the <2µm fraction increases and subsequently results in a decrease in the proportion of interlayered expandable material. van Alphen (2005) reported that illite is mainly found along bedding planes, rarely dispersing in the coal, or is deposited in the cavities in fusinite.

The principal smectite clays (montmorillonite, beidellite, and nontronite) are di-octahedral 2:1 layered silicates and saponite, hectorite and sanconite are tri-octahedral. Smectite minerals have multi-structural layers with significantly higher loading capacity of cations in comparison with kaolinite and illite clays. They also have marked cation exchange properties that can enable their multi-layer structures to absorb more water or organic molecules and result in expanded structures (Velde, 1985; Chamely, 1989; Deer et al., 1992).

Gaigher (1980) found that South African coals contained major clay minerals (kaolinite and illite), silicate oxide (quartz) and minor carbonate minerals (calcite, dolomite and siderite) as in Table 2.2. Gaigher (1980) stated that there was a strong association between clay minerals and inertinite, but a negative association between clay minerals and vitrinite.

Table 2.2: Percentage clay distribution of selected South African Collieries (after Gaigher, 1980)

Colliery	**Seam**	**Coalfield**	**Kaolinite %**	**Illite %**	**Expandable clays %**
Eikeboom	2	Witbank	87.90	3.60	8.50
Springbok	2	Springbok Flats	63.30	35.80	0.90
New Clydesdal	2	Witbank	64.20	29.10	6.10
Albion	2	Witbank	55.40	43.60	1.00
Delmas	2	Witbank	88.50	0.70	10.80
S.Witbank	4	Witbank	90.60	5.10	4.30
Anglo Power (Kriel)	4	Highveld	92.50	2.70	4.80
Blesbok	5	Witbank	52.40	22.40	25.20
Springbok	5	Springbok Flats	55.40	14.70	29.90
Greenside	5	Witbank	76.60	9.70	13.70
Navigation	5	Witbank	65.00	15.30	19.70

Quartz derived from igneous, sedimentary and metamorphoric rocks is found as an accessory mineral and as a secondary mineral in veins and metasometic deposits (Glikson and Mastalerz, 2000; van Alphen, 2005). Quartz can occur as fine or coarse particles dispersed within the coal matrix. According to Glikson and Mastalerz (2000) and van Alphen (2005), wind and water can transport sub-micron grained quartz particles that could be derived from the conversion of smectite-dominated clays into illite or could be an intrinsic component of the plant material, introducing them into the peat forming swamps. Quartz present in bituminous coals may be detrital in origin, but the majority of quartz occurs from diagenetic transformation (Glikson and Mastalerz, 2000; van Alphen, 2005; Ward, 2002).

Ward (2002) suggests that coals that contain a significantly higher proportion of quartz occur beneath intra-seam claystone bands apparently of pyroclastic origin. During hydrothermal alteration of the volcanic glass, feldspars and other minerals in the pyroclastic sediment, the infilling quartz which represents silica is released. This silica will re-precipitate in the pores of the peat, just below the introduced pyroclastic substance arising after the hydrothermal alteration process.

The percolation of salty ground water, containing carbonate anions and Ca and Mg cations, through existing coal seams precipitates carbonates (dolomite and calcite) in stress fractures and cleats in the coal seam. This is another source of metals that deposit as carbonate minerals is the organic matter (Glikson and Mastalerz, 2000; Ward, 2002; van Alphen, 2005). The precipitation or deposition of carbonate minerals in the coal is normally late-syngenetic or more commonly epigenetic and precipitated carbonates can occur, filling the cell cavities of fusinite (Diessel, 1992; Glikson and Mastalerz, 2000; van Alphen, 2005).

Pyrite (FeS_2) can occur in various forms. Diessel (1992); Glikson and Mastalerz (2000); and van Alphen (2005) noted that raspberry-shaped pyrite framboids containing spherically sub-micron crystals of pyrite (0.1-2µm in size) were bonded in some cases by interstitial kaolinite. The pyrite framboids that commonly occur as clusters and are disseminated throughout the coal seam can reach sizes of 200µm. Pyrite also occurs as lenticular masses, euhedral crystals, and cell infillings, as veins and on cleat surfaces (Ward, 1984, 2002). Rao and Gluskoter (1973) and van Alphen (2005) stated that the colloidal deposition of inorganic species or the activity of micro-organisms (bacterial) could be the source for the formation of pyrite framboids, trace amounts of sphalerite, marcasite and galena. Sub-micron or super-micron grained pyrite particles (in the range of 0.1-100µm) can also be dispersed within the vitrinite and inertinite macerals present in coals. Like precipitated carbonates, precipitated pyrite can fill the cell cavities of fusinite, or appears in fractures, cleats and cracks in the carbon matrix (Rao and Gluskoter, 1973; van Alphen 2005). Stach (1982) stated that a high proportion of pyrite in coal can be attributed to marine influences and also biological reduction of sulphate during deposition of the seam.

The parent of siderite is an acidic fresh water environment that is rich in iron ions, but contains trace amounts of sulphate (Ward et al., 1999a). When carbon dioxide is bubbled through acidic fresh water, siderite will start to precipitate from this water. Siderite is commonly found in coals from Australia, while pyrite is present in South African coals (Ward et al., 1999a). In most cases, siderite is present in the mineral matter of coals which have a low proportion of syngenetic pyrite, such as the Sydney-Bowen Basin seams in eastern Australia (Ward et al., 1999a). Siderite is apparently formed by chemical precipitation during early diagenesis and commonly occurs as spheroidal nodules (Ward, 1984; van Alphen, 2005).

Like syngenetic precipitates of pyrite, kaolinite, quartz and carbonate minerals, trace apatite present in coal is formed by syngenetic precipitation as cell and pore infillings in the original peat bed. Apatite melts at a temperature of greater than 1230°C (Deer et al., 1992). This mineral could lower the melting temperature of aluminium silicates and contribute to clinker formation during the coal gasification.

Attalla et al. (2004) indicated clearly that the mode of occurrence of mineral matter (included minerals, excluded minerals and organically-associated inorganic elements) in coal has a significant effect on ash formation mechanisms during coal combustion. The included minerals can experience conditions which are different (oxidation and reduction) in comparison with the excluded minerals or organically-bound cations. Being associated with carbon, the included minerals can interact with each other at elevated temperatures under more reducing conditions and result in artifact compounds (new aluminium silicate minerals).

Buhre et al. (2005) found that the ash formed from the coalescence of the included mineral is significantly affected by size, type and distribution of the included mineral. During the combustion of the pulverised coal at elevated temperatures, the flame of the burning char particles caused the included minerals to turn viscous and coalesce, due to melting of the inorganic matter (Buhre et al., 2005).

As can be seen in Figure 2.3, the excluded mineral fragmentation produced mainly sub-micron to super-micron-sized ash particles, while the last formation mechanism for included minerals in this figure contributes mainly to micron sized ash particles (Quann and Sarofim, 1982). The amount, size and type of excluded minerals determine the extent of excluded mineral fragmentation. The main fragmenting mineral types in Australian black coals are calcite and pyrite (Yan et al., 2001).

Although extensive fragmentation of these minerals has been noted, the bulk of the newly-formed ash particles are generally super-micron in size (Yan et al., 2001; Ten Brink, 1994). The schematic of ash formation mechanisms during pulverised coal combustion is given in Figure 2.3 on the following page.

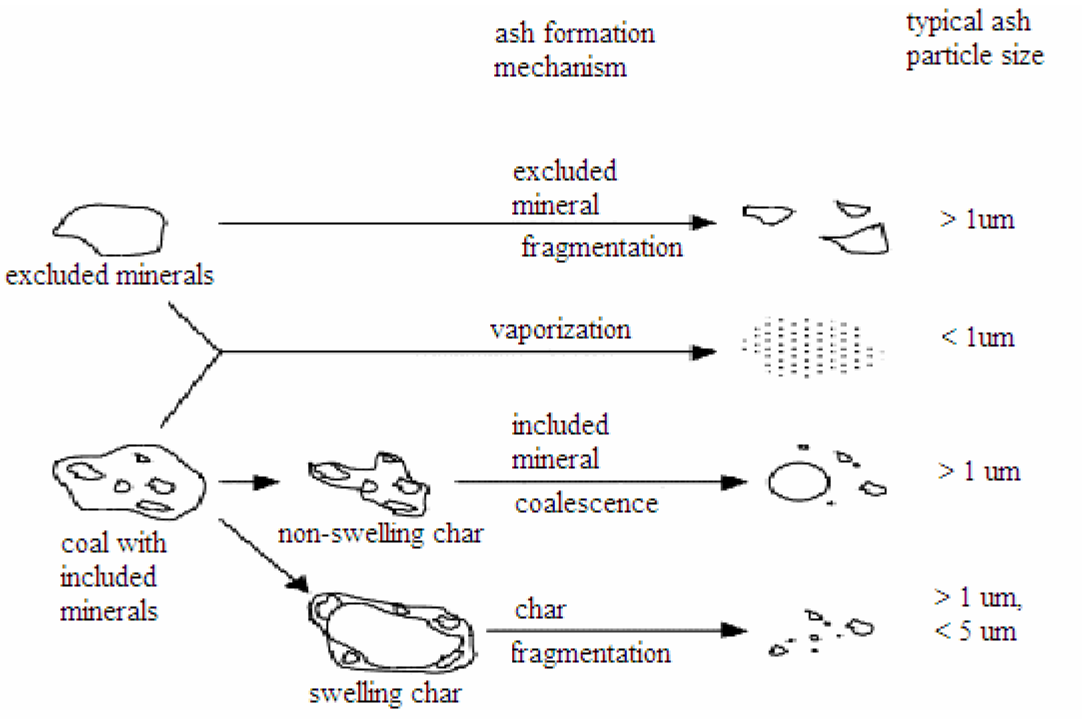

Figure 2.3: Schematic of ash formation mechanisms during pulverised coal combustion (Buhre et al., 2005).

The researchers also found that alkalis, sulphur and phosphorus present in the coal readily vaporise during combustion of coal at elevated temperatures. The extent of vaporisation of the refractory oxides from the included minerals has also been suggested to depend on the size distribution of included minerals containing refractory oxides (Quann and Sarofim, 1982; Eddings et al., 2000; Lee et al., 1990).

2.3 Organic matter in coal

As stated previously, coal is mainly made up of organic matter (macerals). The main objective of this study is to determine which minerals or inorganic constituents are responsible for the sintering of mineral matter at elevated temperatures during coal gasification. Because of this focus, the chemical and physical properties of macerals as well as their behaviour during coal combustion at elevated temperatures are not discussed in detail in this study; only a brief overview follows:

Spackman (1958) defined macerals as organic substances that are contained in coal and have a distinct set of physical and chemical properties.

Macerals are organic components of coal that are closely analogous to the role of minerals in rocks. Macerals and minerals both have reasonably specific physical and chemical properties, and their relative proportions then determine the characteristics of the rock. Spackman (1958), Crelling and Dutcher (1980), Ward (1984) and Gurba (1998) mentioned that coal macerals are divided into three groups:

- Vitrinite group
- Liptinite group
- Inertinite group

Vitrinite group:

Vitrinite is derived from the cell wall material or woody tissue of plants and is the most abundant group that makes up 50-90% of most North American coals (Grelling and Dutcher, 1980). The South African low-rank bituminous coals contain 14-90% vitrinite (Pinheiro et al., 1998-1999). These macerals have reflectance between that of liptinite and inertinite.

Liptinite group:

Liptinite is derived from the waxy and resinous parts of plants such as spores, cuticles and wood resins. These macerals make up about 5-15% of most North American coals. Some of the South African coals contain 2-8% liptinite (Pinheiro et al., 1998-1999). These macerals disappear from coal at a reflectance of 1.35-1.40. They are characterised by significantly higher hydrogen concentration and a high proportion of volatile matter.

Inertinite group:

Inertinite is derived from plant material that has been strongly altered and degraded in the peat stage of coal formation. North American coals contain inertinite macerals in the range of 5-40% and have highest reflectance. The South African low-rank bituminous coals contain 3-28% reactive inertinite and 20-57% inert inertinite (Pinheiro et al., 1998-1999). In the polished section they appear white and opaque and are characterised by significantly higher carbon content and lower hydrogen content in comparison with other macerals in coals of the same rank (Chandra and Taylor, 1982; Ward, 1984).

According to Chandra and Taylor (1982), minerals and macerals present in coals are not significantly transformed at temperatures less than 300°C. However, vitrinite and liptinite macerals could start to deform because of high local stresses during the intrusion process.

They clearly indicated that both vitrinite and liptinite macerals undergo significant petrographic changes at different temperatures (in the range of 300-500°C); in most coals evaluated in their studies the petrographic structure is lost at about 400-500°C. At 500°C structures of liptinite macerals decompose completely and can no longer be recognised. However inertinite does not undergo decomposition during thermal metamorphism below 300°C; its structure starts to change minimally even above 300°C (Chandra and Taylor, 1982).

Gurba (1998) found that liptinite macerals contained a significantly higher proportion of organic sulphur in comparison with the remaining macerals (vitrinite and inertinite). The order for organic sulphur is liptinite > vitrinite > inertinite. No trends were found between the coal rank and organic sulphur determined by electron microprobe. Electron microprobe analysis for samples of coals collected from Sydney-Gunnedah Basins in Australia indicated that Si and Al, which are associated within the organic fraction in coals, are present in macerals (Gurba, 1998).

2.4 Volatilisation of organic sulphur and organically-bound cations

According to Reid (1981), Given (1984), Benson and Holm (1985) and Benson (1987), organic sulphur present in the coal decomposes at high temperatures to first form sulphur dioxide, possibly followed by the formation of sulphur trioxide at a temperature lower than 500°C, under oxidation conditions. Alkali and alkaline earth species present in the fly ash particles formed during combustion of the coal, can preferably interact with the sulphur oxides at approximately 560°C, to form alkali or alkaline earth sulphate (Reid, 1981; Benson, 1987).

Sodium or potassium present in either metallic salts of carboxylic acids, or dissolved in the pore waters, may volatilise in the form of oxides or halides during gasification and combustion. According to Raask (1986), sodium and potassium can react with sulphur from the organic suphur compounds present in the coal under the reducing conditions to form sodium sulphide and potassium sulphide. Hydrogen sulphide can also be formed under reducing conditions. Subsequent to the oxidation of the formed sulphides, sodium sulphate can react with meta-kaolin and coal ash at elevated temperatures to form liquid (Raask, 1986).

Raask (1985) indicated that the temperature and residence time of the ash particle in the flame affect the distribution of volatile sodium between silicate components of the ash and sulphate. Transformed sodium or potassium reduces the viscosity of the molten silicates, resulting in an enhanced rate of sintering.

Wibberley and Wall (1982) found that volatile sodium from the coal reacted directly with silicon-bearing minerals as well as organic sulphur at elevated temperatures, to form sodium silicate and sodium sulphate respectively. In their studies, quartz (pure silica) and silicon-containing minerals in the coal were separately added into a vertical tube furnace and heated to a temperature greater than 1200°C. The results revealed that the formation of sodium sulphate and sodium silicate is sensitive to temperature. Sodium silicate is found to be relatively more stable than sulphates at temperatures from 1200°C to 1600°C. Sodium sulphate is more stable below approximately 1100°C (Wibberley and Wall, 1982).

Attalla et al. (2004) found that trace elements present in the coal volatilise differently during combustion or gasification processes, depending on their modes of occurrence. The trace elements can be classified into three groups as shown in Table 2.3.

From Table 2.3 it is clear that some elements occur in more than one group. The authors suggest that differences in mode of occurrence, operating process conditions (including partial pressure of oxygen, temperature and differing pollution control devices) are most likely responsible for the overlapping of elements between groups. Those elements (As, Cd, Co, Mo, Pb, Se, W and Zn) that have a strong affinity for sulphur (chalcophile), are claimed to be the most readily vaporised as hydrides, halides or metal carbonyls during combustion (Quann et al., 1990). The trace elements listed in Group 1 in Table 2.3 support this (Quann et al., 1990). Those elements (Be, Co, Cr, Cs, Ga, Hf, Li, Rb, Ti, V and Zr) that have a strong affinity for oxygen (lithophile), are expected to coalesce with the aluminosilicate melt (Quann et al., 1990).

Table 2.3: Trace element partition classification after Clarke and Sloss (1992)

Group 3:
Highly volatile, at least partially enriched in the gas phase, depleted in the condensed phases: Hg, Rn, Br, Cl, F, B, Se, I
Group 2:
Volatile, which are enriched in the fly ash, depleted in bottom ash:
B, Se, I, As, Cd, Ga, Ge, Pb, Sb, Sn, Te, Tl, Zn, Ba, Be, Bi, Co, Cr, Cs, Cu, Mo, Ni, Sr, Ta, U, V, W
Group 1:
Low volatility, being evenly distributed between bottom ash and fly ash:
Ba, Be, Bi, Co, Cr, Cs, Cu, Mo, Ni, Sr, Ta, U, V, W, Eu, Hf, La, Mn, Rb, Sc, Sm, Th, Zr

Neville et al. (1981) found that the majority of Mg, Na and Ca that are organically-associated with the organic fraction in the low rank coal was vaporised at 1527°C and produced a sub-micron fume totaling 1.9-9.6wt% of the ash.

Srinivasachar et al. (1990a, b) suggested that refractory metal oxides (including silica) react with carbon at an elevated temperature of 1727°C to form volatile sub-oxides. The sub-micron fraction of the included minerals, being well dispersed within the coal matrix, is most likely the source of those sub-oxides. The results from the experiments with mixtures of finely ground silica and excess carbon in a graphite crucible heated in argon, indicated that substantial volatilisation of silica occurred above 1230°C. It was estimated that for a typical pulverised coal-fired boiler, approximately 1 wt% of the total silica is volatilised in the flame (Srinivasachar et al., 1990a, b). Unlike included minerals under reducing conditions, the excluded minerals experience oxidising conditions at elevated temperatures of greater than 1200-1400°C, fuse and limit the extent of volatilisation of excluded minerals severely.

2.5 Determination of mineral matter (non-minerals and minerals) in coals

As mentioned previously in section 2.1, coal contains both mineral matter and organic matter that play a significant role during mineral transformation at elevated temperatures during coal combustion. A number of different analytical techniques have been utilised to determine concentrations of mineral matter, as well as modes of occurrences of the inorganic species present in coals (Gluskoter, 1965; Miller et al., 1979; Ward, 1986, 1999, 2002; Ward and

French, 2004; Kiss and King, 1977; Miller and Given, 1978; Kiss, 1982; Benson and Holm, 1985). In this thesis techniques that are available for qualification and the quantification of mineral matter in coals are briefly discussed.

2.5.1 Determination of the concentration of mineral matter in coals by oxidation of the organic matter in coals

A number of authors (Gluskoter, 1965; Miller et al., 1979; Ward, 1986, 1999, 2002; Ward and French, 2004; Foscolos et al., 1989) used low-temperature oxygen-plasma ashing (LTA) to oxidise organic matter present in coals at low temperature, without altering the coal minerals. In low-temperature oxygen-plasma ashing, the activated oxygen produced from a radio-frequency oscillator is passed over the pulverised coal particles to selectively oxidise all organic matter at temperatures in the range of 120-150°C, without decomposing the inorganic minerals. They found that the colour of the ash produced at low temperature is grey, indicating that the oxidation process is complete. This technique gave reliable results of the concentration of mineral matter present in higher-rank coals (Frazer and Belcher, 1973; Standards Australia, 2000). A schematic representation of LTA apparatus is given in Figure 2.4.

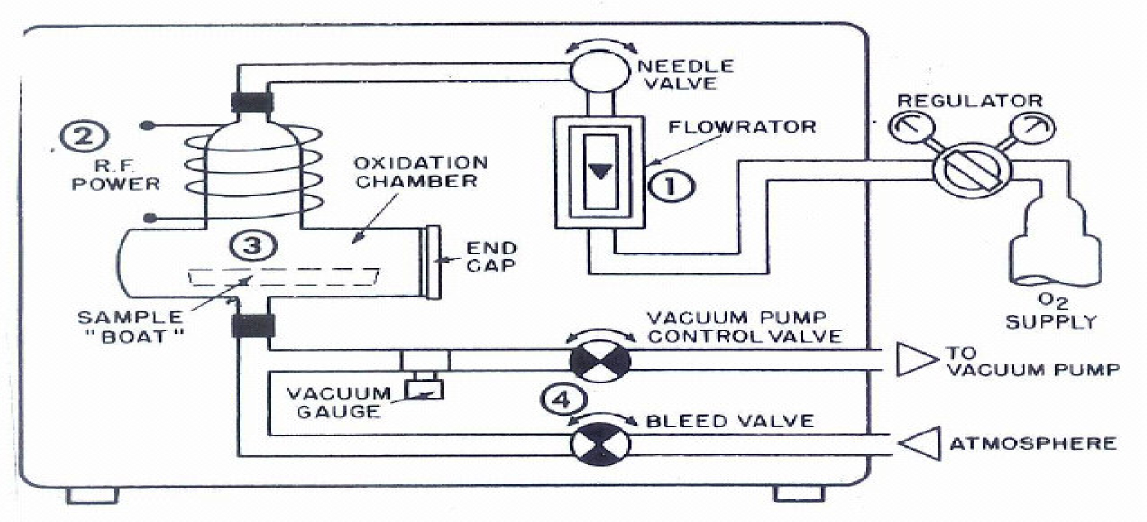

Figure 2.4: Schematic diagram of low temperature asher.

In some cases, the organically-associated inorganic elements in the coal may also interact with each other during plasma ashing to form new minerals (Given, 1984; Benson and Holm, 1985).

The organically-bound elements such as Ca, Mg and Na can also react with organic sulphur to form trace artifact compounds such as bassanite ($CaSO_4.1/2H_2O$), kieserite ($MgSO_4.H_2O$) and thenardite (Na_2SO_4) (Given, 1984; Benson and Holm, 1985).

Other trace minerals (potassium alum ($KAl(SO_4)_2.12H_2O$) and metabasaluminite ($Al_4SO_4(OH)_{10}$) that are also suggested to be artifacts of the plasma ashing process, were detected by XRD (Ward, 1991). Foscolos et al. (1989) found that the low-temperature ash (LTA) from the untreated Greek lignite coal contained ammonium-iron sulphate.

Brown et al. (1959), Nelson (1953), Ward (2001a) and Hicks and Nagelschmidt (1943) heated coal samples to 370°C in the presence of air, to oxidise the organic fraction in the coal prior to the determination of the mineral matter. From their studies they found that coal minerals including siderite, other clays and pyrite start to decompose and result in the alteration of their crystal structures. As a result of mineral decomposition during heating of coal at 370°C, the mass percentage of ash remaining after heating gave unreliable results of the mineral matter content in coals tested.

Nawalk and Friedel (1972) and Ward (1974) noted that the use of hot, concentrated hydrogen peroxide to oxidise organic matter has a negative impact on the crystal structure of carbonates in coals. They suggest that carbonate minerals present in the coal sample dissolve in the organic acids that formed when hydrogen peroxide reacted with organic matter during the oxidation process. Pyrite may also cause spontaneous decomposition of the peroxide and cessation of oxidation. Due to the inevitable reactions between minerals and peroxide, the use of hot peroxide to remove organic matter is not a suitable alternative method for the determination of mineral matter in coals.

2.5.2 Mineral matter determination by chemical analysis

Radmacher and Mohrhauer (1955) used a solution of mineral acid (hydrochloric and hydrofluoric acids) to digest mineral matter present in a high-rank coal sample. The coal sample was weighed before and after digestion with the mineral acids. They concluded that the proportional mass loss represented the content of the mineral matter contained in the coal sample.

The percentage of mineral matter in coals can also be determined by calculation, using the combination of the ash yield of the coal and the proportions of other key inorganic constituents in the coal samples. The simple formulae that were proposed by Parr (1928) and King et al. (1936), are based on the coal's ash yield and total sulphur content and are applied for calculating the concentration of mineral matter from other analytical data. The formula of Parr (1928) was modified to include pyritic sulphur and chlorine, rather than just the total sulphur content (Given and Yarzab, 1978). In the formula of King et al. (1936), known as the King-Maries-Crossley expression or KMC, the carbonate carbon, chlorine, pyritic and sulphate sulphur contents of the coal and the proportion of sulphur retained in the coal ash, as well as the percentage of ash are used to determine the proportion of mineral matter contained in the coal sample. The two formulae are given in Table 2.4.

Table 2.4: Formulae for calculating mineral matter percentages from other analytical data

Parr formula

$MM = 1.08\ A + 0.55\ S$ (original version) (Parr, 1928) (2.2)

$MM = 1.13\ A + 0.47\ S_{pyr} + 0.5\ Cl$ (modified version) (Given and Yarzab, 1978) (2.3)

King-Maries-Crossley (KMC) formula

$MM = 1.13\ A + 0.5\ S_{pyr} + 0.8\ CO_2 + 2.85\ S_{SO4} – 2.85\ S_{ash} + 0.5\ Cl$
(King et al., 1936) (2.4)

Where:

MM = percentage of mineral matter in coal
A = percentage ash yield from coal
CO_2 = percent carbonate carbon dioxide yield from coal
S_{pyr} = percent pyritic sulphur in coal
S_{SO4} = percent sulphate sulphur in coal ash
S = percent total sulphur in coal
Cl = percent chlorine in coal
S_{ash} = percent total sulphur in ash

2.5.3 Determination of the non-mineral inorganics in low-rank coals using a chemical fractionation technique

A chemical fractionation technique which was developed by Miller and Given (1979) and later modified by Benson and Holm (1985) was used to quantify the concentration of non-mineral inorganics such as ion-exchangeable cations, acid-soluble elements and insoluble elements in coals. In the chemical fractionation method, water is used in the first leaching step to selectively remove elements that dissolved in pore waters during coalification (Ward, 1991; Ward and French, 2004). The water-leached coal is then treated with ammonium acetate to extract exchangeable ions from carboxylates within the organic matter. In the last step of the selective leaching, a solution of hydrochloric acid is used to dissolve all the elements present in metallic salts of carboxylic acids or chelates within the coal. The leached residual coal was ashed by a low-temperature oxygen-plasma asher, without decomposition of minerals present in the original coal. Ward (1991) used chemical fractionation to investigate non-mineral inorganics present in Mae Moh coal samples.

The flow diagram for selective leaching of Mae Moh coal samples is given in Figure 2.5.

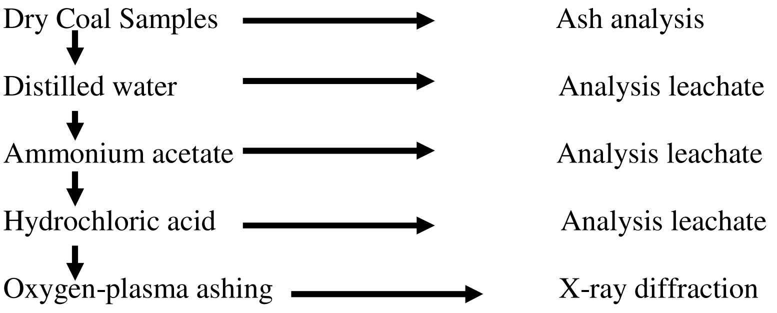

Figure 2.5: Selective leaching scheme used for analysis of Mae Moh coal samples (Ward, 1991).

From results given in Table 2.5, it is clear that the majority of sodium present in the coal sample dissolved in distilled water when water was used as the lixiviant during the sequential leaching step testing. This implies that most of the sodium ions dissolved in the pore water within the coal (Ward, 1991). Results also revealed that calcium occured mostly in ion-exchangeable form (possibly associated with carboxylate compounds and partly in the pore waters and an acid-soluble form). High proportions of sulphur and iron reported to the leached residual coal samples after the selective leaching steps. This suggests that iron and sulphur occur as mineral (pyrite).

The chemical fractionation results reported by Benson and Holm (1985) showed that significant amounts of Ca, Mg and Na present in the lignite coal samples dissolved in ammonium acetate solution during leaching experiments.

Miller and Given (1978), Benson and Holm (1985) and Benson (1987) concluded that the majority of these elements occur in ion-exchangeable form in the lignite coal samples.

Table 2.5: Proportion of selected elements in Mae Moh coals released by different leaching steps (Ward, 1991)

Elements	**% elements removed by water**	**% elements removed by ammonium acetate**	**% elements removed by hydrochloric acid**	**% insoluble in the leached coal**
Na	75.10	20.90	8.50	0.00
Ca	30.70	43.60	25.00	0.10
Fe	0.10	0.00	44.80	55.00
S	19.40	1.40	1.50	77.70

Results given in Table 2.6 are for the oxidised Mae Moh coal from Thailand. Pyrite was found in most samples to be partially oxidised during storage prior to chemical fractionation experiments. It can be seen that the oxidised coal contained significantly higher proportions of water-soluble S, Fe and Ca in comparison with the unoxidised coal (Tables 2.5 and 2.6). Ward (1991) suggested that sulphuric acid, formed during oxidation of pyrite, reacted with calcium from carbonate minerals and iron from the oxidised pyrite during the selective leaching steps.

Table 2.6: Proportion of selected elements in Mae Moh coals released by different leaching steps after pyrite oxidation (Ward, 1991)

Elements	**% elements removed by water**	**% elements removed by ammonium acetate**	**% elements removed by hydrochloric acid**	**% insoluble in the leached coal**
Na	45.60	9.40	29.40	15.60
Ca	73.30	11.50	5.00	10.20
Fe	20.70	0.00	38.60	40.70
S	37.00	2.70	5.90	54.40

As mentioned earlier, low-rank coals contain high concentrations of organically-bound cations in comparison with high-rank coals (Miller and Given, 1978; Benson and Holm, 1985; Benson, 1987; Ward, 1991).

In this study it is suggested that metallic salts of carboxylic acids present in coal will release small amounts of elemental Ca, Na or Mg that may react with some aluminium silicates and assist in lowering the melting points of these silicates.

The organically-bound cations, inorganic elements dissolved in the pore waters as well as dissolved salts interact with each other to produce trace artifacts in low-temperature plasma ashing of higher-rank coals. The chemical fractionation technique (coupled with low-temperature ashing of the coal) significantly improves the accuracy of the mineral matter content in lower-rank coals than just using the direct application of low-temperature ashing techniques (Ward et al., 2001a). Although the leachates produced from CHF experiments done by Ward (1991) were not submitted for Cl analysis, the only major mode of occurrence of chlorine according to Huggins and Huffman (2004), is in the form of chloride in the moisture associated with the macerals in coal. Chlorides can readily volatilise from coals during heat treatment.

2.5.4 Proximate analysis of coal

Proximate analysis is a routine analytical method which is used to determine the relative amounts of light organic compounds (volatile matter) and fixed carbon (non-volatile organic material) present in coals. It is also used to quantify the amount of moisture in the coal, and gives a measure of the inorganic components that are left as a residue or ash after the burning off of the organic matter from the coal (SABS 924, ISO 589), ash content (ISO 1171) and volatile matter (ISO 562).

Volatile matter in the coal represents light organic components, excluding the moisture content, released from either the organic matter or mineral matter when coal is heated at an elevated temperature under oxidising conditions (Ward, 1984). If the concentration of volatile material in the coal is to be utilised to classify coals for a particular application, correction for that derived from inorganic sources (carbonates and clays) must be made in order to obtain accurate results (Ward, 1984). The determination of the concentration of volatile matter in coals involves heating the coal under rigidly specified conditions. The standard methods required for the determination of volatile matter content in coal vary from one country to another. According to the A.S.T.M. (1979), the coal sample must be transferred into a platinum crucible in a vertical electric furnace, and heated to 950°C.

However, for British and Australian Standards, coal must be added to the cylindrical silica crucible in a muffle furnace of specified conditions and heated to 900°C for 7min (Standard British, 1973; Standard Australian, 1979). The results for the same coal, using different procedures from various countries, give slightly different results. A modified A.S.T.M. procedure, involving two stages, of heating, is essentially required for low rank coal or sparking coals in order to improve the accuracy of the results (Ward, 1984).

Coals contain four possible forms of moisture, namely: (1) surface water (extraneous water) which is held as films on the surface of coal particles; (2) hygroscopic moisture (water inside the capillaries of the coal substance); (3) decomposition water (water which is incorporated in some of the organic compounds) and (4) mineral moisture (water of crystallisation that is bonded to clay in the coal). The total moisture content of the sample is the difference between the mass of the sealed sample as received from the mine or stockpile and the dry sample (Ward, 1984).

The following known methods can be used to fully dry samples from the mine in order to determine total moisture in coals (Ward, 1984):

A known mass of the sample is dried at 105-110°C in a minimum free-space oven in the presence of the flowing nitrogen and a relative mass is obtained. This method is suitable for the determination of the total moisture as well as the inherent or air-dried moisture in coals of all ranks. It is possible that samples of low-rank coals may undergo oxidation during heating.

For the determination of the moisture content of high-rank coals, a known mass of coal as received in the laboratory is heated to 105-110°C in a laboratory oven in the presence of air and the relative loss of mass is determined.

When coal is heated at elevated temperature in the presence of air or oxygen, the organic fraction of the coal is released as carbon dioxide and water vapour, while mineral matter transforms to form the non-combustible inorganic residue which is termed ash. Ash makes up a smaller mass fraction of coal in comparison with mineral matter concentration (Ward, 1984).

In coal utilisation, coals with low ash content are preferable to coals with a high ash proportion. A smaller amount of ash in the coal will need less energy when compared with coal with greater mass of high ash material, during either the combustion or gasification process. In addition, a smaller amount of waste (ash) will be generated from the low-ash coal combustion or gasification process.

During the determination of ash present in the coal, both the specified temperature and time are required to obtain accurate ash content.

Methods that are employed for the determination of ash content in coals are as follows:

In British and Australian practice, a known mass of the sample of coal to be analysed is heated slowly from room temperature to 815°C until a constant mass of ash (non-combustible residue) is attained (Standard British, 1973; Standard Australian, 1979). In some cases, two stages of heating, namely: using the temperature of 500°C for a certain period of time and then heating coal at 815 °C in the second furnace, are needed.

In America, the nature of the minerals present in the coal sample determines the type of procedure that is suitable for the determination of ash content present in the coal (A.S.T.M., 1979). For calcite and pyrite-rich coals, a two-stage process is required in order to prevent the reaction between sulphur, calcium and aluminium silicate forming mineral artifacts in the ash. In this procedure, coal particles are slowly heated to 500°C for 1h; then to 750°C for 2h, and kept at 750°C until the mass of ash formed during heating becomes constant.

Carbon retained in the coal material after the removal of the volatile matter is termed the fixed-carbon. For the production of coke from the coal, the fixed carbon content is used as an index or as the indicator of the solid combustible material that remains in coal-burning equipment after the volatile matter has been removed (Ward, 1984). For the classification of coals, the fixed carbon can also be used as an index of the coal rank. There is no direct analytical procedure that is used to determine the concentration of fixed carbon present in the coal.

The formula for the calculation of the percentage of fixed carbon (FC) in coals is as follows:

$$FC = 100 - (\text{moisture content} + \text{volatile matter content} + \text{ash content}) \qquad (2.5)$$

2.5.5 Ash analysis

The proximate analysis, which was fully described in Section 2.5.4, shows the ash content present in the coal sample, but it does not indicate the elemental composition of the inorganic species in the ash.

Coal ash obtained during the combustion of coal at elevated temperatures consists almost entirely of the transformed aluminium silicate products, quartz and trace amounts of the untransformed or partially oxidised coal minerals including carbonates, sulphides, etc. (Ward, 1984). The analytical techniques including Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma (ICP), X-ray Fluorescence Spectroscopy (XRF) and Optical Emission Spectroscopy (OES) are used to quantify elements present in ash. Coal ash typically contains Fe, Al, Mg, Mn, V, Ti, Si, Ca, Na, K, P, S and Cr and is reported as oxides (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). The chemical composition of coal ash is used to predict the types of minerals present in coal ash, to calculate the fouling factor and slagging factor for the determination of fouling and slagging propensity of coals (Ward, 1984; Benson, 1987 and van Alphen, 2005). The metal oxides can also be used in the calculation of the iron index, slagging index and acid base ratio.

The following slagging indices, which are generally based on ash elemental analysis (oxide - %) and ash fusion temperature are used to predict the slagging propensity of a coal:

- Base/Acid ratio (B/A)

$$B/A = \frac{Fe_2O_3 + Na_2O + K_2O + CaO + MgO}{SiO_2 + Al_2O_3 + TiO_2} \qquad (2.6)$$

- Slagging factor (R_s)

$$R_s = B/A * \%\ TS \qquad (2.7)$$

%TS = Total Sulphur

Other factors that contribute significantly to the slagging of mineral matter during coal combustion were developed by Attig and Duzy (1969). He found that the developed slagging factor worked quite well for Eastern coals produced from the USA but was not applicable to Western coals.

- Iron Index (F_i)
- $F_i = \%Fe_2O_3 * B/A$ (2.8)

Attig and Duzy (1969) developed a fouling index relating the ash composition to the formation of deposit in the boiler during coal combustion of Eastern coals.

The fouling factor, which is termed, R_{Fi} is given as:

$R_{Fi} = (B/A) * \%Na_2O$ (based on A.S.T.M. ash). (2.9)

Attig and Duzy defined an additional fouling factor, after including sodium emanating from minerals that is likely to volatilise in the flame during heating. It is given by:

$R_{Fi} = (B/A) * \%$ water soluble Na_2O.

2.5.6 Determination of minerals in coal and coal ash by X-ray diffraction (XRD) analysis

X-ray diffraction is an established technique which is used to qualify and quantify crystalline phases that are made up of atoms or molecular groups arranged in a regular three-dimensional pattern in solids. Minerals present in solids can be characterised by their unique combination of atoms and molecules, as well as their unique d-spacings. XRD has the capability for measuring d-spacings of the individual mineral present in the solid sample from the combination of internal planes in mixtures (Ward and French, 2004). During XRD analysis of the pulverised solid samples, an X-ray detector (scintillometer) measures the intensity of the diffracted rays from the powdered sample with a smooth surface of even texture, which has been placed in a flat holder at the centre of the rotating goniometer at 2θ to produce a diffractogram. The XRD pattern obtained in this way is matched with the pattern of the reference or standard mineral, in order to identify the mineral present in the sample.

The XRD techniques can produce results of higher accuracy for coals if it is applied to low-temperature ash samples with high concentrations of minerals produced from the coal by low-temperature oxygen-plasma ashing, described previously in Section 2.5.1. (Gluskoter, 1965; Miller et al., 1979; Ward, 1986, 1999, 2002; Ward and French, 2004; Foscolos et al.; 1989). Although some mineral artifacts are formed in the LTA sample during oxygen-plasma ashing, a sample of LTA contains high proportions of minerals that will provide reliable results of minerals during XRD analysis. Also, it has no signs of organic matter that can dramatically affect the quality of the XRD results (Glukoter, 1965; Miller et al., 1979; Ward, 1986, 1999, 2002; Ward and French, 2004; Foscolos et al., 1989).

A number of researchers have developed several methods to determine the proportions of minerals in the coal and ash samples using the XRD technique (Rao and Gluskoter, 1973; Ward, 1977, 1978, 1989; Russell and Rimmer, 1979; Renton, 1986).

Klugg and Alexander (1974) added a known mass of the internal standard (spike) to the LTA sample produced from the coal sample by oxygen-plasma ashing, and subsequently compared the intensity of the sample peaks with the intensity of the peaks of the spike added. In addition, the distribution of dominant minerals present in the individual coal seams of the Illinois Basin, USA was studied by Rao and Gluskoter (1973), Ward (1977) and Harvey and Ruch (1986) using the XRD data for the spiked LTA samples and clay-fraction concentrates.

In their studies they found that a calibration curve for each mineral component needs to be prepared prior to evaluation of minor minerals in the spiked samples. They suggested that variations in methodology, as well as differences in crystallinity of the mineral, preferred orientation in the sample mount, as well as differential absorption of X-rays by minerals in the mixture may significantly affect the quality of the diffractogram of the sample. This may also result in substantial variations in the estimated percentages of minerals in the same analysed samples. In their conclusion they proposed that a standard quantitative XRD procedure for the determination of the concentrations of minerals in the LTA sample is required in order to obtain accurate results from the different laboratories.

Rietveld (1969) developed a technique for using the full profile XRD pattern of X-rays to refine the crystal structure of a mineral or other crystalline phase in the samples with the advent of a computer-based data collection and processing system. His approach has been used more recently to evaluate the concentrations of minerals in a powdered mineral mixture. Extension of Rietveld methodology allows a calculated XRD profile of each mineral phase to be generated from its refined crystal structure and the sum of all calculated patterns to be fitted to the observed XRD profile of a multi-mineral mixture by least-squares analysis to find the optimum phase scales. The optimum phase scales obtained in this way are subsequently used in the determination of the proportion of different minerals contained in the analysed sample (O’Connor and Raven, 1988; Taylor, 1991; Bish and Post, 1993; Ward and French, 2004).

A personal computer software system which is referred to as SIROQUANT® was described by Taylor (1991). SIROQUANT® uses X-ray diffraction patterns and Rietveld techniques to quantify the proportions of up to 25 different minerals contained in the mixture form.

Different crystallographic parameters for each mineral present in the sample are simply interactively adjusted within the programme to produce diffraction patterns of high quality, and also to allow for variations due to atomic substitution, laying disorder, preferred orientation and other factors in the standard pattern used. For the application of SIROQUANT® analysis, a library of XRD files that contains expected minerals in the sample must be prepared; in some cases the high level of background radiation caused by the organic matter needs to be removed from the diffractograms of samples (Taylor, 1991).

2.5.7 Determination of the glass content and glass composition in coal ash using X-ray diffraction techniques

The XRD analysis combined with other quantitative methods can be applied to quantify not only the crystalline phase, but also the non-crystalline, amorphous or glassy phases that are typically present in the coal ash and slag samples (Ward and French, 2004). Coal ash contains dominant components of non-crystalline aluminosilicate glass, crystalline minerals (quartz, mullite, anorthite, etc.) and to a lesser extent unburnt carbon particles.

The majority of glass which is the major component of coal ash, is highly reactive and is used in chemical reactions such as the pozzolanic reaction in cement or zeolite production. In some other cases of coal ash utilisation including soil/plant waste stabilisation, glass significantly enhances the retention of trace elements through encapsulation or adsorption during leaching. Although the glass in ash has the capability of adsorbing some trace elements that may have a negative impact on the environment, glass in ash may also be expected to break down with prolonged exposure, releasing elements that can be leached into surrounding environmental systems (Ward and French, 2004).

Ward and French (2004) developed a method for the determination of the glass content and composition using the XRD results, SIROQUANT® software, XRF analysis and stoichiometry of the crystalline phase in the ash sample, where glassy material humps (broaden pattern) in the diffractrograms indicate the presence of glass or amorphous material.

A SIROQUANT® system has the capacity to determine the concentrations of crystalline phases as well as the proportion of amorphous or non-crystalline material contained in the coal ash. To obtain the results for amorphous material using SIROQUANT®, the evaluation of the diffractograms produced from the powder ash samples with a known concentration of the crystalline spike, must be done (Ward and French, 2004).

In conclusion, routine SIROQUANT® processing can be used to determine the percentages of the spike added to the XRD traces along with the other crystalline components. The proportion of all the crystalline components including the spike is normalised to 100%. If the sample contained a significant proportion of amorphous material, the concentration of the spike in this normalised estimate will be higher than the proportion of the spike added before XRD analysis (Ward and French, 2004).

Ward and French (2004) found that the chemical composition of the bulk ash obtained by XRF analysis, the weight abundances of the crystalline phases as well as knowledge of the stoichiometric chemistry of the phases that were identified by XRD, can be used to determine the overall chemical composition of glass contained in the coal ash sample. The concentration of the unburnt carbon in the coal ash was not included in the calculation of the glass composition when using the normalised results for the coal samples studied. The electron microprobe results for identified minerals can be used in the calculation of glass composition, instead of using the assumed stoichiometric compositions of minerals.
A flow sheet for the estimation of glass composition for fly ash from bulk chemistry and quantitative XRD results is shown in Figure 2.6.

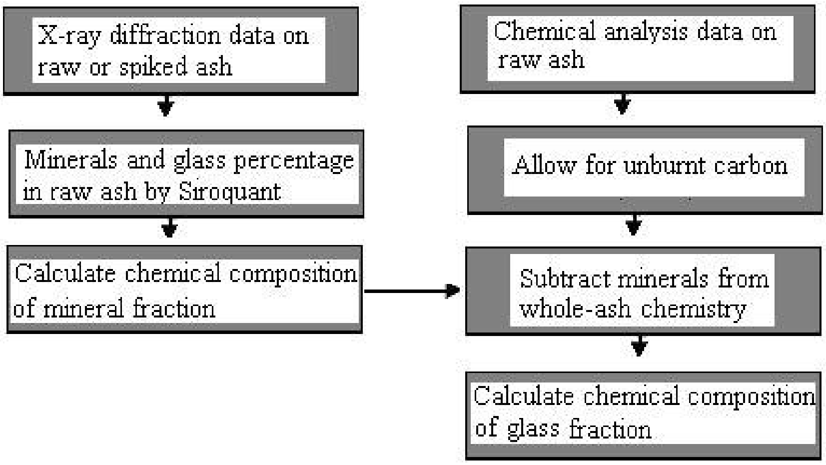

Figure 2.6: Estimation of glass composition for fly ash bulk chemistry and quantitative XRD data (Ward and French, 2004).

During the coal combustion or gasification process, it is imperative to better understand the mineral matter behaviour at elevated temperatures and pressures in order to manage the clinker formation in the boilers or gasifiers, as well as the fouling problem. Traditionally, the slagging or fouling indices that are based on the elemental oxides, thermodynamic modeling based upon the ash chemistry, or direct examination of the end products, either from the gasifier or the boilers, are used to better understand the mineral matter behaviour at elevated temperatures (Ward, 1984; Ward and French, 2004). Dynamic high-temperature X-ray diffraction analysis in conjunction with SIROQUANT® can be used to study coal mineral matter reactions at elevated temperatures under both oxidising and reducing conditions (French et al., 2001; Ward and French, 2004). In addition, the proportions of crystalline phases, amorphous materials (solid and liquid) formed during high temperature X-ray diffraction analysis, can also be qualified and quantified.

2.5.8 Mineral matter qualification and quantification by scanning electron microscopy (SEM)

Scanning electron microscope techniques can be applied to either polished sections of coals or broken coal surfaces to determine mineral matter contained in the coal samples (Creelman and Ward, 1996; Ward and French, 2004). A scanning electron microscope with a light element energy dispersive spectrometer (EDS) and a back-scattered electron (BSE) detector provides comprehensive chemical composition and imaging of the selected individual mineral grains in the polished sections of coals (Creelman and Ward, 1996; Ward and French, 2004).

A combination of SEM and image analyser (computer controlled scanning electron microscopy, CCSEM) is used to evaluate the nature and distribution of minerals in the coal sample (Straszheim and Markuszewski, 1990; Galbreath et al., 1996; Gupta et al., 1999). The CCSEM technique is widely applied for the determination of association, size, composition and abundance of minerals contained in the coal sample which is used in various processes, including combustion and gasification. In the CCSEM analysis, the electron beam is stepped across the selected polished sections in an SEM operating in back-scattered electron (BSE) mode, to evaluate minerals present in the selected coal grains. The size of mineral identified is then measured from the geometry of the selected area with an elevated BSE signal, and subsequently the energy-dispersive X-ray spectrum is acquired from the centre of the selected area. The particles from the selected area are classified into several mineral categories in accordance with the relative abundance of the detected elements. In order to determine percentages of the different minerals present in the coal, the volumetric and weight proportions of the different minerals are calculated (Straszheim and Markuszewski, 1990; Galbreath et al., 1996; Gupta et al., 1999).

Creelman and Ward (1996) noted that the QEM*SEM (quantitative evaluation of materials by scanning electron microscopy) technique can be used for determination of the association of the chemical elements at the individual analysis points on a coal polished section from the output of several X-ray analysers directed at each point in a controlled scan under the SEM. QEM*SEM which was originally designed to determine the proportions of base and precious metals in ores for the mining industry, can also be used to measure size and shape distributions of mineral particles present in the coal. QEM*SEM was modified by Commonwealth Scientific and Industrial Research Organisation (CSIRO) of Australia and is termed QEMSCAN. This equipment can be used in coal utilisation to determine mineral-mineral associations, particle size, mineral compositions and texture of particles in the coal samples (Creelman and Ward, 1996).

2.5.9 Chemical composition of mineral matter and organic matter by electron microprobe (EMP) techniques

The electron microprobe technique is an accurate method that is used to determine the chemical compositions of minerals in coals. As an example, Patterson et al. (1994, 1995) applied electron microprobe techniques for the determination of the chemical composition of different carbonate mineral phases in a range of Australian coal seams. In their studies they found that Australian coals contain pure siderite, pure calcite and dolomite. In some cases siderite was found contaminated by significant amounts of Mg and Ca; ankerite was contaminated by significant amount of Fe. It was found that the presence of Mg and Ca in the siderite is possibly attributed to the deposition of the initial minerals (ferroan, dolomite and ankerite) during plant permineralisation associated with the Foord seam in Canada (Zodrow and Cleal, 1999).

Although the electron microprobe technique is a powerful tool for quantification of inorganic elements that are present on the surfaces of different minerals, this technique can also be applied for determination of chemical proportions of both light organic elements and inorganic elements in the organic matter (macerals) in coals. Bustin et al. (1993), Bustin et al. (1996), Gurba (1998) and Mastalerz and Gurba (2001) applied special analytical techniques for determination of direct light-element concentrations present in the individual macerals in the coal polished sections using the electron microprobe.

These techniques can also analyse sub-micron particles of the inorganic elements that are intimately associated with organic fraction (macerals) in the coal. In some cases, these researchers found that significant proportions of organically-bound calcium, sulphur, aluminium, iron and silicon occur as exchangeable ions attached to carboxylates and elements in metallic salts of carboxylic acids, are present in the different macerals (Bustin et al., 1993; Bustin et al., 1996; Gurba, 1998; Mastalerz and Gurba, 2001). An objective of this present study is to determine the concentrations of the organically-bound inorganic elements in Sasol coals. The determination of the proportions of these elements in coals using electron microprobe techniques may assist in understanding interactions during slagging and fouling.

2.6 Ash Fusion Temperature analysis of coal

It is noted in Section 2.2 that coal consists of not only organic matter, but also of mineral matter which transforms at elevated temperatures to form high-temperature inert metal oxides or ash glass. During the mineral matter transformation at elevated temperatures, the ash fusion of the individual mineral or non-mineral inorganic elements contributes significantly to liquid formation (Ward, 1984; Benson, 1987).

In the laboratory ash fusion temperature test, a cone of ash or a moulded sample of pulverised ash in the form of cube or a pyramid is heated gradually to determine the initial deformation temperature (IDT), softening temperature (spherical) (ST), hemispherical temperature (HT), and fluid temperature (FT) (Ward, 1984; Cumming, 1986). The flow or fluid temperature of the heated ash is reached when the fused ash particles collapse to form a flat button. The temperature values of the above-mentioned temperatures obtained from the ash fusion temperature analysis are critical factors that can be used by the operators or engineers at the combustion or gasification plants to select coals for particular applications as well as to design appropriate boilers or gasifiers.

Huggman and Huggins (1983), Cumming (1986) and Benson (1987) indicated that the ash sample used in the laboratory ash fusibility test had a different chemical composition and particle morphology compared to the fly ash or deposits obtained from the different locations in the boiler.

Variations in the chemical and physical properties of these two samples of ashes result in a discrepancy of the ash fusion temperature values obtained from the laboratory experiments. In addition, Huffman and Huggins (1983) revealed from their research studies that liquid phase formation occurs below the IDT and that the IDT does not represent the solidus temperature.

In most cases, the operators carefully control the operating parameters in the gasification process, including temperature and oxidising agents to manage the physical properties (permeability and particle size distribution) of clinkers. The gasifiers or boilers must be operated at temperatures that are below the bulk melting point of the mineral matter, to avoid massive clinkers or slag. In the present study, the ash fusion temperature was measured as part of coal characterisation.

2.7 Organic matter identification

2.7.1 Ultimate analysis

The ultimate analysis is the fundamental type of routine chemical analysis to determine the concentrations of carbon, nitrogen, hydrogen, sulphur and oxygen in a coal sample (Ward, 1984). The organic matter of coal is essentially made up of carbon, hydrogen, nitrogen, sulphur and oxygen. All of these elements are also found in the coal mineral matter, with the exception of nitrogen. Carbon is also contained in carbonates, sulphur in sulphides and sulphate, and oxygen and hydrogen in hydrous clay minerals (Ward, 1984). Inherent moisture (IM) present in coals mainly consists of hydrogen and oxygen. The concentrations of carbon, hydrogen and oxygen in the organic matter in coals can also be used as indices of rank and as parameters in coal classification (Ward, 1984).

2.7.2 Maceral analysis using electron microscope techniques

Traditionally, a reflected light optical microscope is used to identify various macerals in the polished coal sections in the normal way using oil immersion.

Subsequent to maceral analysis, the electron microprobe technique that was previously described in Section 2.5.9 can be applied for the determination of the direct chemical compositions of the light-elements (C and O) present in the individual macerals in the coal polished sections (Bustin et al., 1993; Bustin et al., 1996; Gurba, 1998; Mastalerz and Gurba, 2001).

The proportion of organically-bound inorganic elements present in the individual maceral can also be determined using the electron microprobe. As an example, individual points on the identified macerals in carbon coated polished sections were analysed by a Cameca SX-50 electron microprobe equipped with the Windows-based SAMx® operating system and interface software to determine proportions of C, N, O, S, Fe, Ca, Al, Fe (Gurba, 1998; Ward et al., 2005). The accelerating voltage for the electron beam was 10kV and filament current was 20 nA, with a magnification of 20,000x giving a beam spot size on the sample of around 5 to 10mm in diameter. Standards for S, Fe, Ca, Al, Fe and O that were supplied with the equipment, as well as an independently analysed sample of anthracite received from Canada which was used as the standard for carbon in their studies for the equipment calibration. The detection limit for nitrogen present in the coal macerals, when using electron microprobe under above-stated conditions was found to be 0.5% (Mastalerz and Gurba; 2001). Goldstein et al. (1992) found that the minimum detectability limit of various inorganic elements such as Na, Mg, Al, Si and Ca in the minerals using the electron microprobe with an WDS detector ranges from 0.01 to 0.02%.

2.8 Mineral reactions at elevated temperatures

Mineral matter (included mineral, excluded mineral and the organically-bound inorganic elements) occur in coal in different modes of occurrences (Ward and French, 2004). During coal combustion or gasification, the included minerals and excluded minerals experience different temperatures and they react differently to form ash particles (Attalla et al., 2004; van Alphen, 2005). As defined previously, included minerals are finely dispersed within the coal matrix and can undergo both reduction and oxidation during coal combustion/gasification (Srinivasachar et al., 1990a, b). It is proposed that these minerals are most likely responsible for the inevitable sintering of ash particles that result in clinker formation in the gasifier.

Furthermore, included minerals may have a lower melting point and may account for the volatilisation of the inorganic constituents in the locally-reducing conditions of the burning char during pulverised or coarse coal combustion.

As defined previously, the excluded minerals may be in the form of ultra-fine material on the surface of coal or rock fragments (siltstone or sand stone) originating from contamination of the mined product by roof or floor strata. They are also liberated from the organic fraction of coal during milling or pulverisation. These minerals can readily oxidise to form metal oxides during coal combustion (Ward, 2004).

According to Ward and French (2004), mineral matter, including minerals and other inorganic constituents present in coal, interact with each other and also with the organic fraction at elevated temperatures during combustion, gasification and coking of coal. Subsequent to coal gasification or combustion, mineral matter transforms to fly ash and bottom ash, fuses and crystallises to form slag deposits, vaporises and condenses to form deposits and interacts with each other or internal boiler components to produce corrosion.

At elevated temperatures, the organically-associated inorganic elements in low-rank coals may react differently from elements in the crystalline or true mineral form.

Kawamoto et al., (1994) conducted research work on types of carbons using different carbon contents to determine the effects of carbon content on the melting rate of carbonate minerals (Na_2CO_3, Li_2CO_3, $MgCO_3$, $BaCO_3$ and $CaCO_3$). In their study they found that the melting rate of carbonate minerals increases as the carbon content decreases. This indicates that there may be an effect of residual carbon content on the melting of mineral matter in the coal to form slags or clinkers.

2.8.1 Excluded mineral mechanisms

As was mentioned earlier in this section, the excluded minerals experience more oxidising combustion conditions than included minerals; this may enhance the rate of fusion, enlarge the clinker size and also reduce the volatilisation of inorganic elements during coal combustion or gasification.

The possible reaction mechanisms of the excluded coal minerals that take place during combustion are discussed below:

It is well documented that quartz (SiO_2) is often regarded as essentially non-reactive in combustion processes, although it undergoes a series of transitions on heating (Bryers, 1986; Watt, 1969; Ward and French, 2004; van Alphen, 2005). At room temperature, quartz is known as low quartz or a quartz, but upon heating to 573°C, it changes to other polymorphs, α-quartz, β-quartz (573-870°C), β_2–tridymite (870-1470°C) and β_2–cristobalite (1470°C-high temperatures) to form a liquid. β_2-tridymite melts at 1670°C; whereas β_2-cristobalite melts at temperatures greater than 1713°C. Watt (1969) mentioned that in the last two transformations of quartz, the structure of its polymorph opens and reacts with alkali ions to form carnegieite and nepheline.

According to Ward and French (2004), tridymite and cristobalite may be formed by solid-state reactions, but the low rate at which reactions take place often allows much of the original quartz to persist through combustion processes.

Quartz is a hard mineral and it contains coarse grains, which may be responsible for an abrasion and erosion hazards in the furnace operation. Finer-grained quartz, which is often associated within the carbonaceous matter in coal, can be produced as residues during the burning of char. In addition, the residues of quartz formed during coal combustion can build up to reduce the heat transfer capacity of the combustion system (Ward, 1984).

At temperatures of between 425°C and 525°C, kaolinite ($Al_4Si_4O_{10}(OH)_8$) in the coal starts to lose hydroxyl water and dehydration is complete at around 800°C. An amorphous material which is termed metakaolinite is formed. The three final products of the transformation of kaolinite which are formed at 950-1000°C, are gamma-alumina (Al_2O_3), mullite ($3Al_2O_3.2SiO_2$) and cristobalite (SiO_2) with a silicon spinel ($2Al_2O_3.3SiO_2$) occurring as an intermediate. As the temperature of the boiler increases to about 1600°C, mullite and cristobalite appear to persist as solid phases (Grim, 1962; Bryers, 1986; Unsworth et al., 1987b; Ward and French, 2004; van Alphen, 2005). The final transformation products melt at temperatures greater than 1600°C, which is much higher than the maximum temperatures of the existing boilers.

The loss of hydroxyl water from illite ($K_{1.5}Al_4(Si_{6.5}Al_{1.5})O(OH)_4$) starts at about 400°C and may continue to about 900°C, forming spinel and mullite at around 950-1050°C. Grim (1962) found that the dehydration of illite is very slow in comparison with kaolinite.

On heating illite, Grim and Bradley (1940) found that spinel is formed at 850°C; as the temperature increased to about 1200°C the amount of spinel also increased.

These investigators suggested that the octahedral sheet of the illite lattice carrying the alumina, magnesium oxide and iron goes into the spinel formation; the alkalis and the silica from the tetrahedral layers yield an amorphous glass. They also found that at 1300°C the spinel dissolved in the glass; mullite appeared at 1100°C and persisted to at least 1400°C. During their investigation, no evidence of quartz was found at elevated temperatures. Ward and French (2004) similarly reported that illite and other clays, excluding kaolinite, fuse at around 1200°C to 1350°C to form glassy components, resulting in relatively low ash fusion temperatures and possible slag development.

Srinivasachar et al. (1990b) conducted research on the excluded crystalline illite particles and illite grains included within a carbon matrix in a laboratory scale reactor to address the physical and chemical transformation of illite particles during the combustion process. The results from their studies show that illite starts to decompose at temperatures above 1167°C, losing its crystalline structure and completely transforming to a glass. During their investigation, no vaporisation of the potassium species occurred from the liquid from either the excluded or included illite particles, but formation of cenospheres (ash components that contain unburned carbon particles of different types from coal combustion, unaltered quartz, other mineral grains and hollow silicate spheres that float on water) was observed.

Combustion of synthetic chars containing illite inclusions showed coalescence of these inclusions to form larger ash agglomerates (Srinivasachar et al., 1990b). Comparison of these results with ash particle compositional data obtained from the combustion of a bituminous coal containing illite, showed intermediate compositions indicating interaction between the molten illite and quartz, kaolinite and pyrite (Srinivasachar et al., 1990b). Hence liquid derived from illite is responsible for the dissolution of ash particles during the pulverised coal combustion process. Similarly, in this thesis it is proposed that potassium or sodium from the illite particles present in coarse coal, together with the included pyrite particles, contribute to the sintering of mineral matter during the gasification of the coarse coal at elevated temperatures and pressures.

It is well documented that trace amounts of excluded carbonate minerals including calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), siderite ($FeCO_3$), ankerite ($(Fe, Ca, Mg)CO_3$)) are found in most bituminous coals.

Bryers (1986), Ward (1984), Bogwardt and Bruce (1986), Raask (1984) and Ward and French (2004) indicated that calcite decomposes at elevated temperatures of around 1000°C to form quicklime (CaO).

This lime may react with water and sulphur oxides to form portlandite ($Ca(OH)_2$) and anhydrite ($CaSO_4$) respectively. At low temperatures, CaO also reacts with sulphur oxides to form bassanite ($CaSO_4.1/2H_2O$). At high temperatures CaO interacts with reactive aluminium silicates, such as meta-kaolin ($Al_2O_3.2SiO_2$) to form gehlenite ($Ca_2Al_2SiO_7$) and anorthite ($CaAl_2Si_2O_8$), the latter fusing at about 1400°C to 1500°C. They also found that dolomite decomposes in a two-stage process at elevated temperature to form lime and periclase (MgO).

van Alphen (2005) used a Drop Tube Furnace (DTF) to study the high temperature transformation of minerals present in South African pulverised fuel during heating. In this study, the selected coal was screened to produce coal fractions which were suitable for the experiments. Each coal fraction was added into the DFT and subsequently combusted at different temperatures and under both oxidising and reducing conditions to obtain fly ash for analysis. The results obtained from this study were also used to validate the fly ash model. The experimental results showed that the excluded calcite in South African fuel transformed into calcium oxide; excluded dolomite transformed into Ca-Mg-oxide. The excluded quartz and excluded orthoclase remained excluded in the fly ash and did not readily interact with the other mineral phases. The excluded pyrite transformed into Fe-oxide or Fe-O-S melts.

It is known that mineral matter containing high concentrations of alkali elements in low-rank coals are responsible for the slagging and fouling of inorganic species at elevated temperatures (>1000°C) (Raask, 1985; Benson, 1987). In contrast these problems are potentially lower in fluidised bed combustion (FBC) operating at much lower temperatures (ca. 700-900°C). Vuthaluru and Ke Zhang (2001) performed testwork with sand, South Australian lignite calcite ($CaCO_3$), Ca-treated coal and magnesium ($MgCO_3$) to investigate the role of Ca and Mg in agglomeration and defluidisation during coal combustion. Combustion tests were carried out in the laboratory-scale spouted bed combustion system operating at 800°C.

Experiments were performed with the crushed coal sample (in the range 1.4-3.35mm) from Bowmans coal from Australia.

A known mass (100g) of a bed material (calcite, magnesite and sand) was added into the fluidisation vessel from an opening at the top end of the reactor. Coal was then fed into the combustor using a screw feeder at a rate of 500 g h $^{-1}$. Ash samples were collected in the cyclone and ash-coated bed particles were collected from the combustor and analysed by electron microprobe and XRD.

The results from the experiments revealed that tests with calcite (as the bed material) indicated no agglomeration and defluidisation tendencies for longer operating periods (12h at 800°C). Mg-bearing compounds were found to be superior in terms of controlling defluidisation in comparison with other bed materials. They also found high concentrations of Ca (either in coal or in the bed material) to delay and decrease the severity of agglomerates formed under the above-mentioned operating conditions. High concentrations of Ca and Mg in ash significantly enhanced the presence of anhydrite, calcite, lime, periclase, and dolomite, talc, and feldspar phases; and reduced the cementing material (low temperature eutectics). The researchers of this investigation concluded that the reaction mechanism mentioned above is responsible for the reduction of agglomerate formation and fouling problems observed with the use of Ca/Mg-based bed materials and Ca-treated coal.

Bailey (1999) heated the excluded particles of pure mineral and sink fraction of coal (obtained by density separation) to combustion temperatures of 1100°C and 1600°C in order to understand the behaviour of siderite particles during coal combustion. The results from his investigation revealed that excluded siderite (containing various levels of Ca, Mg and $MnCO_3$) fragmented during heating without the formation of liquid. The author also used the FeO-MgO-CaO ternary phase diagram in order to predict the behaviour of excluded siderite grains under combustion conditions, clearly indicating that the excluded siderite is unlikely to form sticky or completely molten particles at 1600°C, unless $MgO < 5$wt %, $CaO < 37.5$ wt % and $(MnO + FeO_n) > 60$wt %. The chemical compositions of the different collected sintered particles of ash also agreed with this prediction. From his visual observation, residues from excluded siderite particles are found to be sticky at higher temperatures (1380°C compared to ~1080°C for pyrite (Bailey, 1999).

The excluded pyrite (FeS_2) present in coals breaks down to form iron oxides (hematite, maghemite and magnetite) during coal combustion (Srinivasachar et al., 1990). These authors also mentioned that pyrrhotite (FeS) particles, from the high temperature transformation of pyrite under reducing conditions, melts at 1227°C to form an iron oxysulphide droplet (Srinivasachar et al., 1990). Ward and French (2004) indicated that pyrite can undergo an exothermic reaction; burns due to interaction of its oxygen and sulphur before forming an iron oxide residue. During the heating of pyrite in the presence of carbon, the released iron can react with active inorganic elements or substances to form a range of minerals, including spinel, magnesioferrite, calciumferrite, srebrodolskite and brownmillerite.

Briggs and Lindsay (1986) selected a few samples of pure minerals, including clays, pyrite and calcite in order to study minerals that are responsible for the slagging of mineral matter when they transform at elevated temperatures. In this study, a known mass of individual minerals or mixtures of minerals was placed in the crucibles and heated. As expected, pyrite transformed to pyrrhotite, calcite to quicklime and carbon dioxide, while clay transformed to silicate liquid during heating. They found that with a mixture of either illite or montmorillonite in the presence of pyrite and calcite, liquid formed at temperatures of 600-650°C. When illite or montmorrilonite was totally replaced by kaolinite, the liquid formed at higher temperatures of 750-760°C.

A list of the most common phases reported in various high temperature materials, emanating from the coal combustion process, is given in Table 2.7. Decomposition and melting temperatures of the selected coal minerals and high temperature metal oxides formed during coal combustion are given in Table 2.8. Knowledge of these minerals, in relation to the mineral matter characteristics of the original coal, provides a basis for a better understanding of the interactions or reaction mechanisms that take place between the different mineral matter components at the high temperature associated with coal utilisation.

Table 2.7: Principal minerals identified in high temperature phases associated with coal utilisation ……………(compiled from various sources) (slightly modified after Ward and French, 2004)

Mineral	**Composition**
Quartz	SiO_2
Cristobalite	SiO_2
Tridymite	SiO_2
Metakaolin	$Al_2O_3.2SiO_2$
Mullite	$Al_6Si_2O_{13}$
Sanidine	$KAlSi_3O_8$
Albite	$NaAlSi_3O_8$
Anorthite	$CaAl_2Si_2O_8$
Corundum	Al_2O_3
Pyrrhotite	$Fe_{(1-x)}S$
Oldhamite	CaS
Anhydrite	$CaSO_4$
Aragonite	$CaCO_3$
Vaterite	$CaCO_3$
Portlandite	$Ca(OH)_2$
Lime	CaO
Periclase	MgO
Wuestite	FeO
Hematite	Fe_2O_3
Maghemite	Fe_2O_3
Magnetite	Fe_3O_4
Spinel	$MgAl_2O_4$
Magnesioferrite	$MgFe_2O_4$
Calcium Ferrite	$CaFe_2O_4$
Srebrodolskite	$Ca_2Fe_2O_5$
Brownmillerite	$Ca_4Al_2Fe_2O_{10}$

Table 2.7 (a): Principal minerals identified in high temperature phases associated with coal utilisation ……………… (compiled from various sources) (slightly modified after Ward and French, 2004)

Mineral	**Composition**
Wollastonite	$CaSiO_3$
Gehlenite	$Ca_2Al_2SiO_7$
Merwinite	$Ca_3Mg(SiO_4)_2$
Melilite	$Ca_4Al_{12}MgSi_3O_{14}$
Whitlockite	$Ca_3(PO_4)_2$

Table 2.8: Decomposition and melting temperatures of selected coal minerals and combustion ash products (Goblirsch et al., 1984)

Mineral	**Composition**	**Decomposition and Melting points (°C)**
Kaolinite	$Al_2Si_2O_5(OH)_4$	800-1000^{d}, 1810
Illite	$K_{1.5}Al_4(Si_{6.5}Al_{1.5})O_{20}(OH)_4$	400-1167^{d}, 1200-1350
Pyrite	FeS_2	800^{d}, 1171
Marcasite	FeS_2	800^{d}
Apatite	$Ca_5F(PO_4)_3$	>1230
Aragonite	$CaCO_3$	875^{d}
Calcite	$CaCO_3$	925^{d}
Dolomite	$CaMg(CO_3)_2$	775^{d}
Ankerite	$(Fe, Ca, Mg)CO_3$	725^{d}
Siderite	$FeCO_3$	525^{d}
Rutile	TiO_2	1827
Quartz	SiO_2	1710
Anhydrite	$CaSO_4$	1450
Szomolnokite	$FeSO_4.H_2O$	480^{d}
Thenardite	Na_2SO_4	885
Arcanite	K_2SO_4	1069

Table 2.8 (continued): Decomposition and melting temperatures of selected coal minerals and combustion ash products (Goblirsch et al., 1984)

Mineral	**Composition**	**Decomposition and Melting points (°C)**
Glauberite	$Na_2Ca(SO_4)_2$	900
Vanthoffite	$Na_6Mg(SO_4)_4$	800
Keiserite	$MgSO_4.H_2O$	1120^d
Pyrrhotite	$Fe_{(1-x)}S$	1025
Lime	CaO	2570
Wuestite	FeO	1369
Hematite	Fe_2O_3	1567
Magnetite	Fe_3O_4	1592
Cristobalite	SiO_2	1740
Corundum	Al_2O_3	2052
Mullite	$Al_6Si_2O_{13}$	1850
Sanidine	$KAlSi_3O_8$	1512
Leucite	$KAlSi_2O_6$	1650
Albite (plagioclase)	$NaAlSi_3O_8$	1100
Nepheline	$NaAlSiO_4$	768-1250
Nosean	$Na_2Si_2O_5$	874
Nosean	Na_2SiO_3	1088
Nosean	Na_4SiO_4	1018
Anorthite	$CaAl_2Si_2O_8$	1553
Wollastonite	$CaSiO_3$	1554
Gehlenite	$Ca_2Al_2SiO_7$	1590

Note: d – decomposes

Excluded minerals are unlikely to interact with each other in the bulk gas, due to the low probability of collision (Bryers, 1996). Attalla et al. (2004) indicated that during coal combustion or gasification, excluded minerals undergo fragmentation and transformation to residual ash. They also stated that a limited amount of vaporisation of the inorganic species occurs from mineral matter experiencing high temperatures. At high temperatures the excluded minerals can also undergo fusion and subsequently solidification, depending on the melting points of the individual minerals present in the coal.

Based on the results from the literature review on the excluded mineral mechanisms, various minerals (pyrite, and illite, and to a lesser extent calcite) can be expected to react with kaolinite at elevated temperatures to form silicate glass, resulting in slagging of ash during pulverised coal combustion. The literature review on the reaction mechanisms of the included minerals that interact differently from excluded minerals, is given in the following section.

2.8.2 Included mineral mechanisms

During coal combustion the included minerals generally reach peak temperatures in excess of the surrounding gas temperature and react quickly by coalescence, due to the close proximity to one another (Attalla et al., 2004). The inorganic species in the heated particles of the included minerals may undergo reduction and may volatilise partially.

Attalla et al. (2004) and van Alphen (2005) found that fly ash particles produced by different mineral matter transformations during pulverised coal combustion have different particle sizes. Residual ash was formed from the excluded minerals; the included minerals produced finer ash particles by coalescence of the included minerals during combustion. Attalla et al. (2004) also indicated that vaporisation of the inorganic species from sub-micron grains of the included minerals, and from metallic salts of carboxylic acids, together with the subsequent condensation of the inorganic volatiles during cooling, are responsible for the formation of sub-micron ash (in the range of 0.01 to 1 micron).

As stated earlier, according to Quann and Sarofim (1986) low rank coals contain significantly higher concentrations of the alkaline earth metals that are atomically dispersed, present as cations on the carboxylic and phenolic groups. Neville et al. (1981) stated that almost all of the organically-bound cations present in low-rank coals vaporise at 2627°C as sub-micron fumes totaling 1.9 to 9.6 wt% of the total mass of ash produced during coal combustion. The sub-micron ash particles contain MgO, Na_2O and CaO. In bituminous coals, metals occur in discrete minerals which decompose during char oxidation to form refractory metal oxides such as SiO_2, FeO, CaO and MgO. Srinivasachar et al. (1990a, b) stated that if included silica is fine and well dispersed within the coal matrix, it can be reduced to sub-oxide (SiO) and volatilises during combustion.

Srinivasachar et al. (1990a) found that the included pyrite particles react with clays (aluminium silicates) at an elevated temperature of about 1227°C to form iron-potassium aluminosilicate melt during coal combustion, whereas the excluded pyrite particles fragment and oxidise to form smaller particles of either magnetite or hematite

The model that was developed by van Alphen (2005) predicts that fine included kaolinite present in the carbon fraction is released during combustion to form fine excluded kaolinite fly ash particles. Included kaolinite can coalesce with calcite, dolomite and /or pyrite to form kaolinite/calcite, kaolinite/dolomite and kaolinite/pyrite ash particles respectively. A small proportion of the included kaolinite can coalesce with quartz to form quartz60kaolinite40 (60% heated quartz reacted with 40% high temperature transformation product of kaolinite) and quarz80kaolinite20 (80% heated quartz particles reacted with 20% high temperature transformation product particles of kaolinite) ash phase particles. The author also concluded that the majority of kaolinite is released on combustion; a small proportion of the included kaolinite coalesces with pyrite, calcite and dolomite and to a lesser extent with quartz.

2.9 Sintering studies of coal ash

The sintering of solid material normally occurs when loose or compacted powders of the solid particles are subjected to heat treatment at elevated temperatures. The solid particles with substantially low melting points start to partially melt. In the solid-state sintering process, the solid particles contact each other and subsequently form a new solid material with different shape and size. A reduction of the net surface energies of the solid-vapour and solid-solid interfaces is responsible for the sintering process during heating. The heated solids may shrink, due to the rearrangement of particles, resulting in a change of pore shape, grain size and shape (Kingery et al., 1976).

According to Al-Otoom et al. (2000) the inevitable sintering of ash (which is associated with the coal combustion process) is responsible for different operational problems such as: bed agglomeration, ash deposition on gas circuits, heat exchanger tubes as well as ash build-up and bridging on hot gas filtration systems. Raask (1985) found that the viscous flow mechanism dominates during the sintering of coal ash at elevated temperatures. A model for the viscous flow mechanism was developed by Frenkel (1945), equating the change in the surface energy with the energy dissipated by the flow of material.

In his studies, the author suggested that crystalline material can behave like an amorphous material under the influence of surface tension. The equation of the viscous flow mechanism of coal ash sintering is given as follows:

$$1-(\epsilon / \epsilon_0) = 9\gamma/4\eta r_0 t \qquad (2.10)$$

(Frenkel, 1945)

Where η is the apparent viscosity, γ is the surface tension, and ϵ and ϵ_0 are the pore volume at time t = t and at time t = 0 respectively.

Zagar (1975) applied Frenkel's equation for determination of the change in the porosity with time. The results from the equation showed that the range of applicability of Frenkel's equation is limited to a small time period in the initial stages of sintering. In an attempt to enhance the accuracy of the model of the viscous flow mechanism, at a later stage it was modified by Lemaitre et al. (1976).

The modification of the Frenkel's equation was based on the hypothesis that the viscosity of the material changes linearly with time at a constant temperature during sintering by the following equation:

$$\eta = \eta_0 (1+\alpha t) \qquad (2.11)$$

(Lemaitre et al., 1976)

Where η_0 is the initial viscosity

α is a rate constant for the change of viscosity with time. The results from the modified Frenkel's equation indicated that the material lost its excess surface energy by dissipating this energy into the deformation of this material, subsequently becoming less amorphous in behaviour during sintering. They also found that viscosity increases with time. Al-Otoom et al. (2000) noted that a new technique for the measurement of the sintering kinetics of coal ash was developed. The technique involves the use of the pressure-drop of a gas across the ash pellet, providing more information about changes that occur within the pellet during sintering. The measurement of pressure-drop of the airflow through the pellet can also be used to determine the sintering temperature of the ash pellet, as well as the rate of change of its porosity with time.

A number of researchers used the technique that involves slowly heating an ash pellet and subsequently measuring the electrical resistance across the pellet, to determine the sintering temperature of the coal ash (Raask, 1985; Conn, 1984; Cumming et al., 1986; Tangsathitkulchai, 1986). It was found that the electrical sinter point of ash, which is referred to as the sintering temperature of coal ash, was always below the initial deformation temperature of the ash as determined in the A.S.T.M. ash fusion temperature test (Cumming et al., 1986).

Jung (1996) heated samples of low-rank coal ash at elevated temperatures to gain a better understanding of the ash sintering characteristics. In his studies, several factors including ash composition, ash particle size distribution, sintering temperature and reducing and oxidising conditions (that are believed to contribute significantly to sintering) were evaluated. The results (employing the electrical resistance method) indicated that the sinter point of coal ash particles substantially decreased as the particle size distribution of coal ash was decreased. The author also found that the strength of the sintered coal ash significantly increased when increasing the sintering temperature.

Crushing strength measurements were used by Barnhart and William (1956), Gibb (1981), Conn (1984) and Tangsathitkulchai (1986) to determine the sintering temperature of the coal ash. The strength measurements for the coal ash were favourably compared to a known slagging factor of the coal ash. In contrast, the strength values for the coal ash were not correlated with the measured electrical sinter point.

Nowok (1996) noted that densification occurred when a large fraction of the sample pores were completely filled with liquid formed during a liquid-phase sintering process. In this sintering phase, the majority of solid particles melted to form a liquid.

The author of this thesis proposed that sintering reactions between the included fluxing elements-bearing minerals (calcite, pyrite, ankerite and dolomite), as well as the organically-bound inorganic elements and kaolinite in coal may take place to form high temperature aluminium silicate minerals under reducing and oxidising conditions during the gasification of coal.

It was also suggested by the author of this thesis that fluxing elements-bearing minerals (calcite, dolomite, ankerite and pyrite) that are associated with kaolinite in the coarse coal particles, could initiate the sintering and slagging processes at elevated temperatures and pressures during coal gasification. The proposed mechanisms are as follows:

Organic calcium + Organic sulphur → Calcium sulphate (Bassanite) T= >120°C
Bassanite ($CaSO_4.1/2H_2O$) + Kaolinite ($Al_2Si_2O_5(OH)_4$) → CaO.metakaolinite + SO_2
T= > 400°C
Pyrite + kaolinite → Pyrite(kaolinite) T = > 700°C
Pyrite +calcite + kaolinite → (Pyrite, Calcite)Kaolinite T = > 900°C
Dolomite + kaolinite → Dolomite (kaolinite) T = > 1000°C
Calcite + kaolinite → Calcite (kaolinite) T = > 1100°C.

The (pyrite) kaolinite, (pyrite, calcite) kaolinite, (dolomite) kaolinite and (calcite) kaolinite products of the included fluxing elements-bearing minerals and kaolinite formed in the above proposed reactions denote Fe-aluminium silicate, Fe-Ca-aluminium silicate, Ca-Mg-aluminium silicate and Ca-aluminium silicate glasses respectively.

As stated earlier in the present study, the effects of these minerals and elements on the sintering of coal ash during gasification were determined using the various analytical techniques (XRD, XRF, QEMSCAN, SEM-EDS, CCSEM and EMP).

2.10 Formation of glass phases in coal ash

During pulverised coal combustion, mineral matter (silicate minerals, carbonate minerals, sulphide minerals and organically-bound inorganic elements) may interact at elevated temperature to form ash particles. Due to the availability of silicates in the coal, the ash particles contain mainly amorphous or glass-like material. The factors that influence the glass formation from the liquid are the concentrations of dissolved inorganic elements, the rate of crystallisation of inorganic species and the cooling rate of the liquid (Kingery et al., 1976). According to Benson (1987), a number of researchers studied the physical and chemical properties of crystals from the molten solution in order to be able to manage the glass properties.

According to Kingery et al. (1976) and Ward (2004) the alkali silicates melt readily during the combustion of coal; alkali atoms provide the neutrality by occupying random positions throughout the structure of molten silicates. A sufficient quantity of either alkali or alkaline earth elements, added to the glass structure significantly affects the structure of silicate due to the increased oxygen to silicon ratio. The modification of a silicate structure, by the addition of alkali and alkaline earth elements can eventually lead to crystallisation of inorganic species from the solution to form new crystals (Kingery et al., 1976).

2.11 Crystallisation of the dissolved inorganic elements from the ash-derived melt

In liquid-phase sintering, which is the last stage of the sintering process, much of the solid mass may melt. Solid particles with relatively higher melting points (greater than the flame temperature of burning material) will remain undissolved in the melt. These particles may undergo rearrangement, if they have sufficient mobility for effective densification through the sintering process. On cooling the melt, the dissolved species may start to precipitate preferentially or crystallise to form artificial minerals.

According to Kalmanovitch (1983) the phase diagram CaO-FeO-Al_2O_3-SiO_2 can be used to predict the crystallisation path of coal ash melts during the liquid-phase sintering process. In his method, the ash composition was normalised to the four components CaO-FeO-Al_2O_3-SiO_2. The liquidus temperature was estimated and the composition of the residual liquid phase calculated by following the crystallisation path.

Suzuki et al. (1997) used limestone and sewage sludge incineration ash as feedstock for the production of glass-ceramic. In his laboratory experiments, the mixture of limestone and sewage sludge incineration ash (that consisted of high proportions of silica and alumina and trace amounts of hematite, sulphur and carbon) were heated to 1450°C to form a melt. The glass-like material formed by cooling of this melt was reheated at different temperatures (in the range of 800-1100°C) for various times ranging from 1h to 2h. The authors found that carbon readily reacted with sulphur trioxide produced during heating to form elemental sulphur, which interacted with ferric oxide at 800°C to form a colloidal ferrous sulphide.
Their studies revealed that ferrous sulphide behaved as a nucleant during crystallisation of anorthite from the molten solution.

In this present study, ferrous sulphide from the transformation of coal pyrite, as well as from the interaction of organic sulphur and iron-bearing inorganic species during gasification, may act as a nucleant during the crystallisation of anorthite, from the liquid derived from possible high temperature reaction between fluxing elements-bearing minerals (calcite, dolomite, ankerite and pyrite) and aluminium silicate minerals.

2.12 FactSage modeling

In this study, the thermodynamic package FactSage 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. This model runs on a personal computer (PC) operating system under Microsoft Windows® and consists of a series of information, database, calculation and manipulation modules that enables one to access and manipulate pure substances and solution databases. Additional information is available at www.FactSage.com.

FactSage not only enables calculation and manipulation of phase diagrams, but has been established mainly in the field of complex chemical equilibrium and process simulation. For example, with FactSage it is possible to access both Fact (slag, matte, salt, ceramic and aqueous) and alloy databases, import and export streams and mixtures and also import Chem-Sage data files. Another advantage of FactSage is that it can take carbon-mineral reactions into account and the gas composition and atmosphere can also be varied. The FactSage solution database contains critically evaluated thermodynamic data for SiO_2-CaO-Al_2O_3-Cu_2O-FeO-MgO-MnO-Na_2O-K_2O-TiO_2-Ti_2O_3-Fe_2O_3-ZrO_2-CrO-Cr_2O_3-NiO-B_2O_3-PbO-ZnO (Bale, et al., 2002). In addition, Jak et al. (1998), (2000) and (2003) found in their studies that the FactSage can be used to predict liquidus temperatures of coal ash slag. They also stated that the addition of CaO and FeO as fluxing agents to the coal mineral matter, as well as the aluminium to silicon ratios in the coal, has a significant impact on liquidus temperature of the slag during coal combustion. The change in liquidus temperature of coal ash slag can result in the formation of anorthite and mullite, depending on concentrations of CaO and FeO added to the coal during coal-conversion processes. The most-used module for this study was Equilib, where the Gibbs energy minimisation component of FactSage was utilised. It calculated the concentrations of chemical species when specific elements or compounds reacted or partially reacted, in order to reach a state of chemical equilibrium.