

CHAPTER 8

RESULTS AND DISCUSSION - FACTSAGE MODEL

In the next section (8.1) the FactSage results for high-temperature equilibria of the inorganic material from the feed coal, float fraction, sink fraction as well as selected clinker and heated rock fragment particles are discussed.

8.1 FactSage Model

8.1.1 FactSage results for the feed coal

The expected equilibrium phases in the coal ash were predicted by using the "Equilibrium" module of FactSage (Bale et al., 2002), considering as possible phases: liquid slag, several solid-solution phases (including spinel, anorthite, monoxide, wollastonite, pyroxenes and olivine) and all pure compound solids between the inputs. In first calculations, to show broad trends, the following oxide composition was assumed: 56.0% SiO₂, 26.1% Al₂O₃, 9.1% CaO, 3.4% FeO, 3.0% MgO, 1.1% TiO₂, 0.9% K₂O and 0.4% Na₂O (note that it is effectively assumed that all the pyrite in the coal is oxidised to FeO in the lower regions of the gasifier). The composition is the average of the gasifier ash originating from the coal minerals and the rock fragments. By using this composition, it is effectively assumed that there is full interaction between the coal minerals and the rock fragments. In fact, there is only partial interaction, as was explored in further calculations.

Based on other models of the gasifier, the temperature at the ash grate is predicted to be 335°C, with the peak temperature in the combustion zone being some 1390°C, with the gas composition changing from an O₂-H₂O mixture at the ash discharge point to H₂O-CO₂ in the combustion zone. This does imply that much of the iron would be in the trivalent form at equilibrium. Since FeO is a strong fluxing agent for silica, oxidation to Fe³⁺ would affect the formation of liquid slag. However, in the calculations presented here, it was assumed that all the iron is present as FeO.

The presence of glass (supercooled molten silicate) indicates that the ash and clinker formed from phases which included a large amount of liquid slag. Hence, the equilibrium calculations were performed for the temperature range 1100-1400°C, where a substantial amount of liquid

slag was predicted. The results are given in Figure 8.1. As Figure 8.1 shows, the mineral matter of the coal is predicted to be largely molten at the peak temperature (1390°C), with anorthite the main solid phase upon cooling below 1300°C (the "anorthite" was modelled as the $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ - $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ solid solution, here containing 93-94% of $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). In comparison with this, CCSEM or XRD did not detect any appreciable levels of cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) or leucite (KAlSi_2O_6), but confirmed the occurrence of glass, anorthite, mullite and quartz. Comparing the CCSEM, EMP, SEM-EDS results (Figure 7.4, Figure 7.5, Figure 7.6, Figure 7.16,,Figure 7.14, Figure 7.15) to FactSage model (Figure 8.1), it is proposed that rising steam and oxygen quenched the molten slag, preventing the crystallisation of cordierite, effectively freezing the structure which had been present at temperatures estimated to be between 1220°C and 1390°C. This is confirmed by the occurrence of crushed ash fragments ranging from pure glass, with no evidence of any anorthite crystals, to fragments in which anorthite is the dominant phase (Figure 7.4). Note that the quartz in the coarse ash originated from coarse-grained sandstone rock fragments or included quartz in siltstone/mudstone rock fragments, not from crystallisation during cooling of the ash slag. Hence, the observation of quartz in the coarse ash is consistent with the proposal that the phases in the ash represent the structure as quenched from temperatures above 1220°C, where quartz and cordierite are not stable under equilibrium conditions.

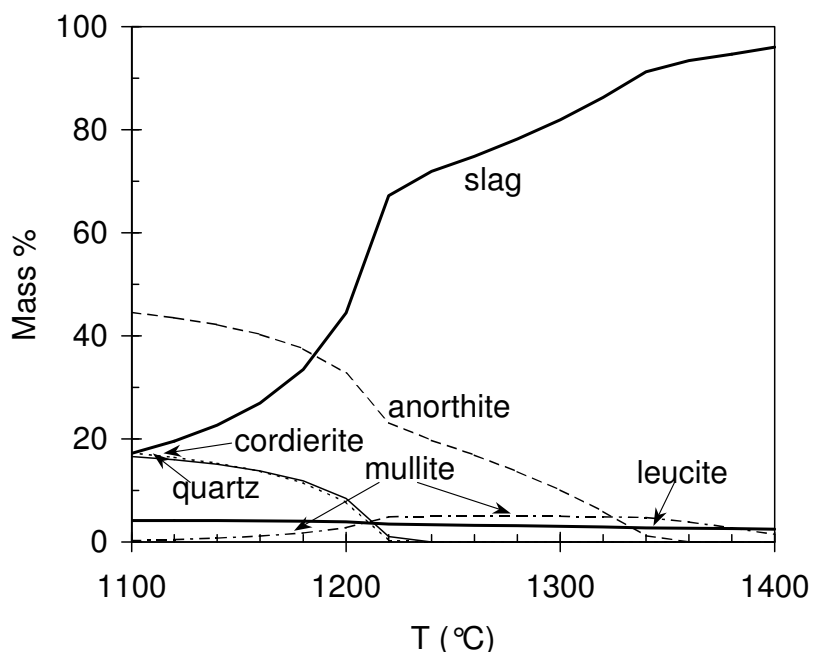


Figure 8.1: Predicted mass percentages of phases in ash (composition 56.0% SiO_2 , 26.1% Al_2O_3 , 9.1% CaO , 3.4% FeO , 3.0% MgO , 1.1% TiO_2 , 0.9% K_2O and 0.4% Na_2O).

8.1.2 Predicted equilibrium phases in the float and sink fractions of the feed coal

As was stated earlier in this study, the included minerals in the coal are responsible for the clinkering and slagging of mineral matter during coal gasification, hence the equilibrium phases in the float fraction (containing a significantly higher proportion of included minerals) and sink fraction were calculated by FactSage. The chemical compositions of ash samples of the float and sink fractions used in the calculation were given in Table 5.13.

The FactSage results (Figures 8.2 and 8.3) indicate broadly similar trends, with anorthite and mullite the dominant high-temperature solid phases, but with higher proportions of anorthite and a smaller proportion of slag in the float fraction in comparison with the sink fraction. Significant proportions of Fe deriving from the pyrite mineral and Si from silicate minerals in the rock fragment present in the sink fraction, contribute to the predicted fayalite and ilmenite. These minerals (and cordierite) are not generally observed in the gasifier ash, but significant proportions of glass are observed. This is in line with the suggestion that rapid cooling in the lower part of the gasifier prevents crystallisation beyond the formation of anorthite and mullite.

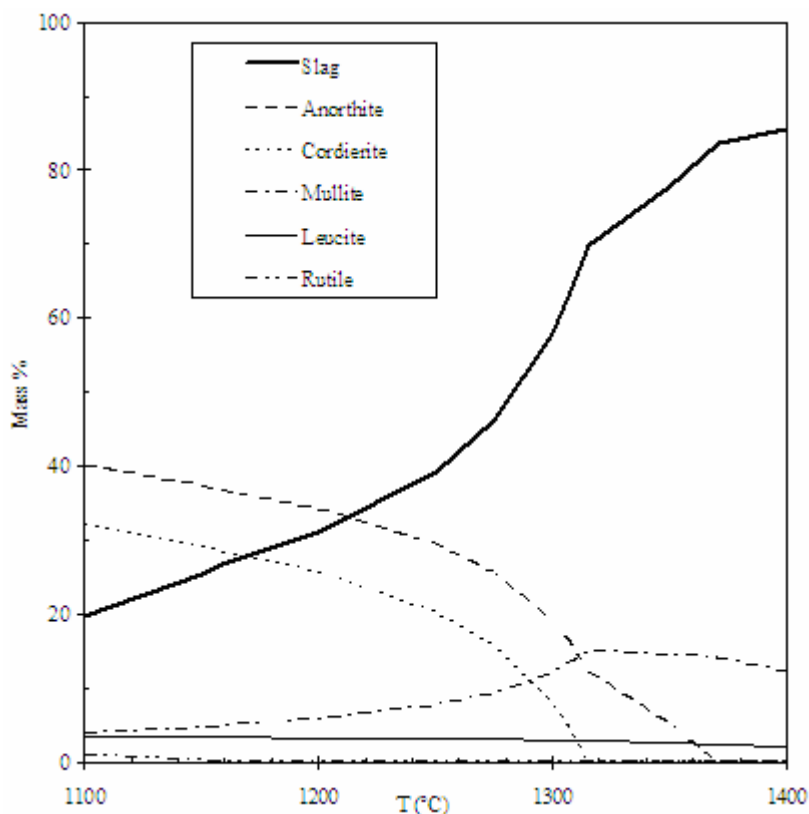


Figure 8.2: Predicted mass percentage in the ash of the float fraction ($<1.5\text{g/cm}^3$).

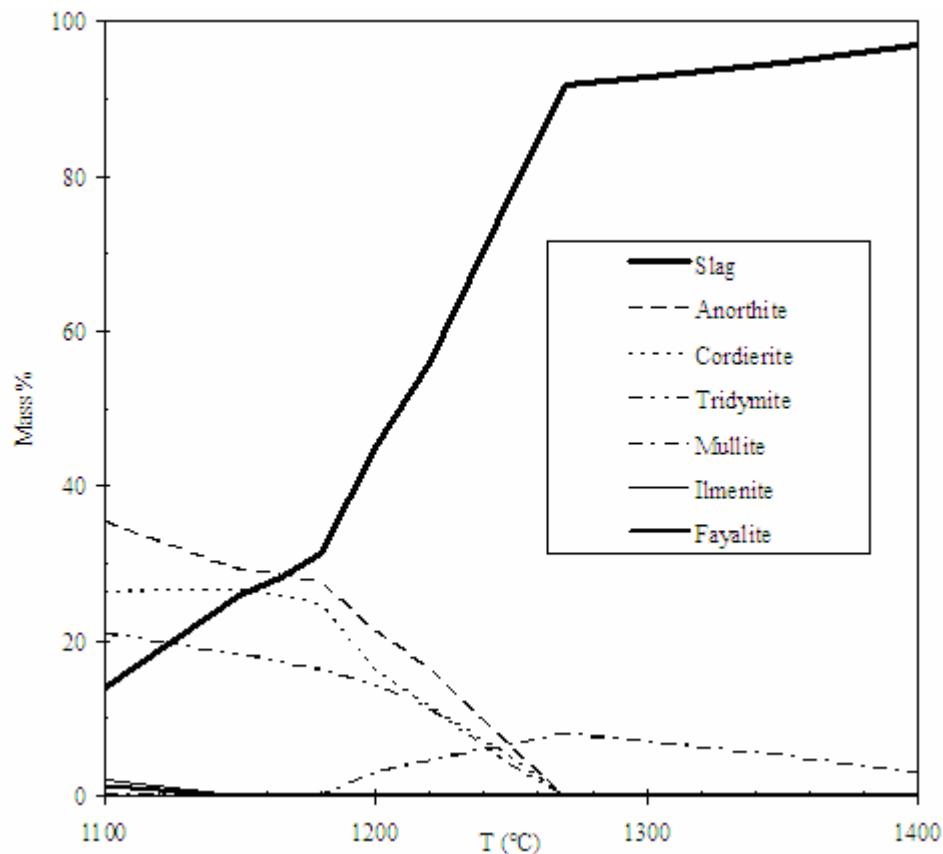


Figure 8.3: Predicted mass percentage in the ash of the sink fraction ($>1.8\text{g/cm}^3$).

8.1.3 Predicted equilibrium phases in the hand-picked dig-out samples

FactSage 5.5 was used to predict the expected equilibrium phases present in the selected fragments from the dig-out samples 6D and 7D. In the present study area analyses (Tables 8.1) of the selected areas of these dig-out samples (determined by SEM-EDS) were used for the input compositions. The predicted equilibrium phases formed at the different temperatures after using the chemical compositions of the selected areas in the heated rock fragments were compared to minerals in the selected areas of the coal ash that were detected by SEM-EDS (Figure 8.4). Note that the major differences in composition are the high CaO content in the coal ash, compared with low CaO (but higher Al_2O_3) in the rock fragment.

Table 8.1: Area analysis of the selected spot fragments of samples taken from the gasifier during the dig-out test (wt %)

Metal oxide	7.4D	6.7D
Na ₂ O	0.60	0.40
Al ₂ O ₃	32.83	38.40
SiO ₂	42.54	58.70
TiO ₂	2.40	0.67
CaO	13.21	0.42
MgO	0.80	0.00
FeO	3.50	0.32
K ₂ O	1.70	1.09
P ₂ O ₅	1.80	0.00
Total	100.00	100.00

Note: 7.4D = Image of selected region of the dig-out sample 7D shows reacted coal ash (Figure 8.4)
6.7D = Area analysis of rock fragment in Figure 8.4 (bottom right)

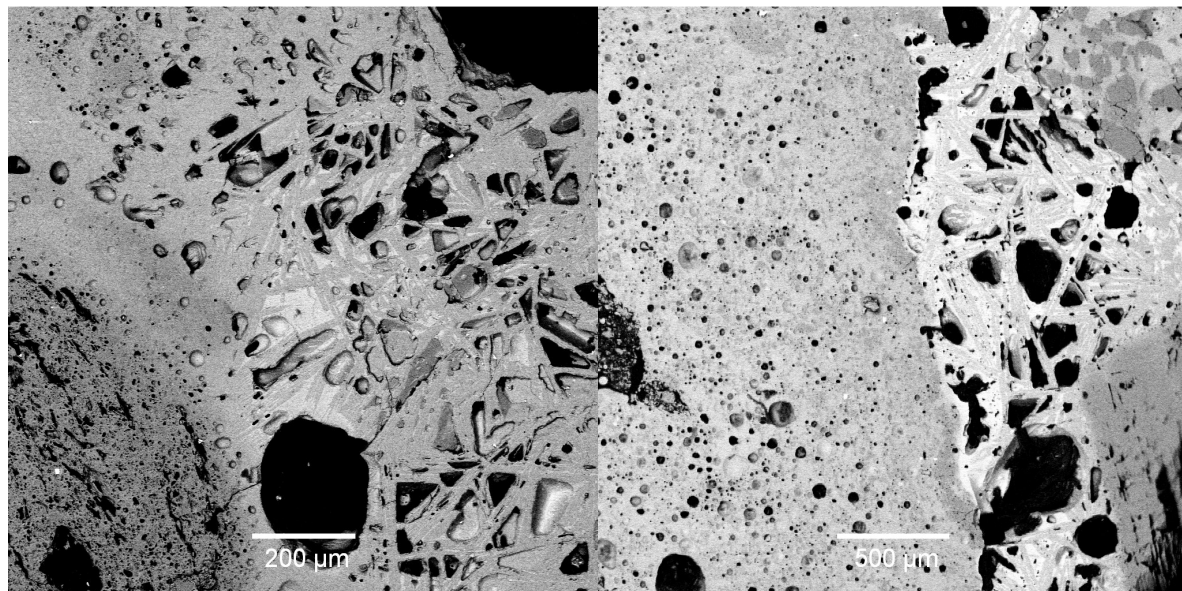


Figure 8.4: Left: BSE image of sample 7.4D showing reacted coal ash, containing anorthite crystals in glass; the region at the bottom left is a heated rock fragment (not included in the area analysis).

Right: Reaction interface in sample 6.7D, showing reacted ash and a rock fragment; the area analysis was taken from the rock fragment at bottom right.

The FactSage results show that mullite is the main solid phase in the heated rock fragment (Figure 8.5), persisting at 1400°C. In contrast, the main high-temperature solid in the coal ash (Figure 8.6) is anorthite. This difference in the identity of the primary solid phase, results from the differences in oxide composition: higher CaO levels favour anorthite formation, while higher Al₂O₃ levels favour mullite formation.

Substantial liquid formation requires high temperatures: for the two examples shown here, approximately 50% liquid is predicted to be presented at 1400°C. The extent of liquid formation depends on the oxide composition. As Figures 8.1 to 8.3 indicated, substantial liquid formation can occur at lower temperatures, for compositions with lower CaO/SiO₂ ratios.

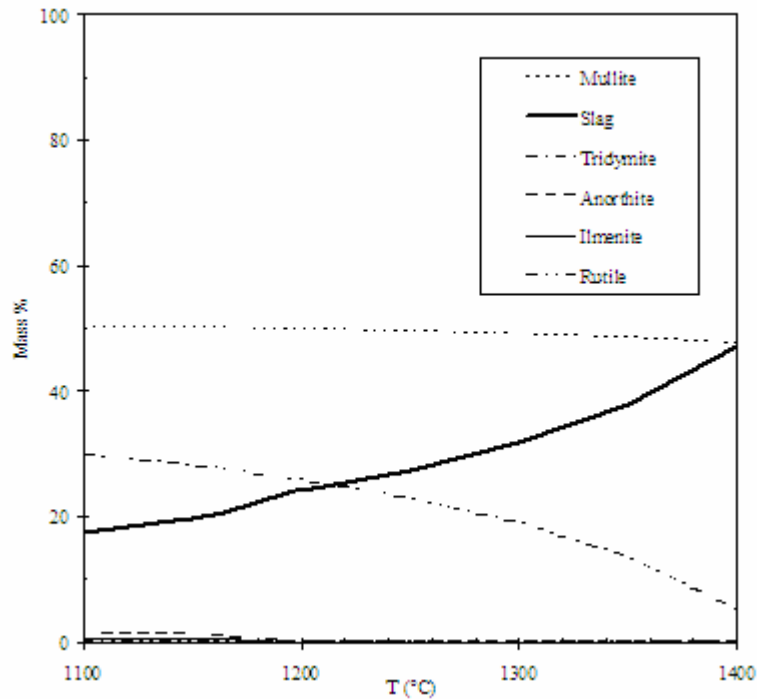


Figure 8.5: Predicted mass percentages of phases in the heated stone 6.7D.

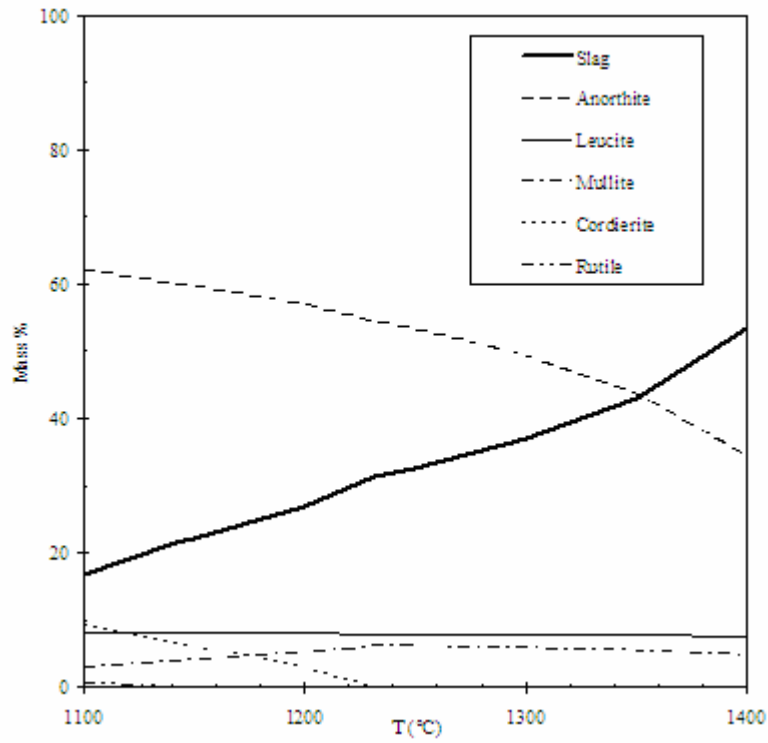


Figure 8.6: Predicted mass percentages of phases in the heated stone 7.4D.

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

The feed coal to gasification consists of coarse coal particles mixed with rock fragments (>6mm coal fraction) derived from the various sources. During coal gasification or combustion, minerals with fluxing elements (Mg, Ca and Fe²⁺) in the rock fragments and coal macerals interacted with kaolinite at elevated temperatures and pressures to form a melt. On cooling the melt with steam, the anorthite and mullite phases crystallised out from the melt and the heated rock fragments attached to the cooled melt to form clinkers in the gasifier. The clinker formation could significantly affect the permeability for syngas (mixture of carbon monoxide and hydrogen), which is produced by gasification. In some cases, the carbon particles that are supposed to be converted to syngas were encapsulated by the melt and reported to the ash particles during coal gasification.

The principal objective of this study was to test the hypothesis that the included fluxing elements-bearing minerals that are associated with the included kaolinite, lowered the ash fusion temperature of this clay at an elevated temperature of greater than 1000°C, to form a melt. The other objective of this study was to use conventional and advanced analytical techniques to qualify and quantify mineral associations that are responsible for the sintering and slagging of mineral matter in the coal during the gasification process. From this, advances in the management of clinker formation are envisaged, which include decreasing carbon loss in the ash fraction and understanding the influences on the production efficiency of a mixture of carbon monoxide and hydrogen.

This thesis describes the detailed characterisation of coals from mines in the Highveld coalfield, feed coal, gasification ash particles (heated rock fragment and clinker particles), coal fractions from density separation, coal and corresponding ash samples from the selected gasifier, gas liquor and char samples from the pyrolysis experiments and, turn-out and dig-out samples from the different gasifiers, as well as coal and liquid samples from the chemical fractionation method. As stated earlier in this thesis, the different forms of mineral matter are responsible for many of the problems (e.g.

abrasion, stickiness, slagging, sintering, corrosion and pollution) associated with coal handling and use. The conclusions of results for coal and ash samples from the different experiments are discussed in this section.

Chemical analyses of coals from six different Highveld coal mines and feed coal to the coal conversion process

The primary constituents in the ashes of coals from the six different Highveld coal mines including the feed coal were SiO_2 , Al_2O_3 , CaO , Fe_2O_3 , MgO , SO_3 and TiO_2 . Minor proportions (<1.0%) of K_2O , Na_2O , P_2O_5 , SrO , BaO and Mn_3O_4 were also present in both cases.

Mineralogical analyses of LTA of coals from the different mines and feed coal

Low-temperature oxygen-plasma ashing indicated proportions of mineral matter in the coals ranging from 25 to 45%. These are higher than the proportions of ash indicated by conventional proximate analysis (22-30%) reflecting the breakdown of the different mineral structures at the higher temperatures used in the proximate analysis process. XRD analysis of the low temperature ash indicates that kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and to a lesser extent quartz (SiO_2), dolomite ($\text{CaMg}(\text{CO}_3)_2$), illite and/or mica are the major minerals present. Minor proportions of fluxing elements-bearing minerals such as calcite (CaCO_3), pyrite (FeS_2) and siderite (FeCO_3) were also found in some LTA samples.

The XRD technique also detected small amounts of the goyazite group (aluminophosphate) minerals in the LTA samples, along with small proportions of anatase (TiO_2) and bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$). More detailed XRD analysis of the clay fraction of the LTA samples, using ethylene glycol and heat treatment further identified the nature of the expandable clay minerals (smectite and interstratified illite/smectite) present in the coal samples.

QEMSCAN analysis of turn-out sample 32T feed coal confirmed high proportions of kaolinite (15.81%), quartz (6.5%), dolomite (2.67%), calcite (2.18%), organic matter (68.76%) and low proportions of pyrite (1.63%), siderite (0.02%), rutile (0.94%), illite (0.42%), apatite (0.07%) and organic sulphur (0.94%). QEMSCAN and SEM-EDS

show that calcite grains are strongly associated with the carbon-rich fraction and are also associated with dolomite, kaolinite, quartz and apatite. Due to the presence of the fluxing elements-bearing minerals in the coal, this mineral association could contribute significantly to the sintering and slagging of mineral matter at elevated temperatures during coal gasification or combustion.

Petrographic analysis

Petrographic analysis indicates that coals are relatively low in vitrinite (20-25%) and rich in inertinite (70-75%), with minor proportions of liptinite also present. Sample from mine 5 had slightly higher proportions of vitrinite and less inertinite than the other coal samples. Mean maximum vitrinite (telocollinite) reflectance was 0.7 to 0.75%.

Elemental composition of individual coal macerals in the coals from the six different Highveld coal mines by electron microprobe

The vitrinite had significantly higher concentrations of nitrogen and organic sulphur than the inertinite macerals in the same coal samples. Minor proportions of organically-bound inorganic elements, including calcium, aluminium, silicon, magnesium and titanium, were identified in the macerals, especially (for Ti) in the vitrinite components.

The overall proportions of carbon, oxygen and nitrogen for the whole-coal samples, expressed to a dry, ash-free basis (Table 4.2) are intermediate between the carbon, oxygen and nitrogen contents for the vitrinite macerals on the one hand and the inertinite macerals on the other (Table 4.8), as determined by the electron microprobe study. The sulphur in the macerals is also significantly lower than the total sulphur in the coals, as it does not incorporate the additional sulphur present separately as pyrite particles.

Chemical fractionation method

Water washing had no particular effect on the mineral matter in the bituminous feed coal sample. Treatment with ammonium acetate (at 70°C) removed most of the carbonate minerals from the bituminous coals. The removal of carbonates by the acetate suggests that the common assumption of such solutions providing only an ion-exchange reaction, needs to be re-evaluated. However, hydrochloric acid treatment did remove almost all the Ca and Fe from the coal samples.

Close evaluation of the ash analysis data suggests that some of the Al in the coals was also removed by the selective leaching process. This may reflect a solution of organically-associated Al from the maceral components (cf. Matjie et al., 2007; Li et al., 2007).

The loss of Ca and other fluxing elements from the coals, induced by the different selective leaching processes, is associated with an increase in the different ash fusion temperatures in all cases.

With high pyrite coals, in some cases, the sulfides may oxidise during the extraction process, resulting in a decrease in the pH of the solution, causing the extraction of acid-soluble elements from the minerals. In this leaching step iron, vanadium, titanium and chromium were not dissolved in ammonium acetate solution, indicating that these coals used in the chemical fractionation experiments were not oxidised. These elements are present in Highveld coals in the form of minerals that are insoluble in ammonium acetate.

Characterisation of coal size fractions and density fractions and feed coal by analytical techniques

The -75+53mm size fraction contains high proportions of pyrite, calcite and dolomite and a low proportion of kaolinite, compared with the other coal fractions. Pyrite predominantly occurs as extraneous cleat fragments and to a lesser extent associated with medium to coarse-grained sandstone rock fragments. Calcite in this size fraction also occurs as extraneous cleat fragments and is to a lesser extent included in carbon-rich matrix.

The CCSEM results for the coal size fractions indicated that the proportion of extraneous particles decreases with a decrease in size, while the proportion of carbon-rich particles containing included minerals increase with a decrease in size.

In this context, “extraneous” particles are principally derived from extraneous rock fragments (“stone”), coarse (>1mm) pyrite and/or calcite rich cleats transecting the coal and possibly from mineral-rich layers in the coal.

The mineralogical and petrographic analyses of the density fractions of coal analysed in this study showed the following interesting trends:

- The increase in SiO_2 , K_2O and Fe_2O_3 proportions to the $>1.8\text{g/cm}^3$ density fraction is attributed to the increase in the proportion of quartz (Si), microcline (K) and pyrite (Fe), from arkosic sandstone fragments in the 1.8g/cm^3 density fraction.
- The $>1.8\text{g/cm}^3$ density fraction contains a higher proportion of calcite (CaCO_3) than dolomite ($\text{CaMg}(\text{CO}_3)_2$). This is attributed to calcite occurring as coarse extraneous cleat fragments, whereas dolomite tends to mainly occur as inclusions in carbon matrix or cleats transecting the carbon matrix.
- Kaolinite, which is a predominant mineral in the feed coal, concentrates in the $1.5\text{-}1.8\text{g/cm}^3$ density fraction and to a lesser extent in the $>1.8\text{g/cm}^3$ density fraction. A high proportion of kaolinite occurs as fine inclusions in carbon matrix and to a lesser extent as a component of mudstone and siltstone rock fragments.

Pyrolysis of coal samples from Highveld coal mines

The mineralogical and FactSage results of the coal and char samples show that some of the inorganic elements in the minerals transformed to form new minerals without significant volatilisation, reporting to pyrolysed coal. Further, the XRD analysis of the char samples indicates that some coal minerals are still contained in the char samples produced during the pyrolysis of coal at 600°C and 26bar under reducing conditions.

ICP-MS and IC analyses of all gas liquor samples indicate that Mg, Ca, Fe, Al, Si, Ti, Na, K, NH_4^+ , SO_4^{2-} , HCO_3^{2-} , Cl^- , F^- and CO_3^{2-} are present in these liquid samples produced during the pyrolysis experiments. Most of the elements were found to volatilise in relatively high amounts from the mine 5 and mine 6 coals (which had higher inertinite and lower vitrinite contents than the other four coals).

Except for some of the Na, all the metallic elements volatilised from the coals studied during the pyrolysis tests, appear to be associated with the carbon matrix in the coals.

Chemical and mineralogical analyses of gasification ash samples

The mineralogical signature of coarse feed coal and corresponding coarse ash/clinker samples offers an insight into clinker formation.

The first stage of clinker formation is the dehydration of kaolinite and muscovite/illite in the carbon-rich particles and rock fragments and devolatilisation of coarse pyrite (yielding SO_2 , S_2 or H_2S) and carbonate (yielding CO_2) cleat fragments. Dehydrated rock fragments, Fe-S-oxide and Ca-Mg-oxide particles are formed. As the ash-bed gravitates towards the hotter zone of the gasifier, the fluxing effect of Ca/Mg and Fe (derived from respectively included carbonates/organically bound cations and pyrite) lowers the melting points of included kaolinite and quartz, causing a CaO- and FeO-bearing aluminosilicate melts to form. The reducing conditions (maintaining iron in the divalent form) and higher particle temperatures of carbon-rich particles promote the formation the molten phase. The molten material encapsulates devolatilised rock fragments, coarse Fe-oxide of rich particles, coarse Ca-Mg-oxide particles and char fragments.

Sintering is initiated by the crystallisation of anorthite and mullite from the molten material upon cooling. Mullite crystallisation starts at approximately 1400°C and anorthite at 1360°C , depending on melt composition. As the combustion of the carbon progresses, the residual molten/rock fragment ash load gravitates to the rotating grate and is cooled/quenched by the rising steam and oxygen that are introduced at the base of the gasifier. With a decrease in temperature, crystallisation of anorthite and mullite

is halted and the remnant molten material solidifies to form the CaO/MgO- and FeO-bearing aluminosilicate glass. Predicted quenching temperatures range from 1220°C to as high as 1390°C. This is the final stage of clinker formation.

The bulk gasification ash, heated stone and clinker samples produced by the gasification process contain fragments of heat-altered rock materials, set in an often vesicular, partly crystalline glassy matrix. Quartz and possibly K-feldspar in the feed coal or admixed non-coal rocks may pass unaltered into the bulk gasification ash, along perhaps with titanium or iron-titanium oxides and aluminophosphate minerals. Although products of solid-state reactions may be preserved in some of the heat-altered fragments, anorthite that has crystallised from molten aluminosilicate material is contained within a glassy matrix in a manner analogous to the formation of igneous rocks.

The main objective of this study was to test all hypotheses mentioned in Chapter 2 of this thesis. The CCSEM results indicated that feed coal to gasification consists of three components:

- Carbon-rich coal particles with included mineral matter: The proportion of mineral matter can vary significantly. The major minerals are kaolinite, quartz, dolomite, calcite and pyrite;
- Extraneous rock fragments or “stone”: These rock fragments are derived from footwall, hanging wall and in-seam partings. The major rock fragments are mudstone, siltstone, carbonaceous shale and arkosic sandstone. These fragments have varying proportions of kaolinite, quartz, muscovite/illite and microcline;
- Extraneous calcite-rich and pyrite-rich cleat fragments: These are derived from coarse cleats transecting the coal seam, footwall and hanging wall.

The coarse ash sample is characterised by black porous glass, partially or totally enclosing rock fragments. The included rock fragments are significantly finer than the original rock fragments in the coal feedstock.

A significant proportion of the minerals in the rock fragments transform in-situ. Typically, kaolinite dehydrates and forms a devolatilised aluminosilicate. Mullite was

detected by the scanning electron microscope in the rock fragments. Quartz tends to crack. Muscovite/illite transforms into K-bearing glass with an Al/Si ratio similar to muscovite/illite or microcline.

Based on the CCSEM results for the turn-out samples it is clear that carbonates (dolomite or ankerite, siderite and calcite) associated with kaolinite lower the ash fusion temperature of kaolinite at elevated temperatures, forming a melt. Interestingly, a low proportion of iron-bearing phases derived from the reaction between kaolinite and pyrite was found in the turn-out samples. This implies that pyrite and its composition products contribute minimally to sintering or slagging of mineral matter at elevated temperatures during coal gasification.

FactSage results of coal and ash particles taken from the dig-out test

FactSage results predict that it is not possible for Fe, Na, Al and Si to be removed from the coal during pyrolysis as volatile inorganic compounds. Some of the halogens (chlorine and fluorine) are predicted to be removed from the coal as HCl and HF during pyrolysis.

The area SEM-EDS analysis of the selected spots of clinker and heated rock fragments taken from the dig-out samples were used in the FactSage model to predict equilibrium phases such as anorthite and mullite at temperature between 800°C and 1200°C. In most cases, these phases completely melted at 1400°C. The presence of the equilibrium anorthite and mullite phases are in agreement with the anorthite and mullite crystals produced from the cooled melt, which was formed by the interaction between high temperature transformation products of the included dolomite or ankerite and calcite, associated with the included kaolinite during coal gasification.

RECOMMENDATIONS

This study has highlighted a number of mineralogical features and described a few techniques, which could be used to further understand clinker formation in the rock fragments present in the feed coal to gasification. The following is recommended:

- The types of rock fragments (siltstones, sandstone, mudstone and carbonaceous shale) in the feed coal to gasification, as well as the heated rock fragment particles in the ash, should be examined, e.g. by a scanning electron microscope (such as a QEMSCAN) to determine the proportions of fluxing elements-bearing minerals (minerals containing calcite, dolomite, siderite and pyrite) as well as mineral associations that are responsible for the slagging of mineral matter during heat treatment.
- The impact of rock fragments on the crystallisation of the anorthite and mullite should be determined. The heated rock fragments may initiate the crystallisation of mullite and anorthite, depending on the proportions of calcium, silicon and aluminium in the melt. It is also proposed that some anorthite and mullite particles in the heated rock fragments may form by solid-state reaction. This needs to be confirmed.
- The proportion and mineralogical compositions of the “stone” in the coal feedstock and the “stone” in the corresponding gasifier coarse ash should be measured.
- High temperature XRD should be used to monitor the transformation of individual minerals in the stones under high pressures and oxidising and reducing conditions. It should also be used to analyse molten glass beads formed by heating coal particles under pressure. This data is extremely important for predicting transformation, solidus and liquidus temperatures.
- Combine all the analytical data and methods and develop a clinker prediction model. This model should be used to predict the “clinker” formation propensity of varying coal feedstocks and whether it is possible to manage clinker formation.

A detailed characterisation of South African coals using electron microprobe and QEMSCAN equipment should be done in order to determine the proportions and the chemical structures of the organically-associated inorganic elements present in the individual macerals in these coals. The organically-associated inorganic elements in the coal macerals could contribute significantly to the volatilisation of inorganic species at low temperature under the reducing and oxidising conditions.

The significant volatilisation of inorganic elements derived from the organically-associated inorganic elements is responsible for precipitation of the dissolved metal ions from the gas liquor in the pipe and heat exchangers during the treatment of this liquid.