



Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Behaviour of coal mineral matter in sintering and slagging of ash during the gasification process

Ratale H. Matjie^{a,b,*}, David French^c, Colin R. Ward^{c,d}, Petrus C. Pistorius^{b,*}, Zhongsheng Li^d

^a Sasol Technology (Pty) Ltd, P.O. Box 1, Sasolburg, Free State 1947, South Africa

^b Department of Materials Science and Metallurgical Engineering, University of Pretoria, South Africa

^c CSIRO Energy Technology, PMB 7, Menai, 2234, Australia

^d School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney, 2052, Australia

ARTICLE INFO

Article history:

Received 21 December 2010

Received in revised form 4 March 2011

Accepted 4 March 2011

Available online xxxx

Keywords:

Sintering

Slagging

Coal mineral matter

QEMSCAN

ABSTRACT

The mineral matter in typical feed coals used in South African gasification processes and the ash derived from gasifying such coals have been investigated using a variety of mineralogical, chemical and electron microscope techniques. The mineral matter in the feed coals consists mainly of kaolinite, with minor proportions of quartz, illite, dolomite, calcite and pyrite plus traces of rutile and phosphate minerals. The calcite and dolomite occur in veins within the vitrinite macerals, and are concentrated in the floats fraction after density separation. Some Ca and Ti also appear to be present as inorganic elements associated with the organic matter.

Electron microscope studies show that the gasification ash is typically made up of partly altered fragments of non-coal rock, bonded together by a slag-like material containing anorthite and mullite crystals and iron oxide particles, with interstitial vesicular glass of calcic to iron-rich composition. Ash formation and characteristics thus appear to be controlled by reactions at the particle scale, allowing the different types of particles within the feed coal to interact with each other in a manner controlled mainly by the modes of mineral occurrence. Integration of such techniques provides an improved basis for evaluating ash-forming processes, based on quantitative phase identification, bulk and particle chemistry, and the geometric forms in which the different phases occur.

© 2011 Published by Elsevier B.V.

1. Introduction

Mineral matter present in coal may occur as minerals, mineraloids and as organically-associated inorganic elements [1], which may interact in different ways during combustion [2–7], coking [8] and gasification processes [9–13]. A distinction is sometimes made between “included minerals” and “excluded minerals”, especially in pulverized fuel combustion. Included minerals are those minerals that occur in intimate association with the coal matrix at the grain size under consideration. In the coarse-crushed coals (>6 mm) used in certain commercial gasifiers [14–17], the excluded minerals may include discrete rock fragments, such as siltstone or sandstone, originating from contamination of the mined product by intra-seam bands, roof or floor strata, in addition to material particles or aggregates liberated from the organic fraction of the coal during the crushing process. The included minerals are typically represented by polymineralic aggregates of mineral components, intimately mixed in varying proportions with organic matter [18].

The mineral matter of the coal used in such commercial gasifiers is thus not a homogeneous material, but is made up of individual aggregates of minerals with or without organic matter. Each such aggregate or particle has its own composition and internal texture, and these provide different opportunities for interaction among the components during the gasification process. As well as the bulk chemistry of the feed coal ash as determined in traditional quality assessment, it is becoming increasingly important to understand the nature of the mineral matter in the coal, including both the percentages of the different mineral components and the occurrence of any inorganic elements in the macerals that make up the organic matter. Especially with the coarse particle size and the heterogeneity of the individual particles in gasification feedstock, it is also necessary to understand the geometric relations between the minerals and macerals in the coal and any associated non-coal contaminants, so that the interactions at a particle scale in the different parts of the gasifier can be better understood.

Although coals of higher or lower rank may be used for gasification in other countries, the coals typically used as feedstocks for commercial gasifiers in South Africa are low grade, medium-rank C (bituminous) coals (Table 1), derived from several different mines in the Highveld coalfield. The coarse-crushed coals (>6 mm), which

* Corresponding author at: Department of Materials Science and Metallurgical Engineering, University of Pretoria, South Africa.

E-mail address: henry.matjie@sasol.com (R.H. Matjie).

typically include admixed rock fragments, are blended to form a product suitable for use as a gasification feedstock. The feedstock is processed in the gasifiers at elevated temperatures (peak temperature > 1350 °C) and pressures (> 20 bar) to produce a raw gas, also referred to as syngas [14], which is further treated to generate a range of other products.

During gasification the mineral matter in the different coal and ash particles may fuse, melt and partially crystallise on cooling to form a number of new phases (e.g. mullite, anorthite, cristobalite, diopside and magnetite) in association with an amorphous or glassy component [16]. With fusion and sintering of the individual particles the ash that emerges from the gasifier is therefore extremely heterogeneous, ranging from fine material to large, irregularly shaped aggregates that vary from 4 mm to + 75 mm in diameter and from red and white to various shades of grey in colour. Especially when processing high ash content coal, the discarded ash is a significant co-product of gasification, and its nature, properties and processes of formation are an important focus for on-going research programs.

The main objective of the present study was to evaluate the modes of mineral matter occurrence in typical feed coal supplied to a gasifier unit, using a combination of chemical and mineralogical analyses, conventional SEM observation, and a recently-developed SEM-based image analysis technique (QEMSCAN). The QEMSCAN technique, initially developed as QEM*SEM [19,20], is an extension of more generic CCSEM (computer-controlled scanning electron microscope) techniques [21], incorporating a high-speed “species identification program” (SIP) to identify, map and perform a range of image analysis operations on the minerals and other phases in coals, coal ashes and other mineral products from point-by-point SEM-EDX data [22]. A secondary objective, based on integrating the results of these studies, was to evaluate the chemical, mineralogical and textural characteristics of the ash particles derived from the gasification process in relation to the different feed coal components.

2. Experimental techniques

2.1. Mineral matter in feed coal

A sample of the bulk feed coal supplied to a commercial gasifier was crushed to <1 mm, and a representative portion finely ground and subjected to low-temperature oxygen plasma ashing as described by Standards Australia [23]. The low-temperature ash (LTA) produced by this process was subjected to mineralogical analysis using powder X-ray diffractometry (XRD), with the Rietveld-based Siroquant data processing system [24] used to quantify the relative proportions of the different phases present. Another representative portion of the finely ground coal was ashed at 815 °C, and the resulting high-temperature ash (HTA) fused into a borosilicate disk [25] and analysed by X-ray fluorescence (XRF) spectrometry techniques.

Another sample of <1 mm feed coal was separated into float-sink fractions using mixtures of toluene and bromoform with densities of 1.5 and 1.8 g/cm³. The floats (<1.5 g/cm³) fraction was expected to contain a high proportion of included minerals and the sinks fraction

(>1.8 g/cm³) a high proportion of excluded minerals, based on separation at the 1 mm particle size. Samples of the floats (<1.5 g/cm³), middlings (1.5–1.8 g/cm³) and sinks (>1.8 g/cm³) materials were also subjected to low-temperature ashing and powder XRD, and to high-temperature ashing and XRF analysis, to provide further data on the modes of mineral occurrence within the <1 mm material.

Samples of crushed coal were mounted in epoxy resin and prepared as polished sections, as for conventional coal petrology studies. The coal in the polished sections was studied using a scanning electron microscope (SEM) with associated energy-dispersive X-ray (EDX) elemental analyzer, to evaluate more fully the modes of occurrence for the different mineral components.

Another sample of crushed feed coal was mounted in carnuba wax and prepared as a polished section for study using QEMSCAN, an integrated SEM and image analysis system described more fully for coal applications by French et al. [22]. The QEMSCAN system uses the back-scattered electron image to initially identify individual particles of coal or mineral matter in the polished section; the individual particles are then scanned on a grid and the X-ray signal used to assign each pixel to a particular mineral species (Fig. 1). Typically 100,000 individual X-ray analyses can be acquired and processed in one hour of measurement. The carnuba wax provides a better discrimination between the organic matter of the coal and the mounting medium than epoxy resin, thereby allowing the organic matter, as well as the mineral matter, to be included in the analysis process.

3. Results and discussion

3.1. Mineralogical and chemical characteristics

XRD analysis of the LTA from the feed coal (Table 2) shows the material to consist mainly of kaolinite, quartz and dolomite, with minor proportions of illite, calcite and pyrite and traces of apatite, goyazite (an aluminophosphate mineral) and rutile. As discussed more fully in the literature [1,26], the bassanite (CaSO₄·½H₂O) in the LTA is thought to be the product of interaction between organically-associated Ca and S in the coal during the low-temperature ashing process. Similar mineralogy has been found in a number of other coals from the Witbank and Highveld coalfields [27,28]. The presence of up to around 0.1% Ca, up to 0.6% Ti and possibly traces of Mg is also indicated in the macerals, especially the vitrinite macerals, of similar South African coals from light-element electron microprobe studies of the individual organic components [28], using techniques first described by Bustin et al. [29,30].

The chemical composition of the coal ash is given in Table 3. The inferred chemical composition of the feed coal ash, interpreted from the XRD data [31], is also shown in Table 3. As with other studies of South African coals using these techniques [27,28], the inferred composition is close to that obtained by actual ash analysis, confirming the validity of the quantitative XRD data.

Mineralogical analysis of the float sink fractions (Table 2) indicates that kaolinite and dolomite tend to be concentrated in the lighter (floats) fraction of the <1 mm coal, whereas quartz, illite, calcite and pyrite tend to be concentrated in the denser or sinks fraction. Bassanite is also more abundant in the LTA of the less-dense fractions, consistent with its formation from Ca and S in the organic matter.

Chemical analysis (Table 3) provides data consistent with these observations; Al₂O₃, CaO, MgO and SO₃ are more abundant in the ash of the floats fraction and SiO₂ and Fe₂O₃ are more abundant in the sinks fraction. Phosphorus appears to more abundant in the floats and middlings fractions, possibly due to the occurrence of phosphate minerals as fine-grained petrifications in the organic matter [32,33]. The greater abundance of TiO₂ in the floats fraction than in the sinks fraction is also consistent with the occurrence of significant proportions of Ti in the vitrinite of such coals, as indicated by electron microprobe studies [28].

Table 1
Proximate and ultimate analysis data for typical gasifier feed coals.

Proximate analysis and total sulphur (wt.% air-dried basis)					
Sample	Moisture	Ash	Volatile matter	Fixed carbon	Total sulphur
1	3.1	30.7	19.6	46.6	1.4
2	3.4	25.1	21.9	49.6	1.0
Ultimate analysis (wt.% dry, ash-free basis)					
Sample	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen
1	79.0	3.9	2.0	2.1	12.9
2	78.8	4.1	2.0	1.4	13.7

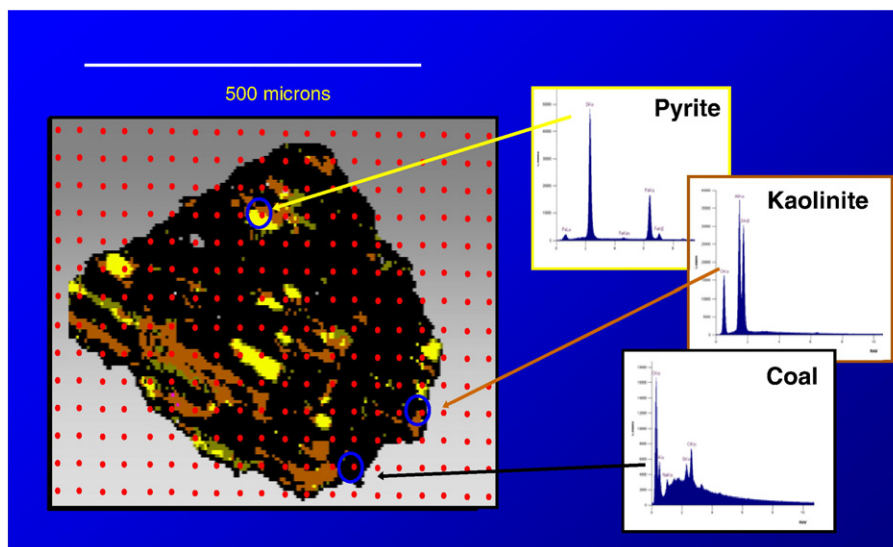


Fig. 1. Operating principles of QEMSCAN, showing EDX spectrum captured at selected points on a coal particle and assignment of mineral identification based on that spectrum [21].

3.2. Modes of mineral occurrence

Scanning electron microscope studies (Fig. 2) show three different modes of mineral occurrence within the individual coal particles. Fine-grained mineral particles, shown by EDX analysis to represent mixtures of quartz and kaolinite, with illite and/or pyrite in some cases, occur interbedded with the organic matter, especially but not only infilling the pores of the inertinite components. As discussed in a broader context by Ward [1], these may represent either detrital minerals washed or blown into the original peat swamp or authigenic precipitates formed in the pores of the peat bed at an early stage of coal formation. Individual crystals and aggregates, commonly of pyrite, are also seen dispersed within the macerals, especially in the vitrinite bands.

The third mode of mineral occurrence shown in Fig. 2 is the presence of carbonate-filled veins, typically confined to and cross-cutting the vitrinite bands in the coal samples. These probably represent infillings of micro-cleats within the coal, filling fractures that were opened up after burial and rank advance. Detailed study shows many of them to contain two separate mineral phases, with calcite (represented by the light colour in Fig. 2B and C) at the outer part of the veins, adjacent to the host organic matter, and dolomite in the central part of the individual cleat infills.

The occurrence of calcite and dolomite in these cleat infills, and the intimate association of the infills with the vitrinite components, serve to explain the higher concentrations of dolomite in the mineral matter

of the floats fraction of the <1 mm feed coal (Table 2). Together with the occurrence of Ca in the organic matter, these factors also serve to explain the higher concentrations of MgO and CaO in the ash of the floats fraction. The greater abundance of kaolinite and Al₂O₃ in the floats fraction (Tables 2 and 3) is also consistent with the occurrence of kaolinite in intimate association with the organic matter, especially in the pores of the maceral components.

As well as the coal itself, this specific gasifier feed sample typically contains discrete fragments of different non-coal rock types, including sandstone and siltstone materials. Mineralogical and chemical studies of such materials associated with Highveld and Witbank coals show a wide range of variation, depending on lithology. For example, Pinetown et al. [27] show quartz ranging from 30% to 80%, 5 to 25% feldspar (mainly the K-feldspar mineral microcline), 5 to 50% kaolinite and up to 15% illite and illite/smectite in such rocks, together with minor proportions of calcite, dolomite, siderite and pyrite.

A scanning electron micrograph of a polished section prepared from one such particle, made up of very fine grained sandstone, is shown in Fig. 3. This shows relatively uniformly sized particles of quartz, feldspar and rock fragments packed together and set in a matrix dominated by clay minerals. Such particles will also be affected by the elevated temperatures developed in the gasifier [16,17], and must be taken into account in assessing the links between feed coal and gasification ash characteristics.

Table 2
Mineralogy of LTA from coal samples using XRD plus Siroquant and using QEMSCAN.

	Feed coal [16]	Floats (<1.5 RD)	Middlings (1.5–1.8 RD)	Sinks (>1.8 RD)	Feed coal QEMSCAN
LTA %	34.6	11.4	30.4	74.5	49.1 ^a
Quartz	18.2	9.7	14.4	25.7	13.0
Kaolinite	53.3	60.2	60.2	49.4	56.9
Illite	5.6	5.3	5.1	9.1	2.8
Mica				4.2	
Dolomite	11.2	9.6	9.4	3.8	5.9
Calcite	2.7	0.7	0.4	2.0	10.8
Siderite				0.2	
Pyrite	2.8	1.4	0.9	2.4	4.7
Goyazite	1.9	1.4	3.4	1.8	
Apatite	1.0				
Rutile	1.1	0.0	0.6	0.3	5.6
Bassanite	2.2	11.8	5.6	1.5	0.1 ^b

Notes: a = weight percent visible minerals; b = measured as gypsum.

Table 3
Chemical analysis of 815 °C ashes by XRF spectrometry.

Ash %	Feed coal [16]	Floats (<1.5 RD)	Middlings (1.5–1.8 RD)	Sinks (>1.8 RD)	Feed coal (calculated from XRD data)
		9.4	24.6	64.0	
SiO ₂	54.3	43.5	50.3	55.0	54.1
Al ₂ O ₃	28.2	29.9	29.6	23.2	28.1
TiO ₂	1.3	2.4	1.5	1.2	1.3
Fe ₂ O ₃	2.2	2.2	2.0	5.5	4.9
MnO	nd	0.1	0.1	0.0	nd
CaO	7.8	8.5	7.8	7.4	6.2
MgO	2.9	3.3	2.9	1.6	2.1
Na ₂ O	nd	0.8	0.4	0.1	0.0
K ₂ O	0.6	0.7	0.8	1.0	0.6
P ₂ O ₅	1.3	1.4	0.9	0.3	1.3
SO ₃	1.4	7.2	2.9	6.1	1.4
Total	100.0	100.0	99.2	101.4	100.0

Note: nd = not determined.

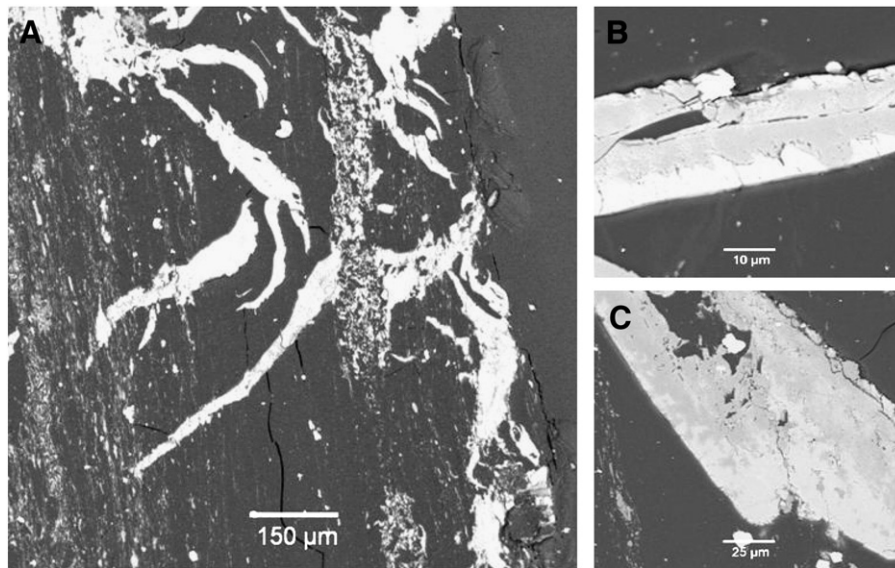


Fig. 2. Scanning electron micrographs of feed coal polished section in back-scattered electron (BSE) mode. A: general view showing cleats filled with carbonate minerals (white), confined to the vitrinite and cross-cutting the bedding of the organic matter (black), and fine particles of kaolinite, quartz and pyrite (spotted patterns) interbedded with the organic matter. B and C: detail of cross-cutting cleat infills, showing calcite (white colour) at the edges and dolomite (light grey) in the centre of the veins.

3.3. Information from QEMSCAN studies

A false-colour image showing the mineralogy and internal texture of the different particles in a crushed sample of the feed coal, prepared using the particle scan option in QEMSCAN, is shown in Fig. 4. The figure shows that, at the particle size studied, many of the quartz, kaolinite, calcite and pyrite particles occur as liberated mineral grains (“excluded minerals”). Some of these are monomineralic, but others are represented by polymineralic aggregates, within which some interaction between the components might be expected to occur during the gasification process. Other mineral occurrences, however, are associated in different ways with the organic matter (referred to, for convenience, as “coal”), sometimes as major and sometimes as minor constituents. Of note in the image is the occurrence of dolomite bonded to coal in discrete particles, consistent with partial liberation of the cleat-filling carbonate observed in the SEM/EDX analysis (Fig. 2).

QEMSCAN was also used to calculate the relative abundance of the different phases in the coal, with the relative volume of each phase combined with a relative density value for each component to give a weight percentage. The overall weight percentage of minerals

recognised by QEMSCAN in the feed coal sample, and also the weight percentage of each mineral as a fraction of that visible mineral matter, is given alongside the results of the XRD analyses in Table 2.

The total weight percentage of minerals estimated by QEMSCAN is slightly higher than that determined for the feed coal directly by low-temperature ashing. This may in part reflect incorporation of some organic matter in the mineral aggregates recognised by QEMSCAN, and in part inconsistencies in the two samples studied. The percentages of quartz, kaolinite and illite identified by the two techniques are similar; the minor differences may reflect sample inhomogeneities, and also possibly difficulties in separately identifying fine quartz particles intimately admixed with more abundant kaolinite.

Although the total percentages of calcite plus dolomite are similar, QEMSCAN has identified a greater proportion of calcite and a lesser proportion of dolomite than the XRD analysis. This may reflect a difficulty in differentiating calcite from dolomite in cleat infillings such as those shown in Fig. 2, where both minerals are present. Since the Ca:Mg ratio of a pixel occupied by a composite of calcite + dolomite would be lower than that of dolomite alone, more of the carbonate could have been assigned to calcite by the species

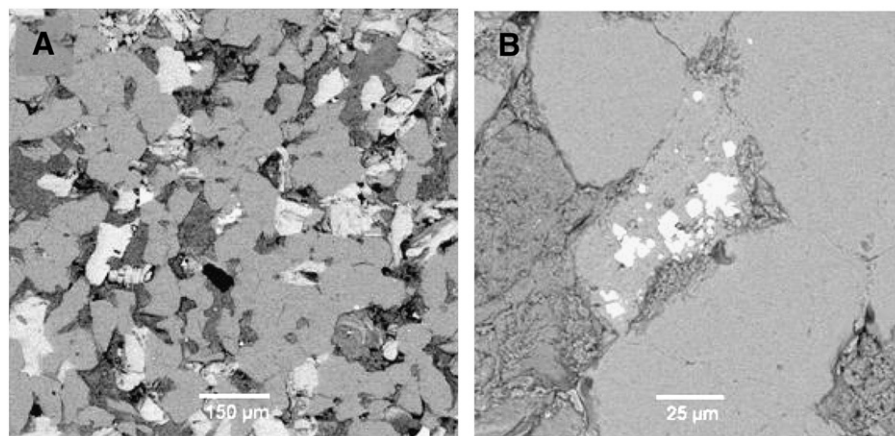


Fig. 3. Back-scattered electron images of very fine sandstone particle included in feed coal. A: General view showing quartz grains (mid-grey), kaolinite (dark grey), potassium feldspar (light grey) and pyrite grains (white). B: Close-up view showing textural relations of quartz grains (homogeneous grey), pyritic fragment (white spotted particle), feldspar particles and matrix.

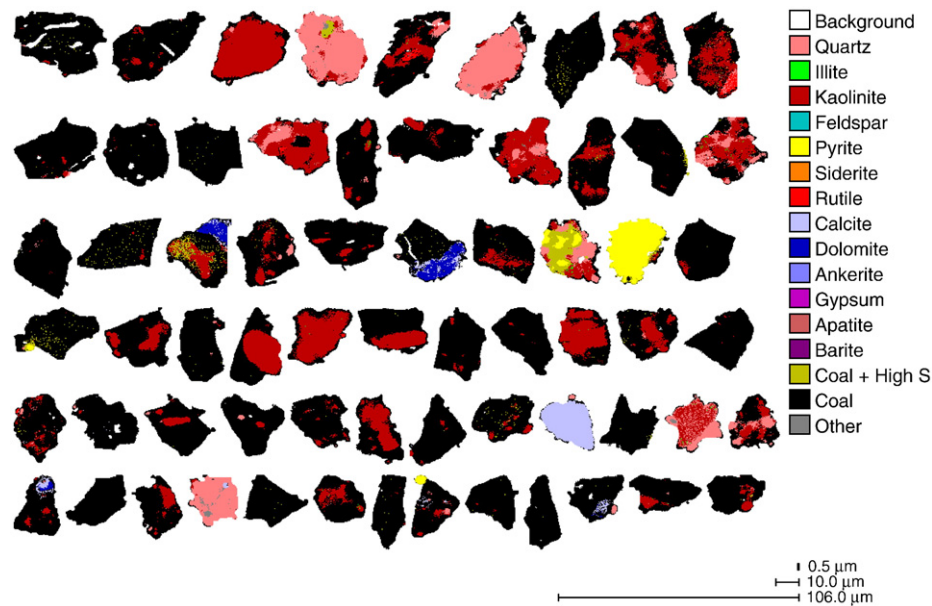


Fig. 4. Particle maps obtained using QEMSCAN, showing modes of mineral occurrence and degree of mineral liberation in finely crushed feed coal particles.

identification program used for the analysis concerned. Traces of siderite and gypsum are also identified by QEMSCAN. The proportion of gypsum, however, is very much less than the proportion of bassanite indicated in the LTA by X-ray diffraction, indicating that calcium sulphates are not present to any extent in the raw coal and thus confirming that the bassanite is an artefact of the ashing process.

The reason for the greater abundance of rutile (TiO_2) indicated by QEMSCAN is still under investigation. However, as indicated by Matjie et al. [28], electron microprobe analysis of the macerals suggests that measurable proportions (up to 0.6%) of Ti are present in the vitrinite of some Highveld coal samples. One possible explanation for the high rutile percentage indicated by QEMSCAN is that some Ti-rich vitrinite particles might have been assigned to “rutile”, rather than to “coal” under the relevant species identification program.

The mineral and coal-mineral associations determined in the QEMSCAN analysis of the feed coal are shown graphically in Fig. 5. Although coarser-crushed coal particles are used in the actual gasification process, the data obtained from the pulverized coal examined in this study can still be used to identify minerals and mineral associations that may be responsible for slagging and sintering of mineral matter during gasification. The “background” in Fig. 5 is the mounting medium used for sample preparation; the transition between background and other phases provides a measure of the degree of liberation, with a high percentage of background-phase transitions indicating a high degree of liberation at the sample particle size.

QEMSCAN analysis of the mineral associations in the pulverised coal particles of the gasifier feed coal (Fig. 5) shows the following:

- Pyrite has an association with high-sulphur coal (most likely vitrinite containing organically bound sulphur) and background, the latter indicating the presence of liberated pyrite grains. Less than 10% of the association is with low-sulphur coal particles.
- Dolomite shows an association with calcite, in agreement with the textural relationships shown in Fig. 2. However, the strongest association is with coal (>50%). The results also show that a small proportion of dolomite grains are associated with the background, indicating that around 3% of dolomite particles are liberated.
- Calcite has a strong association with coal (above 50%), which is supported by the relationships shown in Fig. 2). There is also an association with dolomite and, to a much lesser extent, with

kaolinite, quartz and apatite. A small proportion of the calcite also occurs as discrete grains.

- Kaolinite and quartz are mostly associated with coal. Quartz is also associated with kaolinite, suggesting that the quartz occurs as included grains in some kaolinite particles as shown in Fig. 4. Illite has a strong association with kaolinite and lesser associations with coal and quartz.
- Feldspar is strongly associated with the carbonates and in particular dolomite; there is a weaker association with coal.
- Apatite is strongly associated with calcite and to a lesser extent with coal.

3.4. Characteristics of gasifier ash

As described more fully in other studies [16,17], XRD analysis indicates that quartz, mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$),

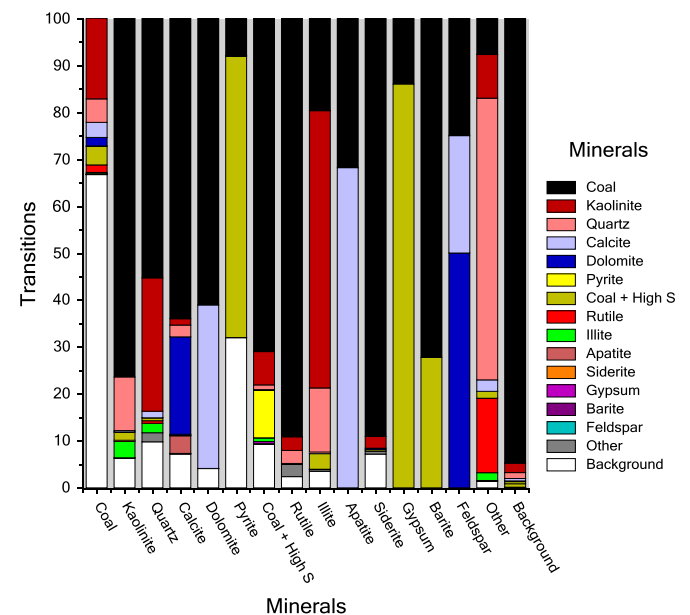


Fig. 5. Plot showing proportion of transitions between each mineral (including “coal” and “background”) and other phases in the fine-crushed feed coal sample.

cristobalite (SiO_2 , a high temperature transformation product of clays such as kaolinite and illite), diopside ($\text{CaMgSi}_2\text{O}_6$) and amorphous glass are present in the ashes derived from the Sasol® FBDB™ Gasification process. The diopside may have been derived from reaction between high temperature transformation products (CaO and MgO) of carbonates (calcite and dolomite) and amorphous silica from the clay minerals. The mullite and anorthite may represent either products of solid-state reaction or crystallisation from molten silicate material formed during the gasification process [11,16,34].

3.5. Electron microscope studies

Fig. 6 shows the general nature of the fused material within typical clinkers obtained from dig-out studies in a gasification plant. Elongate, relatively large crystals of anorthite and smaller more needle-like crystals of mullite typically form a mesh-like structure, with homogeneous or micro-crystalline material filling the interstices. Small to large particles of pyrrhotite and/or iron oxide, apparently derived from pyrite within the coal, also occur in the material. Gas cavities or vesicles, represented in Fig. 6 by black circular bodies, may also be seen in some cases between the crystalline components.

Individual rock (or “stone”) fragments in the feed coal may show only minimal alteration (Fig. 7). The most significant changes appear to be dehydroxylation of the clay minerals, particularly kaolinite. Some incipient melting may also occur, and may be slight permeation of molten material on the margins of some particles from which mullite and anorthite have crystallized on cooling.

Electron microprobe studies [16] show that some of the glass may be calcic in nature, suggesting formation by the interaction of altered clay minerals with the calcite and dolomite in the coal, and also possibly with Ca released from the organic matter. Other glass is more iron-rich, possibly formed by the interaction of clay residues and pyrite; there is little or no evidence for the existence of other significant iron-bearing phases in the feed coal. SEM-EDX studies (Figs. 6 and 7), however, indicate that pyrite particles are commonly transformed to pyrrhotite and hematite, and the mineral does not appear to readily participate in melt formation.

3.6. QEMSCAN analysis

QEMSCAN analysis was undertaken of a polished thin section of a representative portion of a sample of the coarse gasification ash. Two field scans were acquired, one over an area $25\text{ mm} \times 50\text{ mm}$, encompassing the complete thin section, and another over an area $20\text{ mm} \times 20\text{ mm}$, providing a more detailed analysis of a portion of the thin section (Fig. 8). As shown in Fig. 8, the ash is extremely heterogeneous, containing rock fragments set in a glassy matrix. The rock fragments consist of feldspathic sandstone, laminated siltstone, and mudstone, all of which have suffered only minimal alteration. As shown in Fig. 8 at least two different glass compositions can be recognised: one of a calcic nature from which anorthite has crystallised and another of a more iron-rich composition.

The results of the QEMSCAN analysis provide textural evidence of behaviour of the various rock types present in the gasifier coal feed

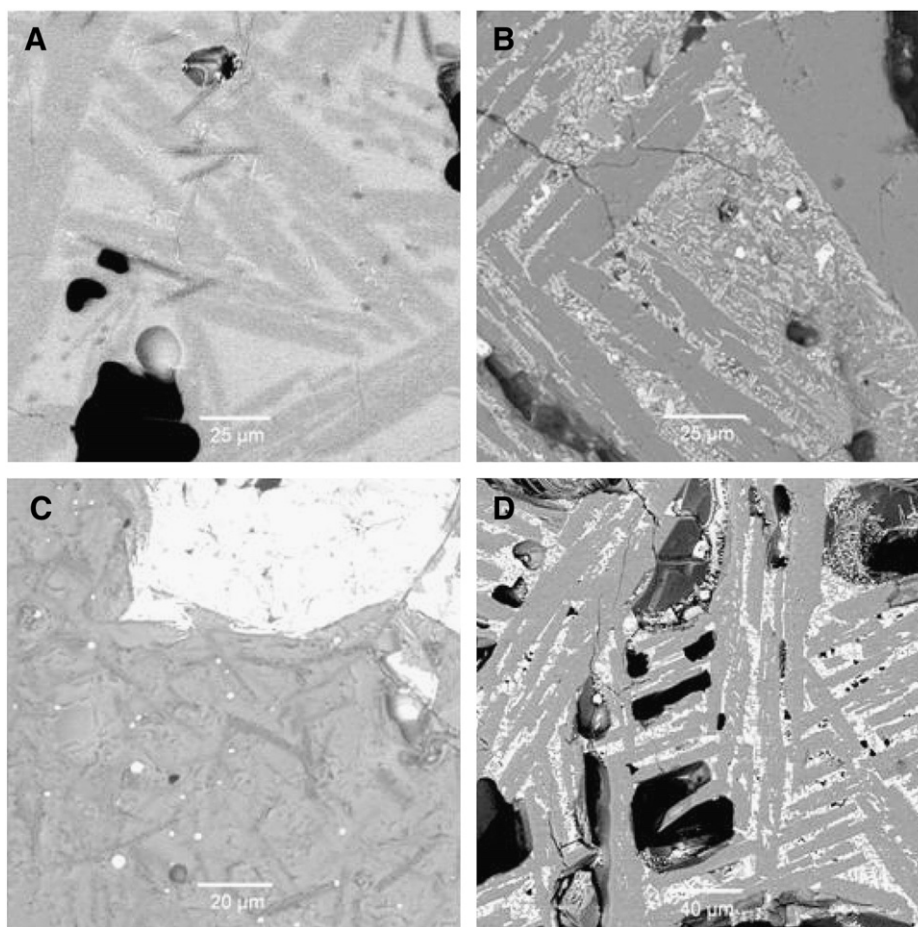


Fig. 6. Back-scattered electron images of clinkers from a commercial gasifier. A: Needles of anorthite and mullite (dark) in a homogeneous glassy matrix; B: Anorthite crystals (dark grey) in a finely crystalline matrix; C: Needle-like mullite crystals (dark grey) in glassy matrix, with white dots of iron oxide in matrix and large iron oxide particle at top; D: Anorthite crystals (mid grey) with interstitial glass and vesicles (black).

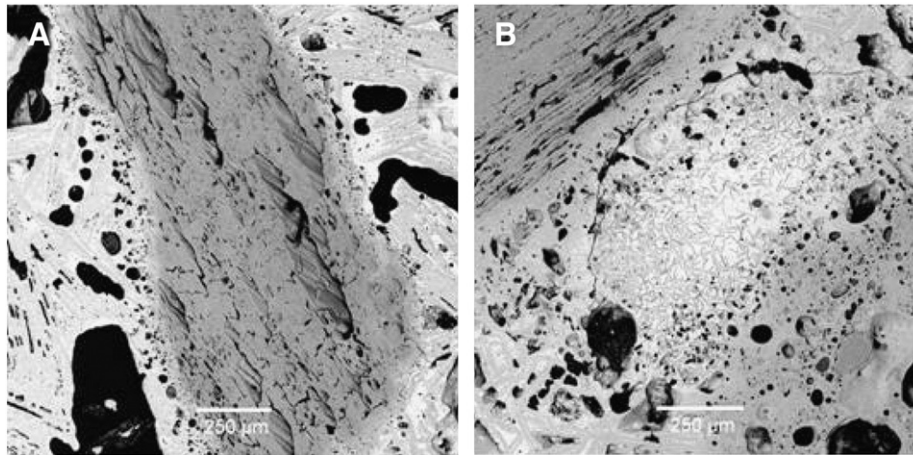


Fig. 7. Back-scattered electron images of heated stone particles. A: Devolatilised kaolinitic mudstone (centre) surrounded by vesicular slag with anorthite crystals; B: Heated carbonaceous shale (upper left) attached to anorthite and mullite crystals in the heated stone.

that cannot be identified from more conventional analyses. The field scan analyses show that the quartzo-feldspathic rock fragments are largely unreactive, and that the glass formation is most likely due to the presence of impure calcareous sediments having a low fusion temperature. Fusion resulted in the formation of a glass from which anorthite crystallised on cooling. It is also possible that the glass may have been derived from the mineral matter associated with the coal, particularly the carbonates and pyrite in association with the silicates; melting of the mixtures could then have formed calcium-rich and iron-rich glasses, respectively.

4. Conclusions

Integrated application of advanced mineralogical techniques such as quantitative XRD and automated electron beam image analysis is a powerful investigative tool for understanding the behaviour of coal mineral matter during gasification. This study has shown that the rock fragments are largely unreactive during gasification, apart from

decomposition of the clay minerals. However, the minerals and inorganic elements in the coal have undergone significant transformations, the nature of which depends not only on the mineralogy but also the mineral association.

Thus the calcic glass from which anorthite has crystallised is most likely the melt product of a calcite + dolomite + kaolinite + quartz assemblage and the iron-rich glass has formed in response to pyrite decomposition. Both of these have formed a matrix in different parts of the mass to bind the largely unreacted rock fragments together. The intimate association of some reactive minerals (e.g. dolomite) with the organic fraction also suggests that many of the mineralogical changes will not occur until later in the gasification process, when most of the coal has been gasified, and may thus take place at higher temperatures at which melting can occur. Studies of mineralogical transformations during gasification must therefore take into account the modes of occurrence of the different components and the associated opportunities for interaction, as well as the bulk chemistry and mineralogy of the coal and ash materials.

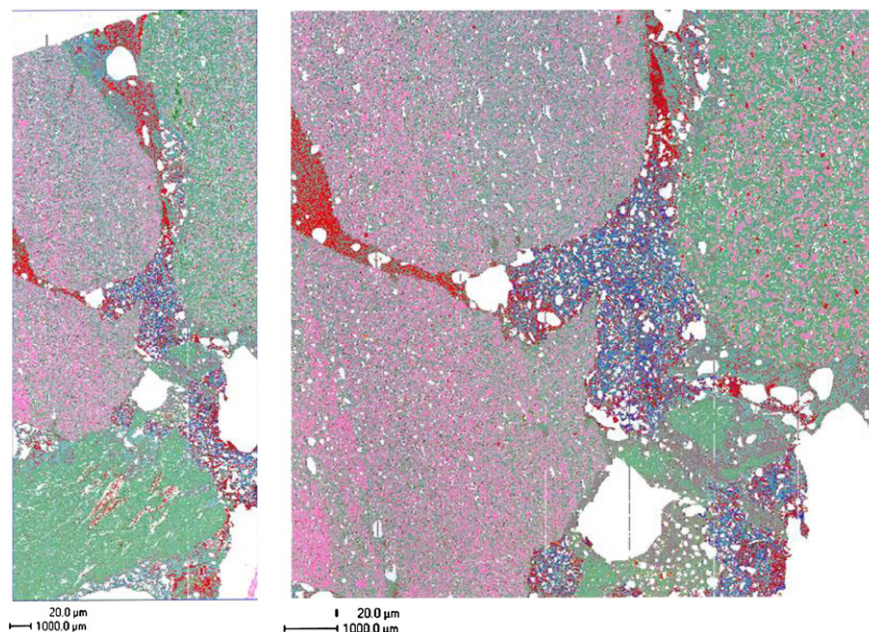


Fig. 8. QEMSCAN field scan of an ash sample, showing general view (left) and close-up view (right) with rock fragments (sandstone and siltstone) containing quartz (pink) and illitic clay (green) set in a matrix of two glass compositions, one iron-rich (red) and one of calcic composition (blue-green) containing anorthite crystals.

Acknowledgement

Mr. Al Cropp of Intellection in Australia is thanked for assistance with the different aspects of the analysis program.

References

- [1] C.R. Ward, Analysis and significance of mineral matter in coal seams, *International Journal of Coal Geology* 50 (2002) 135–168.
- [2] J.J. Helble, S. Srinivasachar, A.A. Boni, Factors influencing the transformation of minerals during pulverized coal combustion, *Progress in Energy and Combustion Science* 16 (1990) 267–279.
- [3] A.P. Reifenstein, H. Kahraman, C.D.A. Coin, N.J. Calos, G. Miller, P. Uwings, Behaviour of selected minerals in an improved ash fusion test: quartz, potassium feldspar, sodium feldspar, kaolinite, illite, calcite, dolomite, siderite, pyrite and apatite, *Fuel* 78 (1999) 1449–1461.
- [4] R.P. Gupta, T.F. Wall, L.A. Baxter (Eds.), *The Impact of Mineral Impurities in Solid Fuel Combustion*, Plenum Publishers, New York, 1999, 768 pp.
- [5] S.V. Vassilev, R. Menendez, D. Alvarez, M. Diaz-Somoano, M.R. Martinez-Tarazona, Phase-mineral and chemical composition of coal fly ashes as a basis for their multicomponent utilization. 1: Characterization of feed coals and fly ashes, *Fuel* 82 (2003) 1793–1811.
- [6] C.G. Vassilieva, S.V. Vassilev, Behavior of inorganic matter during heating of Bulgarian coals – 2: Subbituminous and bituminous coals, *Fuel Processing Technology* 87 (2006) 1095–1116.
- [7] I. Suarez-Ruiz, C.R. Ward, Basic factors controlling coal quality and technological behavior of coal, in: I. Suarez-Ruiz, J.C. Crelling (Eds.), *Applied Coal Petrology: Application of Petrology to Coal Utilization*, Academic Press, Amsterdam, 2008, pp. 19–59.
- [8] M. Grigore, R. Sakurovs, D. French, V. Sahajwalla, Mineral matter in coals and their reactions during coking, *International Journal of Coal Geology* 76 (2008) 301–308.
- [9] F.B. Waanders, A. Govender, Mineral associations in coal and their transformation during gasification, *Hyperfine Interactions* 166 (2005) 687–691.
- [10] K. Matsuoka, Y. Suzuki, K.E. Eylands, S.A. Benson, A. Tomita, CCSEM study of ash forming reactions during lignite gasification, *Fuel* 85 (2006) 2371–2376.
- [11] J.C. Van Dyk, S. Melzer, A. Sobiecki, Mineral matter transformation during Sasol-Lurgi fixed bed dry bottom gasification – utilization of HT-XRD and FactSage modelling, *Minerals Engineering* 19 (2006) 1126–1135.
- [12] N.J. Wagner, M. Coertzen, R.H. Matjie, J.C. van Dyk, Coal gasification, in: I. Suarez-Ruiz, J.C. Crelling (Eds.), *Applied Coal Petrology: Application of Petrology to Coal Utilization*, Academic Press, Amsterdam, 2008, pp. 119–144.
- [13] J.C. Van Dyk, S.A. Benson, M.L. Laumb, F.B. Waanders, Coal and ash characteristics to understand mineral transformations and slag formation, *Fuel* 88 (2009) 1057–1063.
- [14] J.C. Van Dyk, M.J. Keyser, M. Coertzen, Syngas production from South African coal sources using Sasol-Lurgi gasifiers, *International Journal of Coal Geology* 65 (2006) 243–253.
- [15] R.H. Matjie, C. van Alphen, P.C. Pistorius, Mineralogical characterisation of Secunda gasifier feedstock and coarse ash, *Minerals Engineering* 19 (2006) 256–261.
- [16] R.H. Matjie, Z. Li, C.R. Ward, D. French, Chemical composition of glass and crystalline phases in coarse gasification ash, *Fuel* 87 (2008) 857–869.
- [17] T.B. Hlatshwayo, R.H. Matjie, Z. Li, C.R. Ward, Mineralogical characterization of Sasol feed coals and corresponding gasification ash constituents, *Energy and Fuels* 23 (2009) 2867–2873.
- [18] G.H. Taylor, M. Teichmuller, A. Davis, C.F.K. Diessel, R. Littke, P. Robert, *Organic Petrology*, Gebruder Borntraeger, Berlin, 1998, 704 pp.
- [19] P. Gottlieb, N. Agron-Olshina, D.N. Sutherland, E. Ho-Tun, R.A. Creelman, Characterisation of mineral matter in coal and the products of coal combustion, Final Report, National Energy Research, Development and Demonstration Council (NERDDC) Project 1135, CSIRO Division of Mineral and Process Engineering, Clayton, Victoria, Australia, 1990, 190 pp.
- [20] R.A. Creelman, N. Agron-Olshina, P. Gottlieb, The characterisation of coal and the products of coal combustion using QEM*SEM, Final Report, National Energy Research, Development and Demonstration Program (NERDDP) Project 1467, CSIRO Division of Mineral and Process Engineering, Clayton, Victoria, Australia, Report 767, 1993, 164 pp.
- [21] K. Galbreath, C. Zygarrlicke, G. Casuccio, T. Moore, P. Gottlieb, N. Agron-Olshina, G. Huffman, A. Shah, N. Yang, J. Vleeskens, G. Hamburg, Collaborative study of quantitative coal mineral analysis using computer-controlled scanning electron microscopy, *Fuel* 75 (1996) 424–430.
- [22] D. French, C.R. Ward, A. Butcher, QEMSCAN for characterisation of coal and coal utilisation by-products, Co-operative Research Centre for Coal in Sustainable Development, Brisbane, Australia, Research Report, 93, 2008, 103 pp.
- [23] Australia Standards, Higher rank coal – mineral matter and water of constitution, Australian Standard 1038 Part 22, 2000, 20 pp.
- [24] J.C. Taylor, Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile, *Powder Diffraction* 6 (1991) 2–9.
- [25] K. Norrish, J.T. Hutton, An accurate X-ray spectrographic method for the analysis of a wide range of geological samples, *Geochimica et Cosmochimica Acta* 33 (1969) 431–453.
- [26] F.W. Frazer, C.B. Belcher, Quantitative determination of the mineral-matter content of coal by a radiofrequency-oxidation technique, *Fuel* 52 (1973) 41–46.
- [27] K.L. Pinetown, C.R. Ward, W.A. van der Westhuizen, Quantitative evaluation of minerals in coal deposits in the Witbank and Highveld Coalfields and the potential impact on acid mine drainage, *International Journal of Coal Geology* 70 (2007) 166–183.
- [28] R.H. Matjie, Z. Li, C.R. Ward, Determination of mineral matter and elemental composition of individual macerals in coals from Highveld mines, Proceedings of 24th Pittsburgh International Coal Conference, Johannesburg, South Africa, 2007, September 10–14, 2007, Paper 48–5, 14 pp. (CD publication).
- [29] R.M. Bustin, M. Mastalerz, K.R. Wilks, Direct determination of carbon, oxygen and nitrogen content in coal using the electron microprobe, *Fuel* 72 (1993) 181–185.
- [30] R.M. Bustin, M. Mastalerz, M. Raudsepp, Electron-probe microanalysis of light elements in coal and other kerogen, *International Journal of Coal Geology* 32 (1996) 5–30.
- [31] C.R. Ward, D.A. Spears, C.A. Booth, I. Staton, L.W. Gurba, Mineral matter and trace elements in coals of the Gunnedah Basin, New South Wales, Australia, *International Journal of Coal Geology* 40 (1999) 281–308.
- [32] A.C. Cook, Fluorapatite petrifactions in a Queensland coal seam, *The Australian Journal of Science* 25 (1962) 94.
- [33] C.R. Ward, J.F. Corcoran, J.D. Saxby, H.W. Read, Occurrence of phosphorus minerals in Australian coal seams, *International Journal of Coal Geology* 31 (1996) 185–210.
- [34] D. French, L. Dale, C. Matulis, J. Saxby, P. Chatfield, H.J. Hurst, Characterisation of mineral transformations in pulverised fuel combustion by dynamic high-temperature X-ray diffraction analyser, Proceedings of 18th Pittsburgh International Coal Conference, Newcastle, Australia, 2001, December 2001, 7 pp. (CD publication).