Chapter 3: Applied Organic Petrography

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## 3.1 INTRODUCTION

Chapter 2 dealt with the development of coal petrography and introduced the terminology and concepts relating to coal type, rank, and grade. Sample preparation and standardized analytical techniques used in coal petrography were discussed. This chapter focuses on the applied aspects of coal and carbon petrography, expanding on the properties of the different macerals and their technological significance. With respect to the geological origin of coals, maceral and microlithotype data have been used to reconstruct facies and depositional environments. Coal petrography has also been shown to be of use in the assessment of anomalies encountered during mining, handling, processing, and in situations caused by oxidation and / or weathering. Due to the recent focus on shale gas in South Africa, the application of organic petrology to shale gas exploration is also presented. Coal beneficiation is discussed in terms of separation of organic and inorganic matter. The metallurgical industry relies on accurate petrographic assessments of coking coals and their carbonization products, and the gasification and combustion industries benefit from a better understanding of the coal conversion processes via the petrographic assessment of chars. Further detail on these aspects can be found in Bustin *et al.* (1983), Suárez-Ruiz and Crelling (2008), as well as Taylor *et al.* (1998) and Osborne (2013).

## PROPERTIES OF MACERAL GROUPS AND MICROLITHOTYPES

### 3.2.1 Optical Properties

The optical properties of maceral and minerals are discussed in Chapter 2. In brief, as seen in incident light and under oil immersion, vitrinite varies with increasing rank from dark to pale grey and finally to white (Plate 11); these changes are summarised in Table 3.1. Liptinite appears much darker relative to vitrinite in low and medium rank coals (lignite to high volatile bituminous coals). In higher rank coals, liptinite becomes indistinguishable from vitrinite due to devolatilisation and a rapid increase in reflectance. Inertinite is the highest reflecting group maceral, varying from pale grey to white or yellow-white in appearance at all levels of rank.

### 3.2.2 Chemical Properties

Coal is a heterogeneous solid hydrocarbon rock comprised of individual macerals with their own specific chemical and technological signatures. Individual macerals react independently and with each other when the carbon is converted to usable products; hence an appreciation of maceral chemistry is important in order to understand the various conversion processes and products. Advanced techniques to analyse the elemental composition of macerals are discussed in Chapter 4.

Some major differences between the three maceral groups in terms of origin, chemical, and technological characteristics are summarised in Table 3.1. In coals of the same rank, vitrinite contains more oxygen and less carbon than inertinite, whereas liptinite is especially rich in hydrogen and poor in oxygen, and has the highest H/C ratio. As the volatile matter can be related quantitatively to the hydrogen and carbon contents, liptinite produces the largest percentage of volatile matter, followed by vitrinite. Inertinite is relatively poor in volatile matter. These differences in volatile matter, however, diminish with increasing rank (Bustin *et al.*, 1983; Snyman *et al.*, 1984). Similarly, with increasing rank, other chemical characteristics and the physical properties of each maceral group change, but at different rates. Vitrinite becomes more anisotropic with increase in rank due to the increase in aromatization and re-orientation of the molecular structure. This occurs specifically in the mid bituminous range (Bituminous B), after which isotropic textures are noted in lean to anthracitic vitrinite. Calorific value is affected by coal type and rank, with liptinite reporting the highest calorific value at lower ranks, and calorific value increasing with increasing rank in vitrinite; inertinite provides a high calorific value in all ranks. Further detail regarding changes in organic geochemistry with rank can be found in Bustin *et al.* (1983), Taylor *et al.* (1998), and Suárez-Ruiz and Ward (2008).

#### Vitrinite

In low rank coals, vitrinite is composed of various humins (molecules) which consist of aromatic nuclei surrounded by peripheral aliphatic groups (OH-, COOH-, CH3). These molecules occur in a random orientation. With increasing rank, bonds in the aliphatic chains are broken, and the peripheral groups are lost. The aromatic nuclei become larger and are aligned in a more orderly fashion parallel to the bedding plane. The increase in aromaticity and carbon content and loss of volatile components (oxygen content) decreases in an almost linear fashion with increasing rank. Hydrogen initially increases and then decreases from medium volatile bituminous rank to anthracite.

The increase in carbon and loss of volatile matter relative to coal rank can be observed petrographically, as this process relates directly to the amount of light reflecting from the surface of vitrinite, i.e. the higher the carbon content, the higher the reflectance. For this reason, the rank of a coal can be directly determined by measuring the reflectance of vitrinite. In coals possessing more than 80 % vitrinite, rank may also be determined by volatile matter or carbon content, as is the case for most European and American coals. In most southern African coals, however, the presence of high proportions of inertinite masks the increase in carbon content or decrease in volatile matter content with rank as inertinite is carbon-rich and poor in volatile matter in all ranks. The chemical determination of rank in inertinite-rich coals is often, therefore, anomalous, and rank determination by vitrinite reflectance is required. It is for this major reason that the Coal Working Party of the ECE-UN in 1998 declared vitrinite reflectance as the most reliable international parameter to determine coal rank (ECE-UN, 1998).

#### Liptinite

Liptinite in low rank coals is much less aromatic than vitrinite. In general, liptinite has an alphatic-aromatic skeleton with abundant aliphatic side chains, and very small nuclei. It is therefore extremely rich in peripheral groups and yields much higher volatile matter on heating than the other maceral groups in low to mid rank coals. The unique chemical composition of this maceral group, i.e. the waxy sporopollinin and other compounds which rendered the constituents resistant to degradation in the original swamp, yield a wide range of light to heavy hydrocarbons, including exceptionally high proportions of tar and bitumen, particularly in sub-bituminous and low rank bituminous coals. With increasing rank, i.e. in the mid-bituminous range, less heavy hydrocarbons are generated. As rank increases further, i.e. mid to high rank bituminous range, liptinite rapidly increases in reflectance, and is no longer easily recognisable or distinguishable from vitrinite, having lost all its aliphatic compounds.

#### Inertinite

Inertinite is more aromatic than vitrinite or liptinite in all ranks of coal, and the aromatic nuclei are much larger, with few if any aliphatic chains. This maceral group shows very little change in physical and chemical properties with increasing rank. In general, it is characterised by high, tightly-bonded oxygen and low hydrogen contents. In semi-reactive forms, the oxygen is reduced with increasing rank, but no change occurs in highly fusinitized members of the group. Reactive semifusinite exhibits reflectance values close to vitrinite in low ranks, with a comparable volatile yield and swelling capability, and hence will exhibit conversion behaviours closer to vitrinite than inert semifusinite.

Reflectance (and the volatile matter yield) change in reactive semifusinites (pale grey in the low ranks, i.e. those similar to vitrinite in low ranks), and therefore these exhibit behaviour a degree closer to that of the vitrinitic macerals.

#### Microlithotypes

Microlithotype refers to the nature and forms of the associations of organic and inorganic constituents in coal, as discussed in Chapter 2 (Tables 2.7 and 2.8). If minerals are present in proportions greater than 20% but less than 60% by volume (or greater than 5% by volume for pyrite specifically), the inorganic/organic microlithotype is collectively termed carbominerite, irrespective of the number of macerals present.

The chemical properties of microlithotypes are very similar to those of the individual macerals of which they predominantly consist. Where macerals represent less than 5% of the total microlithotype composition, they have virtually no effect on the overall chemical and technological properties. The physical properties of microlithotypes are related to those of the individual macerals, and to the combined effect of their association. For example, vitrite will crush finer than clarite or a vitrinite-rich trimacerite using the same force. This is discussed further below.

**Table 3.1: A Summary of the Major Characteristics of the Three Maceral Groups in Hard Coal (adapted from Falcon and Snyman, 1986)**

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Maceral Group** | **Plant Origin** | **Reflectance** | | | **Chemical Properties** | | | **Technological Characteristics** | | | | | | | | | |
| **Description** | **Rank** | **% Reflected Light** | **Carbon & Hydrogen content** | **Typical Products on Heating** | | **Ignition** | **Burn out** | | | **Smoke** | | **Coke Liquors** | | **Hydrogenation & Liquefaction** | |
|  |  | | |  | |
| VITRINITE | Woody trunks, branches, stems, stalks, bark, leaf tissue, shoots and detrital organic matter gelified / vitrinized in aquatic reducing conditions. | Dark to medium grey | Low- to medium-rank  Bituminous | 0.5 - 1.1  1.1 – 1.6 | Intermediate hydrogen content | Light  Hydro- carbons | Intermediate  volatiles with  decreasing  rank | § § §  § §  §  § | § § §  § §  §  § | | | ††  †  (†) | | †† †††  †††† (†)  † | | § § § § §  § § §  (§) (§) | |
| Pale Grey | High-rank  Bituminous | 1.6 – 2.0 |  | |  |
| White | Anthracite | 2.0 – 6.0 |  | |  |
| LIPTINITE | Cuticles, spores, resin bodies, algae accumulating in sub-aquatic conditions | Black brown  Dark grey | Low-rank  Low rank  Bituminous | 0.0 – 0.5  -0.5 – 0.9  -0.9 – 1.1 | Carbon and Hydrogen rich | Early methane gas | Volatile-rich with decreasing with rank | § § § §  § § §  §  (§) | § § § §  § § §  §  (§) | | | ††††  †††  ††  (†) | | † ††††  † ††  † †  (†) (†) | | § § § § § §  § § § § § §  § § | |
|  | Oil |
| Pale grey  (= vitrinite)  to white shadows | Medium rank  Bituminous | -1.1 – 1.6 | Condensate  Wet gases  decreasing |
| Not observable | High rank  Bituminous to  Anthracite | -1.6 – 6.0 |  | | | | | | | | | | | | |
| INERTINITE | As for vitrinite, but fusinitized in aerobic oxidizing conditions | Medium grey to white | Low rank  Bituminous | 0.7 – 1.6 | Carbon rich Hydrogen poor |  | Low volatiles in all ranks | § | | § | † | |  | |  | |
| Pale grey to white and yellow-white | Medium rank  Bituminous to Anthracite | -1.6 – 1.8  -1.8 – 6.0 | §  (§) | | §  (§) | (†) | |  | |  | |

**KEY: §** Capacity or rate: § § § § = Fast; §§§ = moderate, § = Slow; = Zero; **†** Proportion: †††† = High; ††† = moderate; † = Low; = Absent

### Physical Properties

#### Density

The density of vitrinite increases with increasing rank; i.e. it ranges between relative density (RD) of 1.25 in high volatile bituminous coal to RD 1.8 in anthracites, reaching a minimum of 1.27 in the medium volatile bituminous range (ca. 1.3% reflectance of vitrinite, RoV). Liptinite is the lightest group maceral, ranging in RD from 1.18 to 1.25 with increasing rank in the bituminous rank of coal (Figure 3.1). The inertinite group macerals range in RD between 1.4 and 1.7, changing very little, if at all, with increasing rank. The main difference in density within the inertinite group is related to the inertinite maceral type itself. For reference, the RD of graphite is 2.25, while the densities of most minerals are higher > 2.5 (pyrite is 5.0) (Figure 3.1).

The density of the various microlithotypes consequently also varies with rank, maceral composition, and the size, form and quantity of associated minerals, as graphically depicted in Figures 3.1 and 3.2. For example, in the case of monomaceral microlithotypes, the density is influenced by the specific maceral comprising that microlithotype and its mineral matter content. In the case of combined associations (bi- and tri-maceral microlithotypes), the proportions of the different macerals influence the density of the microlithotype. Liptinite-rich durite may have a density of 1.3 g/ml, whilst a liptinite-poor durite could be 1.6 g/ml. And a mineral-rich particle with a high proportion of liptinite may have a lower density than expected, where the discard product reports a higher volatile matter and hydrogen content, and possibly a higher susceptibility to spontaneous combustion. Such high ash particles may be found in clean density fractions.

Macerals, their distribution in their host microlithotypes and their liberation are important as these factors influence the degree of beneficiation and yield at different densities in the washing process. This is demonstrated in Figure 3.2 and Plates 48-50. Figure 3.11 (discussed later) demonstrates the effect of mineral form on the density of coal particles.

The potential marketability of a coal is tested by density fractionation, or float-sink separation. This is a common laboratory and commercial technique used establish the upgradability of a coal by decreasing the mineral matter. This also concentrates specific macerals and microlithotypes at specific densities, as indicated in Figures 3.1 and 3.2.

**Figure 3.1: Typical relative density ranges of the major constituents of bituminous coal – macerals, microlithotypes, and mineral matter components (modified from Falcon and Snyman, 1986). The range in density values for pure macerals (and consequently microlithotypes) is related to rank (bituminous range considered here) and specific maceral type.**

**Figure 3.2: An example of the effects of beneficiation (heavy media separation) on the distribution of the major constituents of two types of bituminous coal from the Witbank Basin (modified after Falcon and Snyman, 1986).**

#### Microhardness and strength

The difference in hardness of macerals can be observed after polishing for petrographic analysis, with certain macerals showing enhanced relief. The Vickers microhardness technique can be used to quantify the actual hardness by physical testing on specific macerals (Hower *et al*., 2008). A diamond indentor is lowered onto the polished block having selected the maceral or microlithotype of interest, at a specific load for a specified time. On removal, the resultant imprint is measured using micrometers mounted inside the eyepiece. The results have applications in the coking industry (supporting the prediction of plastic behaviour), and coal crushing and milling.

Hardness (defined as the resistance of a material to deformation, indentation, or penetration by means such as abrasion, drilling, impact, scratching, and/or wear) as measured in coal by the Vickers micro**hardness** test indicates that the microhardness of bi- and tri-maceral microlithotypes is always higher (harder) than that of the monomaceral varieties.For example, vitrite and clarite exhibit the lowest range of microhardness, i.e. between 25 and 30 kg/mm2, whilst trimacerite and durite exhibit the highest hardness, i.e. between 80 and 85 kg/mm2.

In terms of tensile strength (defined as the resistance of a material to a force tending to tear it apart, measured as the maximum tension [degree of elasticity] the material can withstand without tearing), liptinite-rich coals have been found to exhibit very high tensile strengths and toughness and, in particular, sporinite and cutinite-rich microlithotypes. Such liptinite layers have been known to prevent breakage across bedding due to their high degree of elasticity.

Within the inertinite category, fusinite occurs in two types in microlithotypes, soft and hard fusite. Soft fusite is relatively soft and friable as the cell cavities are practically free from mineral substances and the carbon-rich material characteristically breaks or crumbles easily. In contrast, the cell cavities of hard fusite are entirely filled with mineral matter, such as calcite, dolomite, or pyrite. In these cases, fusite (classified now as carbominerite) becomes stronger as a result of impregnation and is characterised by greater hardness and resistance to breakage. These hard forms are very characteristic in parts of the seams encountered in the Witbank, Highveld, Free State, Waterberg, Botswana, and Zimbabwean coalfields. As a result of these varying properties, the soft fusinite tends to concentrate in the finer sizes during crushing, while hard fusite remains in the coarser fractions.

The strength of a coal seam and the microlithotypes within it vary due to many additional factors. These include:

1. loss of moisture at some early stage during the metamorphic development (coalification) of the seam. This results in desiccation cracks, particularly within the vitrinite-rich bands, which may potentially render a greater liability to fracturing and crumbling at these points of weakness.
2. loss of moisture due to excessive underground “weathering”. Such weathering effects have been observed in certain southern African coalfields and appear to have been caused by large fluctuations in water table levels, deep penetration of ground-water through rather permeable layers in the overlying sandstones, and the presence of relatively porous semi- to uncompressed inertinite (fusinitic and semifusinitic) layers in the coals. The effect of this weathering, particularly in low-rank bituminous coals, is that porosity and moisture retention capacity is increased and, when mined, this moisture is lost very rapidly. During this process, internal stresses are created and decrepitation sets in.
3. stresses in regions of tectonic movement where uneven compaction or decompression of the strata occur. Whilst such factors are very rare in southern Africa, similar effects have been observed in the proximity of igneous intrusions causing stratigraphic displacements in some seams; and
4. thickness of layers or lenses of specific microlithotypes within a seam. For example, a layer of inertinite, and specifically durite, in the form of fibrous semifusite, several centimetres thick will always show greater mechanical strength than a band of the same material only 0.5 to 1 mm thick. The same is true for clarite and trimacerite layers. These factors have played an extremely important role in the strength and cuttability characteristics in some seams in southern Africa.

In contrast to the weakening effects of cracking and jointing, the strength of microlithotypes is enhanced by the presence of syngenetic mineral inclusions. In particular, strength increases with the decreasing sizes and the uniformity of distribution of the mineral grains intergrown with the coal. Finely dispersed clay minerals and fine grained siderite, pyrite and quartz in the microlithotypes, for example, lead to a significant increase in strength. The effect of mineral impregnation into the cavities of fusite and semifusite (i.e. hard fusite) are especially significant as discussed above.

#### Breakage and grindability

The difficulty in breaking (crushing and grinding) a coal to create smaller sizes (i.e. cobbles (28-100 mm), nuts (71 – 28 mm), peas (6.3 – 25 mm), smalls (0 – 6.3 mm), duff (>6.3 mm)) for specific uses is linked to its resistance to compression, hardness, tensile strength, and friability. These factors arise from the type, grade, rank, and particle size of the coal, all of which contribute to the overall grindability of a coal.

In homogenous layers of vitrain, vitrinite is brittle and fractures angularly, irregularly, and conchoidally (less obvious in southern African coals). This brittleness has been exacerbated by increasing degrees of fissuring in vitrinite. This property frequently results in a concentration of particle sizes smaller than 1 mm (Plate 49).

Liptinite, on the other hand, is characterised by its toughness and high tensile strength, acting in an analogous way to iron rods in reinforced concrete when holding together a spore-rich durite layer. Liptinite therefore increases the strength of coal bands and particles during crushing (Plate 49).

The inertinite maceral group increases the strength of the coal bands in which it occurs, and hence its degree of grindability. Soft fusinite is, however, relatively friable and crumbles to form a high proportion of the dust or fines in coals in which it is a common constituent.

On breakage or crushing, maceral distribution differs in different particle sizes. Malumbazo *et al.* (2013) investigated the influence of coal particle size (5-75mm, 5-53mm, and 5-37.5mm) on char formation and reactivity in a packed-bed reactor. The maceral distribution of the feed coal fractions showed that the smallest size fractions had the highest vitrinite content. Maceral distribution was further divided into total reactive maceral and total inert maceral particles. The largest particle sizes reported the highest inert forms.

## GEOLOGICAL APPLICATIONS

### Application of coal petrography to the determination of facies and depositional environments

As the depositional environment controlled the maceral and mineral composition of coal, detailed petrographic studies provide information pertaining to the peat facies and paleo-sedimentary environment of peat accumulation. Facies analysis of coal seams are based on lithological, petrological, and palynological investigations. Changing facies are considered in Figures 2.2 and 2.3. As stated by Cairncross (2001): time, climate, vegetation, and geological setting are inter-related and inter-dependent prerequisites for coal formation. Peat-forming vegetation controls maceral formation, which is also influenced by geochemical conditions (pH, Eh). As discussed by Hower *et al.* (2013) and O’Keefe *et al.* (2013), the pathways to the maceral types can be complex (Figure 2.4). A general assumption is that coal facies were controlled by oscillating water table levels in the peat mire (Misiak, 2006).

With increasing overlying vegetation and sediment, there is significant compression and volume loss during peatification. The degree of compression can be determined by assessing inclusions, such as secretinite or included minerals, where the coal drapes over the inclusion. Compression ratios of 7:1, 20:1, 6.3:1 are noted in literature (Taylor *et al.*, 1998). In South Africa, due to abundant fibrous semifusinite, compression is regarded to have been on average 10:1 (Falcon, 1986a). According to Taylor *et al.* (1998), 1 m bituminous coal probably represents 6000 – 9000 years of peat accumulation, although it is difficult to place actual times on this aspect.

Unpacking the depositional environment involves consideration of microlithotypes and lithotypes. As stated by Bustin *et al.* (1983): vitrite indicates a forest swamp environment, derived from woody tissues; liptinite-poor clarite originates from strongly decomposed forest litter in a forest moor environment; liptinite-rich clarite probably originated from reeds and non-arborescent vegetation where more resistant liptinite concentrated; spore-poor durite was probably preserved in an oxidising environment where the liptinite was destroyed; spore-rich durite probably originated in subaquatic ooze deposits; vitrinite-rich trimacerites are generally considered to be forest swamp deposits, with fluctuating water tables affecting the degree of oxidation and hence degree of inertite components; and semifusite and fusite may be the result of peat fires or drying out of the peat surface.

As discussed in Chapter 2.3 and indicated in Figure 2.4, woody components accumulating in humic environments leads to vitrinite formation in wet environments, and fibrous inertinite in drier environments, inertodetrinite in reworked environments, and liptinite in all (not highly oxidising) environments. The type of vegetation and degree of oxidation with some microbial activity result in peats of different textures and material composition. This, in turn, gives rise to the suites of coal macerals and microlithotypes found in coal seams today.

Saprophytic environments and decomposing bacteria, fungi, and insects generally resulted in the higher preservation of detrovitrinite group macerals rather than vitrinitic tissue preservation (O’Keefe *et al*., 2013). Detrovitrinite is therefore indicative of significant aerobic decay, having formed from woody remnants after attack by saprophytic and decomposing organisms. Gelovitrinite formed from non-liptinitic cellular contents or migrated materials. Telovitrinite formed from cell walls with little aerobic decay (ICCP, 1998).

The inertinite maceral group is highly diverse, with multiple pathways of possible formation (Hower *et al*., 2013, and discussed in Section 2.3.2). Four main paths of origin have been proposed:

1) fire origin (ie: Scott, 1989; Scott and Glasspool, 2007; Diessel, 2010);

2) oxidation by microbial activity and dehydration in an aerobic environment (Cook, 1981; Hower *et al.,* 2009);

3) biochemical alteration (i.e. Teichműller, 1974);

4) allochthonous environments where partially coalified material is broken up and redeposited (Hower *et al*., 2013).

Peat fires can occur on and below the surface within the peat, and may result in an array of charred to uncharred material with different reflectance values (Scott, 1989). Fusinite displays well preserved cellular structures, reflective of an origin resulting from incomplete combustion due to oxygen deficiency (O’Keefe *et al.,* 2013). This form is known as pyrofusinite.

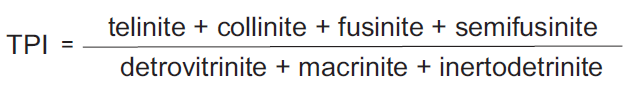
As other inertinite macerals have lower reflectance values compared to fusinite / pyrofusinite, it is plausible that some inertinite, specifically semifusinite, is derived from biochemical alteration or dehydration. It is also possible that fusinite is derived from residual lignin-rich cell walls of plant debris, and semifusinite from the partial removal of the cellulosic layer (Sen, 1999 in O’Keefe *et al.,* 2013). Semifusinite, formed by weak humification, dehydration and redox processes, may exhibit partially visible cell lumens derived from xylem tissues of stems, herbaceous plants and leaves (ICCP, 2001), with Gondwana semifusinite believed to be leaf derived rather than wood-derived (ICCP, 2001). In some instances, botanical cell walls may be preserved by the impregnation of resin or cutin, and thus protected against microbial attack. Some semifusinite reflectance values (specifically reactive semifusinite) change slightly with increasing rank. Semifusinite is extensive in Gondwana coals, with reactive and inert semifusinite readily observed.

Resins or humic gels may be the precursors to secretinite. These are formed by biochemical alteration and subsequently highly oxidized or burnt. Macrinite is not likely to have a botanical origin, rather being a degradation product from microbial activity represented by excreted partially digested remains of plant tissues. The occurrence of inertodetrinite is extensive in southern African coals, consisting of redeposited debris of fusinite, semifusinite and other inertinite macerals as well as vitrinite and included clastics. A more mixed redeposition may indicate wind transport where peat surfaces have dried out or partially burnt; a more uniform graded bedding may indicate redeposition in a more aquatic environment. (O’Keefe *et al*., 2013). Thus, inertodetrinite, detrovitrinite, and possibly even some micrinite, are more likely to have an allochthonous origin. It is also plausible that partially coalified material forming under one set of conditions may continue along different or consecutive pathways, thus explaining the wide variety of macerals observed in coals globally (Hower *et al.,* 2013) (Figure 2.4).

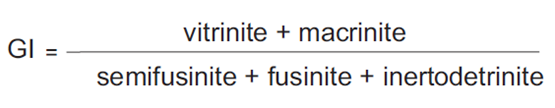
Looking at peat forming environments today, subarctic mires of the northern hemisphere could be comparable to the peat forming areas that typified southern Africa during the Permian. Peat thicknesses in Canada, a current peat-forming environment, is possibly comparable to the prevailing environment in the Main Karoo Basin during the Ecca, varying between 2 and 7 m with an accumulation rate of 0.1-0.8 mm peat per year (Martini and Glooschenko, 1985, in Taylor *et al.*, 1998). The rate of accumulation is low, but so is the rate of decomposition. This is in direct contrast to more tropical environments, where the rate of accumulation and decomposition are both rapid with almost continuous growing seasons. Reed and moss mires tend to dominate in cool climates, and many coal seams originating in temperate or cool climates contain less bright coals. Oxygenated summer waters and desiccation during dry, snow-covered winters result in thinly-banded coals.

Structured and partially gelified inertinite abound in southern African coals, probably related to the climatic conditions at the time of peatification – subarctic to cold temperature. According to Falcon (1986, 1989), the coal forming mires of southern Africa were colonized by sub-arctic mosses, conifers, and deciduous forests with Gangamopteris and Glossopteris floras (arborescent and herbaceous plants), and less dominant lycopods, ferns, cordiataleans or early gymnosperms. Gymnosperms plants had evolved by the Permian. The coals accumulated in well-drained, brackish- to fresh-water mires, resulting in oxidation of the peat and microbial degradation. Varying conditions occurred in each peat forming period ranging from autochthonous, water-logged anaerobic vitrinite-rich environments at the base of the lower seams, and grading up to allochthonous / hypoallochthonous environments in upper peats. A hypoauthochthonous origin is proposed in some seams due to the predominance of detrital macerals over massive cellular macerals, specifically for the Mpumalanga Coalfields. The embayments beyond the main deltaic basin, caused by localized intra and intercratonic, graben or half-graben basins, enabled more extensive sequences of coal seams. These were more authochthonous in nature, frequently with higher vitrinite content, compared to the main deltaic coalfields of Mpumalanga. Plant remains that are more readily decomposed are generally reduced to absent in hypoauthochnous to allochthonous coals, resulting in concentrations of inertinite, corpocollinite, and liptinite. Herbaceous plant communities give rise to much more fine detrital humic matter, richer in cellulose in lower in lignin, than forest peats. According to Taylor *et al.* (1998), funginite and fusinite are more abundant and better preserved in dry conditions. It is interesting to note that fungal remains (funginites) are not observed in southern African coals.

It is well known that the microlithotypes are very important for the understanding of the origin of coal (Silva and Kalkreuth, 2005; Diessel, 1992; Pophare *et al.,* 2010; Teichműller, 1989). Ternary facies microlithotype models by Smyth (1984) and facies model by Diessel (1992) (mostly used in the Northern Hemisphere coal) enable the reconstructed of depositional environments and facies (Figures 3.3 and 3.4). Silva and Kalkreuth (2005) applied the models to the Candiota coal seams of Brazil, indicating deposition of sediments in open-water-limno-telmatic forest moor.

To characterise coals and distinguish between depositional environments, Diessel (1992) introduced the terms “Tissue Preservation Index (TPI)” and “Gelification Index” (GI). The TPI measures the degree of humification that the maceral precursors have suffered, based on the ratio of tissue-derived structured macerals over unstructured macerals. The TPI is defined as follows:

The gelification index relates to the wet conditions of peat formation as defined by high GI and dry conditions by Low GI indices. The GI is defined as follows:

****

Kalkreuth *et al.* (1991; 1999), Scott (2002), Misiak (2006), and amongst others, have discussed and modified Diessel’s method.

**Figure 3.3: The microlithotype facies ternary plot for the reconstruction of the depositional environment of coal in the southern Hemisphere (modified after Teichműller, 1989). In the lower left apex, the term trimacerite was introduced to incorporate the tri-macerals microlithotypes.**

**Figure 3.4: Coal facies diagram of the Tissue Preservation Index (TPI) and Gelification index (GI) in relation to the depositional environment (Silva and Kalkreuth, 2005). This diagram was employed conjointly with the facies model for microlithotypes to gain greater insight of the precursor mires. (Limnic = body of water; limnotelmatic = shallow water; telmatic = water table close to the ground surface).**

### Coalfield and Seam Evaluation

Macroscopically identifiable coal bands or lenses can be difficult to trace or correlate; some may thicken, others thin out and yet others only appear in localised areas. The maceral, mineral, and, in particular, microlithotype composition of a seam can change rapidly, vertically and laterally, in response to the original conditions prevailing during peat swamp development. These changes can usually be seen macroscopically (and recorded in terms of the lithotypes as defined earlier – bright, dull, etc.), but they may be quantified more readily and reliably by a petrographic assessment of the microlithotypes (Figure 3.5). The net overall quality of the mined coal can change dramatically. This may be important if, for example, a slightly enriched inertite lens was to appear in a seam being mined as coking coal or for use in hydrogenation, liquefaction, or pyrolysis; the mined product could then become less suitable for markets requiring such specialised products.

**Figure 3.5: In-seam band correlations based upon microlithotype profiles (carbominerites and minerites excluded). Variable vertical and horizontal distribution of vitrinite and inertinite between the two borehole cores (BH1 and BH2) is indicative of different depositional environments. (Reproduced courtesy of R. Falcon).**

Vitrinite reflectance data can be used to assess rank gradients related to basin geometry, varying geothermal gradients, and proximity to heat sources (sills and dykes), as well as understanding structural deformation. High bireflectance can provide information pertaining to strain and stresses. Plate 70 shows some microfaults determined in some coal particles. Folds and tensional fractures can assist in determining deformation as compressional or extensional. A recent study on coals from Limpopo Province indicated that the coals occurring between two faults reported higher reflectance values than coals of the same seam immediately adjacent to the faults. This indicates that the faults were active during coalification.

In South Africa there is a general trend of increasing rank from the west to east across the coalfields, related to the higher proportions of dolerite intrusion in the form of sills and dykes to the east and geothermal heat in the deeper parts of the main Karoo Basin (Snyman and Barclay, 1989). Studies on coals from the Moatise Coalfield, Mozambique, revealed increasing reflectance with dip, therefore indicating the dip angle was present during coalification possibly affected by increasing geothermal temperature with depth.

Specific mineral identification or maceral types are useful features to use when assessing seam correlations, or determining coal origin. Typically in the Witbank Coalfield the No. 2 seam is richer in vitrinite than the inertodetrinite-rich No. 4 Seam (Plate 69). And the lower Volksrust Formation of the Waterberg is richer in inertinite with a low mineral content compared to the upper Vryheid Formation, which is a mineral- and vitrinite-rich coal. Colloquially referred to as ‘bar-coded’ coals, the latter sequences grade cyclically from mineral-rich coaly sediments into true coal seams over short vertical distances, making sampling and analysis complicated. Incorrect sampling will change the categorization of these coals, as explained by Falcon (2013).

Figure 3.6 indicates different utilization options for southern African coals based on rank and type. A prime coking coal requires a specific coal rank as well as an optimal vitrinite to inertinite composition. Coals of a high rank and rich in vitrinite should ideally be used for direct reduction. Figure 3.7 provides an example of four different southern African coal deposits, plotted according to the ECE-UN classification (ECE-UN 1998), clearly indicating different utilization options for the different deposits.

**Figure 3.6: Major sectors of utilization based upon type and rank of coal. (Reproduced courtesy of R. Falcon).**

**Figure 3.7: Application of ECE-UN (1998) geological classification of coal to four southern African coal deposits. (Reproduced courtesy of R. Falcon).**

Petrographic assessments should be used in conjunction with other analyses (as outlined in Chapter 4), and the results incorporated into quality assessment data for mine-planning, product evaluation, as well as utilization.

### Oxidation and Weathering

Weathering and oxidation are continual geological processes, affecting coal exposed to the elements at the mine face (above or below ground), on stockpiles, during transport, and so on. Coal oxidation, a chemical reaction, may result following exposure to weathering processes immediately after mining, during handling, transportation, and stockpiling. Weathering and oxidation, affecting both the organic and inorganic components, may lead to deterioration of coal properties and alter the technological properties, rendering the coal no longer useful for its intended purpose.

Low rank coals are known to be more susceptible to oxidation than higher rank coals, being more readily oxidizable when exposed to the atmosphere or oxygenated waters. This frequently leads to a high liability towards spontaneous combustion and reduces coal quality as the physical and chemical properties of coal are altered. The rate of oxidation is less well known in the liptinite and inertinite group macerals compared to vitrinite macerals, although it has been suggested that liptinite may be more rapidly oxidized than vitrinite and that inertinite will oxidize at a far slower rate. Rank and maceral composition are therefore important contributory factors in oxidation, potentially influencing the rate of liability to spontaneous combustion (Falcon 1986c).

Oxidized states have been observed in all three group macerals, both in natural underground reserves and in storage situations. All coals, therefore, are potentially oxidizable, despite their variable rates of oxidation. Furthermore, oxidation may occur:

1. Early in peat formation;
2. Subsequently during *in situ* coal seam development and *prior* to mining by the passage of underground waters or deep weathering (primary oxidation and weathering); or
3. *After* mining by exposure to air during handling and storage (secondary oxidation and weathering).

Primary and secondary oxidation and weathering processes affect the coal constituents in different ways and should be identified prior to coal utilisation (Stach *et al*., 1982). For example, the floatability during washing is affected by the changes in surface chemistry; caking propensity is detrimentally affected due to the loss of swelling capability; calorific value is lowered; and the coal may become more friable on handling due to weathering. During weathering, physical breakdown of particles occurs due to the enhancement or occurrence of microsfissures and microcracks, frequently resulting in intense fracturing and friability to the point of granulation. This condition also affects the response to density separation during coal beneficiation. During oxidation, chemisorption of oxygen on aromatic and nonaromatic sites occurs, with the formation of acid functional groups such as –COOH, -CO, and phenolic -OH. Humic acids are believed to form at advanced stages of oxidation, typically observed as oxyrims. Even slight oxidation of coking coals can destroy their fluid properties, with properties determined by Free Swelling Index and Gieseler Fluidity dropping rapidly as oxidation time increases. Other coke properties that are affected include: loss of coke strength; increased amount of coke breeze; increased coking time; increase in coke reactivity, and so on (Crelling, 2008). The weathering of coking coals has been studied by many authors over the years, as listed by Crelling (2008) and Wagner (2007).

Petrographically, natural weathering and oxidation is recognised by particle discolouration, oxyrims, microfissures, microcracks, and possibly devolatilization pores or other signs of heating. Minerals associated with coal will also undergo various forms of transformation due to hydration and oxidation processes (Huggins *et al.,* 1983). Sulphates (gypsum, anhydrite, jarosite, goethite, basanite) are all considered to be oxidation products in coals, not typically observed in fresh samples. Clays may swell causing particles to fragment, resulting in the generation of excess fines.

Spontaneous combustion of coal may result due to oxidation in circumstances where temperatures reach 55oC and above. As oxidation is an exponential exothermic reaction, unless the heat generated is dissipated, self-ignition of the coals may occur. Significant amounts of work have been conducted on understanding spontaneous combustion in coal (Falcon, 1986a; various sections in Suárez-Ruiz and Crelling, 2008, as well as a series of books by Stracher *et al.,* 2011, 2013, 2015). Pone *et al.* (2007) addressed spontaneous combustion in South African coals. From a petrographic perspective, coal rank (lower rank coals), maceral composition (liptinite and vitrinite-rich coals), mode of occurrence of pyrite (framboids), and microstructure (fissures, cracks, available surface area) are all factors that may play a role in spontaneous combustion. Other factors include: moisture content, friability, volatile matter content, as well as accessibility of oxygen and lack of circumstances allowing the dissipation of heat. Spontaneous combustion can occur in seams, or on stockpiles, or during transportation of coals.

Valentim *et al.* (2006) and Wagner (2008) discuss the effect of oxidation features on coal conversion, and both concluded that the oxidation / weathering features resulted in poor combustion efficiency. Falcon and Ham (1988) observed oxidised particles of coal in fly ash obtained from power stations.

### Dispersed Organic Matter

The generation of oil and gas can be related to the rank and organic matter located in a given sedimentary sequence. Finely dispersed organic matter occurs in most sedimentary rocks to some degree or other, although only those with higher concentrations (weight % organic carbon) are considered as source rocks for hydrocarbon generation. By definition, solid hydrocarbons indicate hydrocarbon generation and migration in petroleum systems as a result of thermal conversion of kerogen, detected in shales and siltstones / sandstones that are mature and post-mature. Its absence would indicate thermal immaturity or lack of generative potential in the host rocks, or extreme maturity (above 5% mean RoV). The use of assessing the solid hydrocarbons in rocks devoid of vitrinite or vitrinite-poor rocks can be applied for thermal maturity determination (Landis and Castaño, 1995). Reflectance data should be correlated with or complemented by other data including Rock Eval, Tmax, H/C ratios.

Oil and gas are formed from the breakdown of kerogen, which is a mixture of organic chemical compounds making up a portion of the organic matter in sedimentary rocks. Kerogen alteration or break down is related to the geothermal temperature of the basin. Basins, or sedimentary sequences, are classified as immature, oil generating, gas generating, or over mature depending on the type and rank of the organic matter. Over mature deposits occur where temperatures have been too high, resulting in the cracking of the carbon-carbon bonds.

The van Krevelen diagram shows the evolution pathways of organic matter in source rocks using O/C and H/C atomic ratios (Figure 3.8). The type of organic matter gives rise to Types I – III kerogen. Type I kerogen is rich in aliphatic structures, consisting predominantly of alginate and biuminite; it represents excellent oil generation potential and is hydrogen-rich. Type II kerogen contains large amounts of liptinitic macerals, and could be a good source for oil and gas if the temperatures and time conditions are favourable (Bustin *et al.*, 1983). Kerogen Type III is rich in aromatic structures and is oxygen-rich, mainly consisting of remnants of higher terrestrial plant debris; this type of kerogen may be more prone to gas generation.

**Figure 3:8. A van Krevelen diagram showing kerogen types in relation to maceral / coal groups relative to O:C and H:C atomic ratios (redrawn from Pashin, 2008).**

Hutton’s (1987) classification of the origin of hydrocarbon’s scheme graded the organic matter based on the depositional environment. Terrestrial, lacustrine, or marine environments were proposed to have resulted in the kerogen Types III-I respectively. Terrigenous organic matter dominates in fluvial and deltaic sediments, which will have less hydrogen and more oxygen than aquatic organic matter. Fluvial and deltaic rocks many serve as sources of gas rather than as oil source rocks (Taylor *et al.,* 1998).

Understanding the kerogen concentration, composition, and maturation state are essential criteria for understanding oil and gas formation. The reader is encouraged to obtain further information from Taylor *et al.* (1998), Pashin (2008), Suárez-Ruiz *et al.* (2012), Hackley and Cardott (2016), among others.

## TECHNOLOGICAL APPLICATIONS

### Beneficiation

The density of macerals plays an important part in the washability of coals. Liptinite and vitrinite report to low density levels in their mineral-free form, less than 1.35 g/cm2 in the bituminous range of coal. However they may report to higher densities if the vitrite-clarite particles contain significant proportions of minerals in them. The combined density of such mineral-containing organic particles is termed the relative density (RD) of that particle. Thus, when assessing coals for their washability, the combination of mineral and macerals and their proportions need to be taken into account. The following densities are of importance in coal beneficiation:

Density of water: 1.0 g/cm3

Density of coal (Range 1.3-1.6) average 1.5 g/cm3

Density of shale: 2.4 g/cm3

Density of pyrite 5.0 g/cm3

Higher ranking (anthracitic) vitrinite possesses slightly higher densities, as do weathered / oxidised and heat affected coals. Beneficiation is discussed further in Section 3.5.2 and Plate 48.

### Blending and mixing

The term blending refers to the calculated combination of specific properties of coals for a specific purpose, e.g. low and high sulphur coals blended to meet a moderate sulphur specification. Or a range of blend coking coals blended with a prime coking coal to extend the tonnage of a coke resource. Mixing infers simply combining products for convenience sake, such as fines with sized coal for sale to the market place. In either case, there are compatible and incompatible forms of mixing or blending based largely upon the proportions of type, rank, or grades in coal in the mix. Figure 3. 9 shows coals of a single or mixed ranks exhibiting the same volatile matter %. In the first two cases, a single rank coal or one with overlapping ranks, macerals and microlithotypes will perform in a similar manner. In this case where four or five ranks of coal are observed, ranging from low rank bituminous D to anthracitic, the reactive macerals and microlithotypes in the low rank coals could ignite and burn out before the high rank particles ignite. This would be termed an incompatible mix or blend.

**Figure 3.9: The effect of blending as determined by vitrinite reflectance analysis (Reproduced courtesy of R. Falcon).**

### Pyrolysis

Bituminous coal, when heated at high temperatures, can be converted to various organic gases and light to heavy hydrocarbon products (tars, bitumen,liquid fuels) as it undergoes physical and chemical changes. These changes are important for understanding both the science and technology of coal utilization. Gasification and combustion are the two most common processes for converting coal into gases, liquids, heavy hydrocarbons, and heat energy, both commencing with pyrolysis. Initial coal quality (type, grade, and rank), particle size, boiler / furnace temperature, air to oxygen ratios, and residence times influence the final heat output and syngas formation. Reactive macerals in lignite and bituminous coal essentially follow the same conversion pathway during pyrolysis, varying only in the temperature at which the process of pyrolysis (devolatilisation) is initiated. The higher the rank, the higher the temperature of devolatilisation and ignition, and in the case of vitrinite, the fewer the pore and the lower the swell of the particles. Anthracite particles, irrespective of maceral type, do not swell or form porous chars. The pyrolysis can be tracked optically by petrographically observing the changing forms of the particles (Plates 51 and 56).

Generally, coal conversion occurs as a two-stage process. The initial stage is the thermal decomposition of coal (pyrolysis), which consists of a sudden release of volatiles (devolatilisation) accompanied by significant changes in morphology and molecular structure of the remaining solid leading to formation of char and ash. Pyrolysis is the thermal decomposition of the volatile compounds between 200 – 700oC, generally in the absence of air or oxygen, with up to 70% weight loss occurring in the reactive components. The resultant char particle is dependent on: the maceral and microlithotype composition; the rank of the coal; the particle size (physical properties); and the temperature of char formation (Solomon *et al*., 1988; Bailey *et al*., 1990). The second stage of coal conversion involves combustion or gasification of the char particles.

The pore openings of the softening reactive coal components become blocked due to the high fluidity contributed by the softening coal. Due to this blockage, the volatile matter will be trapped in this fluid and form bubbles. When a large number of bubbles exist, they will overcome the force balance and burst to release volatile matter. Hence, the release of volatile matter and the ultimate char structure will be determined more by the softening coal and the bubble’s behaviour than the original pore structure of the feed coal (Yu *et al.,* 2007). Thus, the devolatilisation process and release of volatiles have a strong influence on the physical structure of char.

The char structure is highly heterogeneous and this usually affects the subsequent char combustion and gasification reactions as well as the ash formation in the second phase of coal conversion (Sadhukhan *et al.,* 2009). The diffusion of oxygen to and within the char particle influences the rate of char burning and release of gases, and therefore the char morphology becomes important (Alexander and Sommer, 1956; Alonso *et al.,* 1999). The chemical and physical properties of char particles are strongly dependent on the properties of the raw coal, while the char structure depends on the heating conditions such as temperature, heating rate, and pressure (Alonso *et al*., 2001; Everson *et al.,* 2015).

Vitrinite and inertinite differ in pyrolysis behaviour, affecting the char yield and morphology. As determined by van Heek and Muhlen (1987), fusain, due to its inert nature, does not exhibit any changes in size during pyrolysis, whereas vitrain exhibits considerable swelling, increasing the particle size two- to four-fold (depending on rank).

The work by Odeh (2015) on the effect of coal rank and pyrolysis behaviour of coals demonstrated that, regardless of the initial coal rank (lignite through to semi-anthracite), by 700oC all coals had reached comparable total reflectance values (4.36 – 4.86 % RoVmr). This indicates that the chemical changes in macerals during heating up to that temperature follow comparable pathways, and to some extent match that of coalification. However, the thickness of the char walls and the degree of porosity varied with rank, with lower rank coals typically having the highest degree of porosity and thinnest walled chars.

### Combustion

Combustion is the process of heating coal in air to produce heat for steam raising and ultimately power generation. As the primary use of coal is for power generation for the foreseeable future, it is important to understand the conversion of the coal particles in the production of heat and energy. A variety of boiler designs convert a range of particle sizes (large to pulverized) in small and large scale power stations. South Africa obtains coal-fired power from power plants ranging in capacity from 214 MW (Kelvin Power Station) to 4800 MW (Kusile Power station – still under construction in 2017). Given the widely varying boiler types in South Africa, it is important to ensure that the coals most suited to each type are used and that the correct operating conditions are set for those coals in order to ensure optimised power production.

As most power stations globally utilize pulverized fuel (pf) injection (particles crushed to 90% passing minus 75 µm), the conversion of the coal to char and ash in this particle size range will be discussed further. Fluidized bed combustion (FBC), including bubbling and circulating fluidized bed combustion (BFBC and CFBC respectively), are heat- and steam- generating technologies growing in importance, but not yet widely applied in South Africa. FBC technology is far more accommodating to coal quality variations than pf technology and operates at lower temperatures, but the conversion principles are comparable to pyrolysis and pf combustion. Vleeskens *et al*. (1988) petrographically examined char from a FBC process.

Coal combustibility is the ability of individual macerals to ignite at certain temperatures. On heating, moisture in the particles is driven off (around 100oC), followed by the release, ignition, and combustion of volatile gases emitted by the macerals (devolatilisation stage). The release of volatile gases can be observed petrographically by the formation of devolatilizing and increasingly porous chars, as occurs typically during pyrolysis. The char forms ignite at slightly higher temperatures and combust until they are burnt out. The rate of combustion and time to burnout varies for different particles types which, in turn, depend on maceral composition, particle size, boiler temperatures, and residence time. Char forms can be quantified and readily linked back to the initial particle types and maceral composition.

The behaviour of individual particles is influenced by rank and maceral composition which, in turn, relates to total volatile matter and carbon content, microlithotype, and the interaction of the macerals with mineral matter (liberated or included). For example, Bengtssen (1986) undertook a detailed PhD study examining the role of coal rank on char formation and combustion. This showed that low rank, high volatile vitrinite-rich coals ignite more readily than higher rank, lower volatile particles. On heating, the “reactive” macerals, namely vitrinite and liptinite, degasify, the volatile gases are emitted to enhance ignition, and the particle ignites and combust relatively easily and rapidly. Liptinite in low rank coals devolatilises and emits tar and bitumen extremely rapidly and at a relatively low temperature, thereafter leaving very little carbon residue to maintain the flame. Vitrinite, on the other hand, softens during devolatilisation, becomes plastic and swells to form a porous char which then presents a larger surface area for combustion to take place. Vitrinite of different ranks will produce chars with different degrees of porosity.

In direct contrast to vitrinite and liptinite, the inertinite macerals (and the more fusinitized and oxidised forms in particular) do not soften, degasify, or become porous. They therefore present a dense or non-porous char with a reduced surface for combustion which is relatively difficult to ignite, takes far longer to burn out, and requires more oxygen and higher temperatures to effect combustion than the “reactive” constituents. The inertinite macerals close to vitrinite in low-reflectance colour (and therefore with higher volatile matter contents than the higher reflecting inertinite particles), are transitional in behaviour as well as appearance. Kruszewska (1989) demonstrated that lower-reflecting inertinite (reactive semifusinite) was semi-reactive during combustion. The proportion of “non-reactive” inertinite is therefore an important factor in most conventional combustion processes, unless the burning units and their conditions have been designed for such constituents. Coal combustion char classification is discussed in Section 3.4.3.

In terms of combustion rate, typically liptinite combusts first, followed by vitrinite, and then inertinite. A according to the microlithotypes the order is: clarite<vitrite<durite<fusite (Suárez-Ruiz and Ward, 2008) for low rank bituminous coals. The proportion of the non-combusted, or partially combusted particles in ash is reported as the ‘carbon in ash’ value; efficient carbon conversion processes will have very low carbon in ash values. Inertinite, at all ranks, is the most common maceral group reporting as unburned carbon in ash.

Ash generated during combustion is typically classified into fly ash and bottom ash. Fly ash is removed from the combustion gas stream via pollution-control devices such as bag houses, fabric filters, or electrostatic precipitators (ESP’s). Fly ash is far finer than bottom ash, and is generally of a greater environmental concern due to its volume (approximately 80% of the total solid residues produced during combustion) and particle size (from PM10 to PM0.1). The minerals occurring in fly ash are either unmelted minerals fed in with the coal (included or liberated), or neoformed amorphous glass (noncrystalline aluminosilicates) and new minerals (typically crystalline). The amorphous glassy phase is typically dominant, with the proportion of quartz, iron oxides, and glass related to the mineral matter proportions in the coal feed. Minerals can include quartz, mullite, cristobalite, magnetite, haematite (Suárez-Ruiz and Ward, 2008), as well as spinels and trace and rare earth elements. Non-volatile rare earth and trace elements are known to concentrate in combustion ash relative to coal. Several researchers have investigated the viability of extraction of valuable metals and elements from ash, but none currently successfully on a commercial scale.

Fly ash can be used for a wide range of industrial applications, depending on the proportion and type of unburned carbon and mineral morphology. The cement industry utilizes low-carbon fly ash as a partial replacement of Portland cement. The construction industry utilize ash as a filler. Applications in agriculture include use as a soil conditioner. Other industries utilize cenospheres extracted from the fly ash as light-weight fillers. Unfortunately, the ash-user industry in South Africa is relatively small, resulting in a large amount of ash dumps which require careful monitoring.

Petrographic unburnt carbon and fly ash classification is discussed further in Section 3.6.5 and Plate 53-54. Additional images of unburnt carbon and fly ash can be located at Suárez-Ruiz *et al.* (2015) and Crelling’s online petrographic atlas of coals, cokes, chars, carbons, and graphites (Crelling and Rimmer, 2015).

Besides petrographic parameters, calorific value, grindability, combustibility, and ash properties are coal characteristics of importance in coal combustion (discussed briefly in Chapter 4). In terms of heat content, the calorific value of a coal depends upon mineral matter content, maceral composition and rank. Work conducted by Nandi *et al.* (1977) demonstrated that proximate and ultimate analyses of the coals tested were not useful in predicting the reactivity behaviour during combustion, and that petrographic properties (rank and reactive maceral content) provided more productive information for predicting coal conversion performance (Table 2.1). XRD and XRF techniques are ideal to assess the minerals in coal and coal combustion ash.

### Gasification

Coal gasification is the process of heating coal in the presence of steam and oxidising / reducing conditions to produce syngas, which is a mixture consisting of methane, carbon monoxide, carbon dioxide, hydrogen, and water (Higman and van der Burgt, 2003). Gasification involves pyrolysis, gasification, and combustion of the coal and resultant char particles to produce syngas and heavy hydrocarbons including bitumen and tars (depending on the gasifier technology and operation). The syngas is reformed to produce a variety of carbons, which are subsequently used for liquid fuels or as chemical feedstocks. The pyrolysis step results in the release of the volatile components and the formation of char. In the combustion step, occurring subsequent to or at the same time as pyrolysis (Wall *et al*., 2002), the char and volatile products react to form carbon dioxide and carbon monoxide, which provides heat for the subsequent gasification reactions. Gasification, which can occur simultaneously with combustion (depending on the gasifier design), occurs as the char reacts with carbon dioxide and steam to produce carbon monoxide and hydrogen via shift reactions. Key differences between gasification and combustion include the role of pressure and oxidizing / reducing environments; gasifiers typically operate under pressure, with reducing environments present in the gasifier. Both these factors influence the conversion behaviours of the char particles.

Gasification performance is dependent on the type of coal and gasifier configuration. A variety of processes may be used to gasify coal, and for each one the most important properties of the feedstocks differ (Wagner, 2008; Ozer *et al.,* 2017). Some processes, such as the fixed bed dry-bottom (FBDB) process, are designed to gasify all coals including inert rich types, whilst other processes, such as the Winkler and Koppers Totzek processes, require low-rank bituminous volatile-rich feedstocks. Certain gasifiers are designed to gasify wet coal slurries, while others use dry fine coal particles or lump coals. The most important organic properties that influence the choice of coal for specific gasification technologies include the rate of devolatilisation, the composition of gases evolved, the burn-out time of the original particles, and the size consistency of the particles. The rate of the gasification reaction is influenced by the particle size, internal surface area, and morphology (structure) of the char, and char consumption rate. The rate of char combustion will significantly influence the release of the heat, temperature profiles, char burn-out characteristics, and unburned carbon in the ash. Both excessively fine and coarse sizes may be problematic in the handling, burning, and flue-gas emission stages of gasification. All these factors can be controlled or influenced by the composition, rank, and possible oxidized state of coal, but most of all by matching coal type with the appropriate gasifier type (Collot, 2006; Wagner, 2008; Ozer *et al.,* 2017).

The carbon conversion profile can be assessed petrographically via char form analysis, and petrography can aid in the selection of the most suitable coal for a specific gasification technology. The maceral content and coal rank significantly affect char formation, which is also affected by the role of temperature, pressure, residence time and particle size (Zhuo *et al*., 2000). Parent coal properties significantly influence the resultant char formation (Wagner and Joubert, 2005; Harris *et al.,* 2006; Bunt *et al*., 2009; Bielowicz, 2016), and, as with combustion, gasification-char morphology can be predicted from the initial maceral and microlithotype composition. Char type has a significant impact on gasification and coals with a high volatile matter content will generally have a lower char yield. Wall *et al.* (2002) demonstrated that the proportion of porous chars increased with the increase in vitrinite content in the parent coal at all pressures and the proportion of vitrinite in a particle will influence the porosity of the char particle. Megaritis *et al.* (1999) concluded that the gasification of inertinite begins at a later stage than liptinite and vitrinite, and that inertinite chars were found to have high gasification reactivity with a longer residence time. Liptinite and vitrinite convert rapidly during pyrolysis and exhibit plasticity, whereas inertinite retains its rigid, well-defined fibrous structure through the gasification zone. Wall *et al.* (2002) also demonstrated that semi-reactive inertinite forms are capable of displaying high fusibility similar to vitrinite under conditions of high pressure. Similar results were reported for coal particles of 4-4.75 mm by Matsuoka *et al.* (2005).

In terms of FBDB gasifier operation and carbon conversion, char morphology classification highlighted definite zones within the gasifier (Wagner and Joubert, 2005; Bunt *et al*., 2009). The carbon conversion process does not appear to be linear, but rather occurs in stages. At the point of these “stages” rapid changes occur. This essentially confirms the concept of defined temperature and reaction zones within the gasifier. Bunt *et al.* (2009) conducted a study on lump coal conversion through a commercial scale Sasol® FBDB gasifier. A petrographic technique, referred to as the carbon particle type analysis, was developed to characterize the physical changes occurring in the carbon particles through the gasifier. The carbon particle type analysis assessed a 50x50 µm field of view, and classified (quantitatively and qualitatively) the carbon form. Unconverted (fresh coal) particles, devolatilized particles, char, and mineral particles where assessed (Figure 3.10. In particles exhibiting bi-or trimacerals, vitrinite bands tended to devolatise more quickly, showing an unequal degree of porosity when compared to inertinite bands (Bunt *et al.,* 2009).

Gasification chars assessed petrographically are generally larger than pf combustion chars, which may cause classification problems when applying the recommended ICCP combustion char classification scheme (Table 3.4). However, as there is no petrographic classification scheme currently for gasification chars, largely due to the wide variety of gasification technologies (Wagner, 2008), conversion processes, and feed particle sizes, petrographers regularly adopt the ICCP classification scheme. Bielowicz (2016) assessed the petrographic characteristics of huminite-rich lignite following fluidized bed gasification applying the char classification scheme proposed by Lester *et al.* (2010), although the char particles were large. Bielowicz (2016) determined in that study that low porosity macerals, such as ulminite, form inertoid chars, and textinite and liptinite swell, forming porous chars.

Solomon *et al.* (1987), Wall *et al.* (2002), Higman and van der Burgt (2003), and Matjie *et al.* (2011) discussed the behaviour of mineral matter during gasification. The mineral matter will typically melt, fuse, and partially crystallise on cooling into new phases (including mullite, anorthite, cristobalite, dopside, and magnetite) in association with amorphous glassy components (Matjie *et al.,* 2011). Mineral matter transformations and slag formation impact the suitability of coal as a feedstock for a specific gasification technology as the mineral properties are related to the coal feed. Most mineral reactions occur at high temperatures, after carbon conversion. In addition to petrography, mineral forms in coal and ash should be assessed using XRD, SEM-EDX, QEMSCAN, etc.

For petrographic consideration of gasification chars and ash, the particles are prepared in polished blocks as per SANS ISO 7404-2. In order to retain the char structure, it is preferable to avoid crushing the sample. The char particles should be assessed in polarised and x-polarised light, possibly with the use of retarder plate, to identify isotropy and anisotropy.

**Figure 3.10: A profile through a fixed bed dry bottom gasifier gasifying lump coals under pressure in a reducing atmosphere (1 being the base where the ash is extracted, 32 being the top where the coal is fed). (Bunt *et al.,* 2009).**

### Hydrogenation and Liquefaction

As discussed above, coals can be converted to liquids or gases which can be refined and used as petroleum products or chemical feedstocks. Liquefaction requires the addition of hydrogen to the coal. The aromatic ring-structures and functional groups are broken down into lighter, more hydrocarbon-like products, and refined into liquid fuels. It should be noted that gasification is considered to be an indirect liquefaction technology, whereas liquefaction is regarded as a direct liquefaction process.

The liquefaction of coal is highly rank and type (ratio of inert to reactive macerals) dependent, and is affected by experimental or operation conditions. In medium rank coals, vitrinite is readily hydrogenated and liquefied, but low and high rank coals require special processes. Liptinite is even more suitable for hydrogenation, particularly in low rank coals, due to its high hydrogen content. Inertinite is, for the most part, not suitable for this process due to its low hydrogen content and high disordered aromaticity.

Solid residues derived from the liquefaction process can be assessed optically. The formation of mesophase can indicate the temperature of the liquefaction conversion.

### Carbonization

Carbonisation is the process of making coke from highly specific “coking coals”. Coke is a valuable metallurgical product, high in carbon, moderately porous and extremely strong designed for use in blast and submerged arc furnaces in the processing of iron, steel, ferrochrome, and other ferroalloys. Metallurgical coke is usually manufactured in coke ovens in plants where up to 100 coke ovens are stacked together. The coal is heated to about 1 000oC in inert atmospheres. The volatiles are driven off as gases and tars are collected for use as by-products. The solid coke is pushed out of the ovens and quenched to prevent combustion when exposed to air. The coke is then used, for example, with iron ore in layers in a blast furnace where the iron ore is converted to metallic iron.

The primary use for coke is to act as a reducing agent in the extraction of various metallic ores. In the early years of coal petrography, the most successful and indeed prime purpose of this analytical technique was to support coke making for the metallurgical industry. This was applied both to (i) the identification of the coals most suitable for coke making, and (ii) to the coke products used in the various metallurgical processes. More specifically, petrography is used to evaluate the applicability of a given coal for coking, to predict the strength of the cokes made from single coals or blends of a number of coals, to predict peak coking pressures, to assess cokes in their various forms by identifying their texture and composition, and to predict coke reactivity.

The properties required for a prime coke include

* **strength** (to resist crushing under the burden of ore in a blast furnace),
* **porosity** (to permit the passage of gases through the burden) and
* **reactivity** (the release of carbon in the process of extracting the metalliferous metal elements such as Fe, Cr, Si, V, and Mn from their host rocks).

Coal petrography has successfully been used to accurately predict coke strength of single coals and coal blends for many years and a number of systems have been developed to achieve this success. The basic model behind the prediction systems is that vitrinite acts as a binder and the inertinite macerals as aggregate reinforcing the cell walls. Thus, as summarized by Crelling (2008), for a vitrinite of any given rank, there is an ideal proportion of inertinite needed to yield the strongest coke. Steyn and Smith (1977) developed just such an accurate prediction system for South African coking coals and cokes, going further by taking into account the unusually high proportions of semi-reactive inertinite (reactive semifusinite macerals) unique to this region. These components were found to contribute to the coke structure in a manner partially equivalent to vitrinite (Cook and Edwards, 1971).

On heating coals at temperatures between 300ᵒC and 500ᵒC in the low-temperature carbonization process, some constituents remain relatively inert, whilst others devolatilise, soften, and become porous; can fuse or bond with other particles; and ultimately harden into coke. Vitrinite typically reacts in this way, but only at specific levels of rank. Liptinite is largely volatized, only providing porosity in low rank coals. Vitrinite-derived coke made from low rank coal is highly porous, thin-walled, frothy in appearance and weak. This type of coke lacks the strength necessary to support the ore burden in the blast furnace. High rank vitrinite (i.e. of low volatile bituminous coals and anthracite) contains too little volatile matter to provide swelling and porosity, and the bonding (caking) capacity is too low, so that poor coke is formed. The best coking coal is made from vitrinite-rich coals in the mid-bituminous range of rank. Here the vitrinite has high swelling properties, good plasticity and fluidity, and firm bonding characteristics, thus forming a strong porous structure with thick walls.

In contrast, inertinite at all levels of rank is, for the most part, inert and will fuse very little or hardly at all. Only certain macerals within this group with a reflectance transitional between inertinite and vitrinite (reactive semifusinite) will soften a little and possibly agglomerate (coke) to some degree. A certain proportion of non-reactive inertinite, however, is always necessary in order to provide strength for the coke walls.

The degree of heterogeneity in a microlithotype is also important in certain carbonisation and combustion processes. For example, the macerals vitrinite and inertinite may be present in equal proportions in a coal, but their associations may vary from thick homogeneous bands of vitrite with inertite distributed throughout this matrix to thin heterogeneous mixtures of macerals, i.e. vitrinertite. Under the latter conditions, the passage of volatiles through the heterogeneous matrix may be impeded by the widely distributed inertinite components, thus causing this coal to exhibit a relatively low swelling capacity despite the presence of vitrinite with good swelling properties. The porosity and size of the reactive surface of the resultant cokes are thus affected.

Similar problems arise in the production of porous chars during combustion and gasification. Clearly vitrite would provide the most porous char or coke on heating, followed by clarite, trimacerite, and vitrinertite. Durite and inertite would provide the least porous products in these processes.

Prime coking coal falls within a tightly specified range of rank, i.e. between 0.9% and 1.6% mean random vitrinite reflectance (Medium Rank Bituminous B) and it contains a specified range of vitrinite, usually between 50% and 85% mmf. Blend coking coals are those coals which possess characteristics closely adjacent to the prime specifications of prime coking coal. Such coals are used in closely controlled proportions with prime coking coal in order to extend the production of metallurgical coal for industry, given the prime coking coals are relatively rare and highly priced.

The petrographic characteristics of metallurgical coke reveal much about its composition and structure and can be used to evaluate its behaviour and formation (Crelling, 2008). Because coke is a hard, porous carbon mass with pores and cell walls, features such as abundance, size and shape of pores, and thickness of cell walls have been studied in an attempt to understand the behaviour of coke. Petrographic studies of coke cell walls textures have been most productive in assessing the behavioural patterns of cokes.

The major requirements for good coking coals therefore are:

1. 50% or more vitrinite;
2. Rank in the mid ranges of the bituminous coal category (vitrinite reflectance 0.8% to 1.8%);
3. Mineral matter and, particularly, sulphur and phosphorous as low as possible.

Calcination is a process commonly used to remove volatile substances in a material in order to improve its electrical conductivity, or to remove water or certain impurities. Also called calcining, this process uses very high temperatures, often over 2000oC or higher, to change the physical and chemical properties of various solid materials, such as anthracite and other [minerals](http://www.wisegeek.org/what-are-minerals.htm), metals, and ores. South Africa uses calcined anthracite for several purposes, one being as a solid carbon “filler” in the manufacturing of electrodes for use in submerged arc furnaces. In this case, electrical conductivity is of prime concern. Calcining re-aligns the carbon molecules into semi-crystalline forms, a process which is easier to achieve in vitrinitic anthracites than inertinite-rich ones.

A wide variety of other carbon materials can also be made from coal, as summarised by Crelling (2008) and pictured in Crelling and Rimmer (2015). This includes carbon fibres and carbon-carbon composites, graphite activated carbons, carbon foams, and, more recently, carbon nanotubes (Moothi *et al*., 2015).In all cases, the coal substrate or precursor and its maceral composition, rank, and subsequent processing control the nature of the products produced.

## TECHNOLOGICAL IMPORTANCE OF MINERALS

The understanding of mineral matter specifically that intricately bound with the organic matter is most important in various technological aspects of coal mining and utilisation. Some of these aspects are mentioned below. The occurrence of minerals in coal is discussed in Chapter 2 Section 3.2.3, with the list of minerals found in coal provided in Table 2.5. Not all mineral forms are readily observable under the petrographic microscope (Table 2.6), but the main mineral groups can readily be determined. A petrographic system to classify mineral distribution in coal is provided in Section 3.4.2.

### Exploration and Mining

Minerals and rocks play an exceedingly important role in the coal mining industry. Information about the properties of the rocks in the hanging wall (roof) and the floor and in particular their response and resistance to water, will facilitate the choice of the appropriate pattern of support in mining. For example, montmorillonite minerals have swelling properties and expand in contact with water, potentially creating hazardous conditions during mining.

The presence of coarse-grained hard minerals also contributes materially to the wear of mining equipment. Examples in the Witbank Coalfield have indicated that “hard fusite”, namely calcite-impregnated fusite, have formed unusually hard layers or bands within the coals seams. Investigations proved that such hard bands reduced the tonnage of coal per unit pick wear on continuous miner equipment from 80 tons per unit pick wear to less than 4 tons per unit pick wear. This resulted in one case to a complete change in mining methods and equipment. Once mined and reporting to the crushing or processing plant, such lumps of coal are so hard they have been known to block the crushers and stop their functioning.

In addition, mineral matter content of the coal and country rock has an influence upon the composition of mine dust in particle sizes below 5 µm. Fine particles in the low micron range are known to impact respiratory problems.

Certain minerals intergrown with the macerals give a useful indication of the condition at the times of coal formation. For example, high concentrations of syngenetic pyrite generally indicates a deposition environment with marine influence. Some mineral bands facilitate identification and lateral correlation of coal seams or partings. Bench 5 in the Waterberg Coalfield, for example, has a unique mineral composition, which distinguishes it from other seams. The high phosphorous content in this seam is problematic for applications in the metallurgical industry, and the seam is selectively mined to prevent contamination with the other benches in this coal deposit.

### Beneficiation

Beneficiation is the process whereby mineral-rich coal (high ash content) is crushed and the particles then separated into low-ash better-quality products, higher-ash middlings products, and very high-ash or rock discard materials. Washability, another term used for achieving this upgrading process, is also used to characterise the potential for a raw coal (whether run-of-mine or borehole sample) to be upgraded and separated into two or more different products. The yield (proportion) of the washed low mineral-matter coal products depends largely upon the forms of minerals contained in the coal, i.e. their size, distribution, and associations within the organic matrix. In essence, the effectiveness of coal beneficiation (level of ash achievable) depends on the nature of the mineral matter in coal.

The breakage characteristics of freshly mined coal and the liberation of the minerals contained therein depend on the mechanical strength of coal and the nature of the mineral content, both of which are determined by the coal’s maceral-mineral (microlithotype) composition. Mineral inclusions may occur intimately associated with organic macerals, either as nodules or fine layers within bands of homogenous vitrite or inertite, or as abundant discreet flakes (tiny nodules or amorphous forms) intimately mixed with granular detrital organic matter in bands of inertodetrite (Figure 3.11). Other mineral forms occur as mineral grains or crystals that precipitated out in cracks and fissures. Such intimately inter-grown minerals include quartz and most clays, i.e. the products of flooding during times of snow melts and high water levels which would have been washed into the early swamps and embedded into the decomposing plant matter. Pyrite, carbonate minerals, and some flocculated clays would have precipitated out in specific water-logged geofacies environments within the organic matrix at the time of peat accumulation or during early stages of peatification. Forms of pyrite and carbonates may also have been deposited within the original cell cavities of fibrous woody layers of fusinite and semifusinite and through groundwater passing through cleats and fractures in the compacted beds of vegetable matter in the later stages of coalification. Fine crystalline forms of pyrite embedded in the organic matrix are difficult to remove during beneficiation.

Those minerals that were washed or blown into the original swamp or precipitated out at that time within the accumulating organic matrix are known as syngenetic minerals (occurring at the same time as peat formation) (Figure 2.7). The minerals introduced after peatification in subsequent cleating of the seams are known as secondary or epigenetic minerals. The epigenetic minerals such as calcite, pyrite, and marcasite are largely liberated through breakage during mining and crushing and can subsequently be removed by washing (>1.8 to 2.0 relative density). Minerals embedded within the coal matrix are more difficult to remove, as indicated in Figure 3.11.The finer the coal particle is crushed, the higher the chance of mineral liberation. The proportions of minerals in a particle will alter the density of that particle, and hence a vitrinite-rich particle with unliberated mineral matter may report to sink fractions.

At a particular size, some of these minerals can easily be liberated by milling and can, therefore, be removed by beneficiation processes. These minerals are termed adventitious, in contrast with those that are not yet liberated which are known as inherent. These two terms have practical connotations. Thus, the preparation of ultra-clean coal (1% ash or less) by depends completely on the form in which mineral matter exists. Petrographic and photographic investigations are frequently used to predict the required sizes for liberation (for example, Plates 48 - 50).

**Figure 3.11: The effect of mineral form on the liberation of mineral matter (modified after Falcon and Snyman, 1986).**

### Impact of Minerals and trace elements on Utilisation

Major, minor, and trace elements associated with minerals as well as organic matter are important considerations in coal utilization. Ash oxide analyses typically report ten major and minor oxides (SiO2, Al2O3, CaO, Na2O, K2O, Fe2O3, TiO2, MgO, P2O5, SO3). These oxides, indicative of common minerals occurring in coal, are known to impact upon coal conversion processes and ultimately to report to the ash; some elements in the minerals may be volatilised. The presence of trace elements in coal and associated coal ash has, in recent years, become an important consideration due to their negative impact on health for humans and animals (Swaine, 1990, 2000). Hazardous air pollutants (HAP’s), including Hg, As, Se, Cd, Pb, and Zn, are subjected to regulation in some counties. The reader is referred to Swaine (1990, 2000), Davidson and Clarke (1996), Wagner and Hlatshwayo (2005), Suárez-Ruiz and Ward (2008), Ketris and Yudovich (2009), and Zhang *et al.* (2004) for further discussion concerning trace elements in coals, as well as Chapter 4 herein.

Table 2.5 documents the principle minerals identified in coals globally. During combustion, most minerals will undergo transformation reactions at different temperatures and in the presence of other elements, thus forming a range of neoformed minerals / mineral phases, as well as amorphous glassy phases (Plate 54). The mineral phase depends on the original minerals present in the coal, the gaseous atmosphere, temperature in the conversion unit, and interactions with other minerals. Quartz typically remains unaltered in ash as the boilers do not attain temperatures suitable for melting or alteration, although silica fumes may be produced.

In terms of low-temperature carbonisation, a maximum quantity of around 10 % mineral matter in washed coal does not usually impair the quality of coke. This, with certain inert organic components, acts as a diluent and, in fact, imparts physical strength to the coke. However, any increase in the proportion of mineral matter exerts an unfavourable effect on coke strength and blast furnace productivity and must be avoided. Excessive pyrite leads to high sulphur contents in the coke products; excessive chlorine leads to corrosion of oven walls. Phosphorous, typically present in coals as apatite, is detrimental to the strength of pig-iron; the metallurgical industry require a total phosphorous level below 0.08 %.

For hydrogenation purposes, mineral inclusions are undesirable and should be removed as far as possible.

In terms of oxidizability, very finely disseminated minerals (pyrite and marcasite in particular) can increase the oxidizability of coal and, thereby, its tendency to spontaneous combustion. Intergrown mineral matter lessens the tendency of coal to form dust as the minerals provide strength to the particle.

In combustion, steam-raising, and gasification, the suitability of a coal as a fuel for specific purposes is also a function of the mineral impurities and their chemical composition. Quartz is highly abrasive, responsible for rapid wear in mills and ducts. Slagging, fouling, ash fusion points, pollution of heating surfaces, and corrosion in heating chambers become important factors when assessing minerals and mineral transformations. Ash fusion temperatures, slagging, and fouling indices will indicate the potential of a coal to be problematic in a boiler, but boiler and operational conditions will also affect the likelihood of these occurrences. Some minerals may melt and coalesce, forming fused or partially fused clinker. Clinker consists principally of silicate glass derived from the decomposition of clay minerals, but can bind other minerals and organic components, reducing the effectiveness of the conversion process. CaO and MgO (from carbonate minerals) and Fe2O3 (from pyrite) modify the fusibility of the clinker. Fused ash tends to corrode iron, steel, and refractory linings of the combustion chamber, whereas solids carried in the combustion gases may cause deposits on the back-end surfaces of the boiler, as well as polluting the atmosphere. The main binding agents in the deposits are alkalis, SO2, SO3, and phosphorous oxides. Slagging and fouling processes are discussed by Suárez-Ruiz and Ward (2008).

The converted mineral matter (now ash) is carried forward in combustion gases, either as solid particles (fly ash), fused, or gaseous forms. Carbonate minerals emit carbon dioxide at low temperatures and will affect the ash fusion temperature of a coal. Pyrite emits sulphur dioxide (combustion processes) and hydrogen sulphide (gasification processes), both of which may be detrimental to respiratory systems and the environment. Quartz may produce silica fumes at high temperatures.

Neoformed (secondary) minerals are crystallized in the ash fraction (fly ash or bottom ash). They include: cristobalite, lime, periclase, gehlenite, anorthite, anhydrite, spinel, mullite, hematite, maghemite, magnetite, and quartz. At around 500oC, kaolinite is one of the first minerals to react, losing the OH units in the crystalline structure, forming amorphous metakaolin, and later mullite with cristobalite (950 – 1000oC). Calcite decomposes to lime (CaO) around 700oC and dolomite will form periclase and lime. Gehlenite and anorthite are neoformed calcium aluminosilicates. Anhydrite will form from sulphur and calcium interactions, retaining sulphur in a solid form rather than the gaseous phase. Spinel and mullite form from illite and smectite around 950 – 1050oC, occurring as glassy compounds by 1350oC. Pyrite and siderite break down to form oxide minerals, including magnetite, maghemite, hematite, or spinels, and a range of other iron derivatives. Quartz, due to its high fusion temperature, is essentially unreactive during combustion up to 1500oC, thereafter becoming amorphous (Suárez-Ruiz and Ward, 2008).

Mineral matter transformations consume heat in the combustion process as the melting reaction is endothermic, thereby reducing the calorific value of coal. Figure 3.12 illustrates the dependence of the calorific value on the ash yield in coals of the same rank; a general rule of thumb is: the higher the ash content in a coal, the lower the calorific value of that particular coal. Even a 1% increase in mineral matter (ash content) will reduce the heat content and boiler efficiency in a combustion process by a significant amount. In processes other than fluidised bed combustion the maximum limit of mineral matter (ash) in a coal is extremely important.

Petrography can be used to study clinkers, slags, carbon soot deposits, and corrosion on boiler tubes and other surfaces. Petrographically it is possible to view a deposit if sectioned and prepared. The inclusion of macerals, unburned carbon, and/or char particles, and the size of particles can be noted, as well as any layering in the deposit. Petrography can play a valuable supplementary role, supporting other analytical tools such as SEM and XRD in investigating the cause of such deposits.

**Figure 3.12: The relationship between Calorific Value and Ash Content (Witbank Coalfield) (Data derived from a series of data sources, courtesy of Papi Kekana)**

## NON STANDARDISED PETROGRAPHIC TECHNIQUES

Standardized coal petrography techniques were discussed in Chapter 2. In addition, in efforts to enhance the available information obtainable by organic petrography, petrographers globally have devised various analytical schemes to consider further aspects in the coal value chain. These include, but are not limited to:

1. Mineral group analysis
2. Coal char petrography
3. Fly ash and unburnt carbon petrography
4. Coke petrography
5. Abnormal condition / weathering and oxidation analysis
6. Dispersed organic matter for thermal maturity assessments in shale gas

### Mineral Group analysis

In order to determine the viability of coal beneficiation, it is useful to gain an understanding of the occurrence and distribution of mineral matter in the coal particles. Falcon (in-house technique) developed a petrographic classification scheme to assess the size distribution of the three main mineral groups: silicates (clays and quartz), pyrite, and carbonates (Table 3.2). The analysis follows the procedure for microlithotype analysis, whereby a 50 x50 µm field of view is assessed and categorized. The percentage occurrence of minerals in the field of view is correlated to the size of the mineral component. With this information, the mineral processing engineer can understand how the mineral matter content (and consequently the ash content) will change depending on the particle size to which the coal is crushed, and the density fraction to which the particle will deport. Minerals observed to represent < 25 % by volume within a field of view are likely to occur as micron-sized small grains finely disseminated through the organic matrix. Such a particle would report to low-density levels in a washing process, and increased crushing will not liberate the mineral component from the organic matter. Minerals representing > 50 % by volume in the field of view (or particle) are likely to occur either as abundant fine grains densely clustered within the organic matrix; as large single nodules; cell infillings; cleats; or a shale, siltstone, mudstone, or sandstone bands containing some organic material. A particle of this type would report to a high-density sink fraction (above 1.9 RD), and the mineral component would be liberated on crushing to finer sizes.

Specific minerals of commercial or environmental concern, such as apatite (phosphorus in coal) and radioactive minerals (zircon and others), are included in the analysis, but as they are very rare they not considered in terms of size and distribution.

**Table 3.2: Mineral Group Analysis (volume %) as proposed by Falcon (in-house technique). Also refer to Figure 3.1 last column concerning mineral mode of occurrence.**

|  |  |
| --- | --- |
|  | % distribution in 50x50 µm area |
| Mineral matter free particles |  |
| Clays | <25 |
|  | 25-50 |
|  | >50 |
| Quartz | <25 |
|  | 25-50 |
|  | >50 |
| Pyrite | <25 |
|  | 25-50 |
|  | >50 |
| Carbonates | <25 |
|  | 25-50 |
|  | >50 |
| Apatite | In field of view |
| Radioactive minerals | In field of view |
| Other minerals | In field of view |

### Coal Char petrography (Plates 51-55)

In order to identify and assess the chars arising from coal pyrolysis and combustion, various researchers have proposed char classification schemes (Table 3.3). Schematic Figure 3.13 very broadly depicts the different types of coal combustion chars encountered optically. An ICCP Working Group on combustion char classification developed a series of classification schemes which were tested via many round robin exercises. The classification scheme published by Lester *et al.* (2010) is the culmination of the Working Group; the scheme is elaborated further in Plate 52, and the logic tree is provided in Figure 3.14.

**Table 3.3: Various char classification systems (modified after Cloke and Lester, 1994; Lester and Cloke, 1999; Wagner, 1999)**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | A | B | C | D | E | F | G | H | I |
| Lester *et al.* (2010) | tenuisphere | crassisphere | tenuinetwork | crassinetwork | mixed porous | mixed dense | inertoid | fusinoid / solid | mineroid |
| Wagner (1999) | thin walled cenosphere | thick walled cenosphere | thin walled honeycomb | thick walled honeycomb | mixed porous | mixed (banded) | inertoid | dense solid / fusinoid | Mineroid / carbomineroid |
| Lester & Cloke (1999) | tenui-sphere | crassi-sphere | tenui-network | crassi-network | fusinoid | fusinoid | solid | solid | - |
| Crelling (1992) | cenosphere | cenosphere | honeycomb | - | unfused char | - | unfused char | unfused char | - |
| Bailey (1990) | tenuisphere | crassisphere | tenuinetwork | mesosphere | fusinoid | mixed dense | inertoid | solid | Mineroid |
| Shibaoka (1986) | vesicular | vesicular | vesicular | - | open solid | mixed | open solid | Solid char | Mineral-rich |
| Oka *et al.* (1987) | thin walled balloon | thick walled balloon | network | - | skeleton | - | unfused block | unfused | - |
| Keesattel (1987) | cenosphere | cenosphere | honeycomb | mesosphere | unfused | unfused | inertosphere | unfused | - |
| Jones *et al*. (1985) | cenosphere | - | honeycomb | - | unfused | unfused | unfused | unfused | - |
| Lightman (1968) | thin walled cenosphere | thick walled cenosphere | lacy cenosphere | solid | solid | solid | solid | solid | - |

**Figure 3.13: Schematic of the various char forms resulting from coal combustion**. **The numbers correspond to those listed in Table 3.4**

**Figure 3.14: Logic tree for the classification system used by the ICCP to classify coal combustion chars (ICCP, 2015).**

### Fly ash petrography and unburned carbon (Plates 53 – 54)

Bailey *et al.* (1990) introduced a fly ash classification scheme based on ash texture (extracts listed in Table 3.3). More recently, Hower (2012) proposed a more generic fly ash classification scheme (Table 3.4), based on modifications from 1995, assessing the neoformed organic and inorganic components and the original components, including components from fuels potentially co-fired with coal. The ICCP proposed a classification scheme for fly ash based on the Commission III Working Group round robin results (Suárez-Ruiz *et al*., 2015). All the classification schemes consider the whole particle or a 50 x 50 micron field of view where the particle is large. The ash samples are prepared as polished block mounts in epoxy resin, although Hower (2012) proposes the use of Sudan Black-laced epoxy to enhance the visibility of the particles. Fly ash samples are typically not crushed further, but bottom ash samples may require crushing to obtain a representative sample as the particles are generally far larger than fly ash.

Whilst fly ash is essentially composed of crystalline minerals and amorphous glass (noncrystalline aluminosilicate glass), it also contains unburned carbon. The proportion of the unburnt carbon in ash varies between conversion processes, being as low as 1 % in a South African power station, up to 25 % in inefficient chain grate stoker furnaces, but more typically around 3 – 5 % in coal combustion ash. The remaining carbon in the ash is generally the determining factor regarding the use of the ash, as the carbon may weaken the ash when mixed with cement, for example. Wagner *et al.* (2008) proposed an unburned carbon classification scheme in order to include the classification of coal, devolatilising coal, oxidised coals and chars, and mineral-rich chars (Table 3.5). The classification was applied to unburned carbon occurring in coarse gasification ash.

The fly ash and unburned carbon classification schemes may be applied to all coal combustion ash and ash from other conversion processes (FBC, gasification, chain grate stokers, for example).

**Table 3:4. Proposed fly ash classification schemes.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Organic fraction | | Inorganic fraction | |
| Suárez-Ruiz *et al.* (2015) | Fused | Unfused | Metallic | Non metallic |
| Dense/massive | Dense/massive |  |  |
| Porous/ vesiculate | Porous/ vesiculate |
| isotropic | isotropic |
| anisotropic | anisotropic |
| Then apply the ICCP Char Classification scheme | | | |
| Hower (2012) | Neoformed | Coal/fuel derived | Neoformed | Coal/fuel derived |
| Isotropic char or coke | Inertinite | Glass | Quartz |
| Anisotropic char or coke | Petroleum coke | Mullite | Sulfide |
|  | Tire-derived fuel | Crystalline silicates | Rock fragments (may have glassy rim, or carbon interior) |
|  | Biomass carbons | Spinel |  |
|  | Carbons in rock fragments | Lime |  |
|  | Partially burnt coal | Sulphates |  |
|  |  | Oxidized minerals |  |
| Valentim *et al.* (2016) | Isotropic |  | Glass | Quartz |
| Anisotropic |  | Glassy rimmed |  |
| Inertinitic |  | Iron minerals |  |
|  |  | Other minerals |  |

**Table 3.5: Unburn carbon classification scheme, based on carbon form characterization proposed by Wagner *et al.* (2008)**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Porous | Dense | Layered/mixed | Carbominerite | Rock |
| Coal |  |  |  |  |  |
| Devolatilized coal |  |  |  |  |  |
| Isotropic carbon |  |  |  |  |  |
| Anisotropic carbon |  |  |  |  |  |
| Oxidised carbon (including oxyrims) |  |  |  |  |  |
| Mineral-rich |  |  |  |  |  |

### Coke Petrography (Plates 59-60)

Petrographic and physical tests are used to identify key properties of coking coals and coke, including: vitrinite reflectance and maceral composition (coals); coke strength (stability) and reactivity; a range of swelling / caking indices (Crelling, 2008; Osborn, 2013). The latter two points are discussed further in Chapter 4.

A coking coal is essentially a coal which, on heating in an inert atmosphere, will devolatilise, the vitrinitic organic matrix softens, swells, binds, and then hardens, forming a porous sponge-like lump of almost pure carbon. During this process, the molecular structure in vitrinite becomes semi-fluid, realigns, and produces a range of semi-crystalline structures ranging from small circular spheres to larger spheres, lenticular, and finally linear ribbon-like forms. These form the “mosaic textures” seen in the walls of coke. Particles of inert forms of inertinite simply retain their shape and structure and are embedded within the walls of the coke where they provide strength in a manner similar to pebbles in concrete (Marsh and Menendez, 1989; Crelling, 2008).

The classification of the cell wall petrography of coke is divided into a binder phase, namely the vitrinitic material that had softened, fused and hardened, and a filler phase, consisting of organic and inorganic inert particles incorporated and fused into the binder material in the cell walls. The binder phase classification consists of isotropic (homogeneous texture) and incipient isotropic phases followed by increasingly anisotropic phases (heterogenous textures) including circular, lenticular, and ribbon-like phases in fine to coarse sizes. The form of isotropy or anisotropy in the binder phase relates to the rank of the original coal, thus allowing the source identification of the coals used in a coke or in a blend. The filler phase of a coke is comprised of fine and coarse inert organic particles such as fusinite, semifusinite, inertodetrinite, macrinite, and oxidised coal particles. Inert inorganic particles retained within the coke are classified as minerals in the filler phase.

**Table 3.6: A coke petrographic classification scheme**

|  |  |  |  |
| --- | --- | --- | --- |
| Binder phase | Isotropic |  | |
| Anisotropic | Mosaic | Fine |
| Medium |
| Coarse |
| Lenticular | Fine |
| Medium |
| Coarse |
| Ribbon | Fine |
| Medium |
| Coarse |
| Filler phase | Unfused inerts |  | |
| Mixed |
| Oxidised |
| Pyrolytic carbon |
| Mineral |
| Other | Green coke |
| Coal |
| Non coal derived (pet coke) |

### Abnormal Condition Analysis (Plates 62 - 64)

The assessment of coal condition is increasingly important as it is known to affect beneficiation and technical performance of coal. Coal stockpiles or waste dumps are being reclaimed and coal particles recovered for conversion, typically combustion. There are a variety of methods used to detect weathering and oxidation in coals, whether natural or laboratory (artificial) induced (Kus and Misz-Kennan, 2017). Many authors have assessed petrographically observable weathering features, including Chandra (1962, 1982), Gray *et al*. (1976), Marchioni (1983), Ingram and Rimstidt (1984), Wagner (2008), Kus (2017), and Kus and Misz-Kennan (2017). Weathering and oxidation features may include cracking and fissuring, particle discolouration, oxy-rim formation, edge effects, and mineral alteration. Berkowitz (1979) stated that all coals, with the possible exception of anthracite, and all macerals, with the possible exception of inert forms of inertinite, will oxidise. However, other petrographers believe that all forms of coal may oxidise when exposed to suitable conditions. Oxidation results in changes to a coal’s chemical and physical characteristics.

Petrographically it is possible to quantify the degree of alteration due to weathering and oxidation, and thus possibly explain anomalous behaviour in coal. In addition to weathering and oxidation features, the analysis may quantify any other atypical features, such as pseudovitrinite, and porous non-compressed fusinite (this material may render the coal sponge-like, retaining a higher than expected inherent moisture content); or *in-situ* devolatilisation of coals due to igneous intrusions. These features may result in anomalous behaviour of coal. Igneous influenced coals have an anomalous chemistry.

Table 3.7 provides two classification schemes to assess oxidation, weathering, and abnormal condition in coals, following that proposed by Wagner (2007) and Kus and Misz-Kennan (2017). The latter was based on the outcomes from the ICCP Commission I Working Group on Oxidised Coals. The former differentiates between primary and secondary weathering features. Primary features are inherent in the mined coal (*insitu* weathering and oxidation), and secondary features are a result of weathering / oxidation after mining, handling, and stockpiling.

**Table 3.7: Classification schemes available to quantify and qualify oxidation and weathering in coals. Adapted from Wagner (2007) and Kus and Misz-Kennan (2017).**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Wagner (2007)** | | | **Kus and Misz-Kennan (2017)** | | | |
| Fresh |  | | Fresh |  | | |
| Inherent / primary weathering | Fissures / cracks |  |  | | | |
| Porous fusinite |
| Pseudovitrinite / desiccation cracks |
| Secondary weathering | Microfissures | Few | Secondary weathering | Microfissures |  | |
| Extensive |
| Microcracks | Few | Microcracks |
| Extensive |
| Holes/ leaching/ cavities |  | Micropores |
| Margin Effect | Cracks/ fissures | Margin Effect | Relief / grain outline |  |
| Dark rims | Oxidation rims/ oxyrim | Dark |
| Light rims | Light |
| Heat affected / lighter in colour |  | Reflectance/ bireflectance |  | |
| Discoloured particles | Discolouration |
| Mineral alteration |  |

### Thermal maturity determination on dispersed organic matter by vitrinite reflectance (Plate 65)

Vitrinite reflectance is a widely used method to determine the rank of organic matter, and its application in assessing thermal maturity is shales is discussed in Section 2.4.3.3. Figure 3.15 shows the correlation between vitrinite reflectance and hydrocarbon potential. Random reflectance at 546 nm using immersion oil and total magnification of x500 in non-polarised light conducted following ASTM D7708-14 (Microscopical determination of the reflectance of vitrinite in sedimentary rocks) is a recommended procedure for thermal maturity determination. Twenty to fifty readings on vitrinite fragments should be taken across the surface of a polished block at a magnification of x500 or higher. Oil generation from kerogen commences around 0.5 – 0.6 % Romax ending by 1.3 % Romax; gaseous products start to occur from 0.8 % Romax, ending between 2.5-3.5 % Romax. There are some intrabasinal differences between these boundaries (Bustin *et al.,* 1983). Reflectance data should be correlated or complemented with other data including Rock-Eval, Tmax, and H/C ratios.

In order to accurately characterise the organic matter, the samples should be viewed under normal white light (preferably in colour), as well as in fluorescent mode (to determine degree of fluorescence), and under crossed-polars (to determine degree of anisotrophy). Liptinitic components can clearly be identified and distinguished from the mineral matrix with UV light or blue light excitation. The combined used of normal white-light and fluorescent light provides a more accurate determination of organic matter in shale samples. ASTM D7708-14 defines a number of types of organic materials that may occur in rocks containing dispersed organic matter. These categories include: bituminite, fusinite, huminite, inertinite, inertodetrinite, liptinite (alginate, lamalginite, telalginite), micrinite, mineral matter (carbonates, clays, pyrite, quartz), semifusinite, solid bitumen, vitrinite (including recycled), and zooclasts (chitinozoan, conodont, graptolite, scolecodont).

The ICCP offers a training course in dispersed organic matter, as well as a training module and ICCP accreditation on the determination of vitrinite reflectance on dispersed organic matter. Suárez-Ruiz *et al.* (2012) provide a thorough update of organic petrology related to dispersed organic matter.

**Figure 3.15: Vitrinite reflectance correlation chart for dispersed organic matter maturation studies indicating the oil and gas window (http://oilandgasgeology.com/.)**