THE CHARACTERISATION OF CARBON REDUCTANTS IN THE METALLURGICAL INDUSTRY – A CASE STUDY

R. Falcon[1], V. du Cann[2], D. Comins[3], R. Erasmus[3], P. den Hoed[4] and A. Luckos[4]

[1]University of Witwatersrand, Private Bag 3, Wits 2050 RSA. E-mail: falcons@icon.co.za
[2]Coal and Mineral Technologies, Building 46, CSIR Campus, Pretoria 0001 RSA.
[3]University of Witwatersrand, Private Bag 3 Wits 2050 RSA.
[4]Mintek, Randburg, Johannesburg RSA.

ABSTRACT

Carbon as a reductant, additive or filler is an essential element in the processing of metallic ores and the manufacture of iron and steel in the metallurgical industry. In most cases, the element carbon is derived from coal and its carbon derivatives. The properties of carbon required for the different processes in each metallurgical sector vary significantly and, for this reason, matching the correct carbon product for each specific process has become an important if not vital function in all sectors of this industry. This selection process, however, has become increasingly difficult. In many cases, the substitution of new products, despite being similar in all relevant chemical specification characteristics to previous products, has resulted in different performance properties relative to that expected. Under these circumstances, the prediction of performance of unknown carbon products has become fraught with difficulties unprecedented in the past.

In order to initiate an investigation into addressing these issues, a test case was selected for indepth study the results of which are reported in this paper. The case concerned the use of a specific carbon feed in a conventional submerged arc furnace which gave rise to an unprecedented amount of unreacted or only partially consumed residue trapped in the frozen slag on the refractory walls of the furnace.

During the course of these investigations, different advanced analytical technologies were employed including, inter alia, Raman spectroscopy, surface dimensional tests, organic petrology and various thermal reactivity factors. All results have been integrated into a multidisciplinary assessment presented in summary in this paper. Based on the above, and previous experience, the concept of an all-embracing 3-D coal-carbon "framework" is briefly introduced.

This approach has succeeded in obtaining greater depth of knowledge and a better understanding of the issues at stake with specific reference to the organic composition, structure, texture, internal surface area and consequent reactivity of the carbon materials concerned. In consequence, it would now appear that various properties of relevance to the metallurgical industry may be predicted with greater precision than has hitherto fore been possible.

1. INTRODUCTION

Carbon as a reductant, additive or filler is an essential element in the processing of metallic ores and the manufacture of iron and steel in the metallurgical industry. In most cases, the element carbon is derived from coal and its carbon derivatives.

The properties of carbon required for the different processes in each metallurgical sector vary significantly and, for this reason, matching the correct carbon product to each specific process has become an important if not vital function in all sectors of the metallurgical industry. Such properties include softening, swelling, fusion and porosity in coke and char making, reactivity or carbon consumption of the carbon reductants for use in various processes using solid, gaseous and molten media, strength related to overburden pressure in blast furnaces, heat production during pre-reduction in pre-reduction kilns and in the Corex process, electrical resistivity related to degrees of graphitisation under various electric arc furnace conditions, and yet other related factors relevant in carbon fillers used in the manufacture of electrodes for electric arc furnaces.

The process used to select the correct or most suitable coal or carbon feed source for each purpose, however, has become increasingly more difficult in recent years, largely because tried and trusted reserves of coal and carbon products have dwindled in many iron, steel and other base metal producing countries and new coal products have had to be substituted. In many cases, despite similarities in all relevant commercial chemical specifications to previous products, the substitution of new products from different sources to replace the old has resulted in significant differences in performance properties relative to that expected or acceptable. Under these circumstances, the prediction of performance of unknown carbon products has become fraught with difficulties unprecedented in the past.

For this reason it has now become necessary to understand in greater detail some of the basic reasons for the variations in feed coals and carbon products available to the metallurgical industry, how these materials change on heating in different processes and then to indicate methods by which properties vital to this industry may be predicted with greater precision than in the past. Of specific relevance in the current paper is the rate of carbon consumption or reactivity in full-scale electric arc furnaces.

To address the problem outlined above, a long term programme is currently being devised in which a wide range of coal forms and their processed carbon derivatives has been selected for comprehensive laboratory testing and analyses as well as full-scale industrial metallurgical use.

The current paper represents the first step in this programme. In essence, it takes the form of an investigation concerning a carbon reductant comprised of a product termed “anthracite” which was introduced into a full scale operating submerged arc furnace, a considerable proportion of which reported as unreacted carbon residue floating on the surface of the molten bath and embedded in the freeze line slag trapped against the refractory walls.

In order to gain a better understanding of the results obtained, and to establish control points from which to draw conclusions as to the significance of the results, other selected coal and carbon products were introduced into this initial study for direct comparative purposes.

The methods by which these coal and carbon products were assessed included the use of (a) chemical analyses of the unprocessed coal-anthracite products in order to establish a base level commercial comparison, (b) coal petrography and coke/char spectroscopy in order to determine the basic organic maceral-mineral-coke-char constituents within the materials, their levels of maturity (rank) and their structures and textures, (c) Raman analyses to determine levels of graphitisation and crystallographic ordering, (d) surface area determinations by means of BET in order to determine the extent of sites for potential reaction and(e) laboratory scale TGA analyses in order to calculate and compare carbon mass loss or “reactivity” relative to CO and CO_2 gaseous environments.

The results were integrated into a comprehensive interdisciplinary overview from which a considerably better understanding of the materials and the reasons for their respective characteristics and consequent reactivities was achieved. From this it has been shown that greater precision in the characterisation of coal and its various carbon derivatives, and an identification of detailed structure, texture and consequent reactivity, is possible. In the test case currently under investigation, the apparent reason for the poor reactivity of some of the feed anthracite was established and discussed in further detail.

Based upon the results obtained and experience in related fields, the concept of an all-embracing “3-D coal-carbon framework” has emerged which will undergo further development in the later phases of the overall coal-carbon research programme. The concept is built upon a 3-dimensional framework in which all ranks and types of natural or raw coals and their heat-processed carbon derivatives are located. Such a framework provides easily identified spatial dimensions on which to locate all these coal and carbon forms as well as their relationships to one another and to the various process conditions under which they are or were formed. Linked to the inherent physical, chemical, structural and textural characteristics of each coal or carbon form at each location, this framework would also provide the basis for understanding the performance-related properties of these materials in various technological processes.

With considerably more tests to enhance the data associated with this framework, it would be possible in time to predict the potential inherent properties of any coal or carbon product under any given set of technological circumstances, based largely upon its location within this diagram. Furthermore, substitution of any given carbon product by another with similar technological properties would be relatively simple to accomplish. Ultimately, the principle of blending of different carbon products in order to achieve an overall material with acceptable performance for use in specific technological processes could also be achieved, limited only by an understanding of the general principles of blending and the effect of extraneous secondary factors such as particle size distribution on the properties of those blends.

2. SAMPLING AND METHODOLOGY

2.1 Sample Identification

The samples used in this investigation were drawn from different sources. The samples are listed in order of rank as follows:

Raw coal:

1. Bituminous coal (BCa) - bright coal (high volatile, high vitrinite, Bituminous C, RoV 0,66%)
2. Bituminous coal (BCd) – dull coal (medium volatile, high inertinite, Bituminous C, RoV 0,66%)
3. Anthracite (ATC) - test case feed anthracite used in the test case electric arc furnace
4. Anthracite (ANW) – alternative anthracite on offer to the metallurgical industry
5. Anthracite (ASM) – alternative anthracite on offer to the metallurgical industry

Carbon materials after exposure to elevated process-induced temperatures:

6. Coke (ISC) – coke used by the metallurgical industry
7. Coke (ASM) – coke used by the metallurgical industry
8. Carbon residue (CTC) – test case carbon material trapped in the freeze-line slag
9. Graphite (GUP) – unused graphite prepared from carbonised petroleum coke for use in electrodes
10. Graphite (GE) – graphite taken from the tip of a used electrode that has been exposed to high temperature electrical charge in the furnace but has not been introduced into the molten bath.

2.2 Investigative Methodology

The samples listed above were subjected to various analyses and tests, outlines of which follow:

2.2.1 Chemical Analysis

Proximate analyses are the first analyses conducted on coal materials. This suite of analyses includes inherent moisture content, ash content, volatile matter content and fixed carbon content (by difference) as percentages on an air dry basis.

2.2.2 Petrographic Analysis

Petrographic analyses are those undertaken microscopically using a light reflecting ore microscope and examination of material under oil immersion at magnifications of approximately 500x. The role of organic petrology is to determine the organic and inorganic (mineral matter) constituents of coal or carbon materials, their degrees of maturity or rank, their conditions of weathering, levels of heat affect, porosity or textural changes and their associations if blends are included within a product. These factors are determined by a series of statistically repeatable measurements conducted on polished blocks of finely crushed or whole particles of coal, as appropriate for the specific analysis. The petrographic methods used fall within the scope of ISO 7404.

The analyses specifically undertaken in the present investigation included the following:

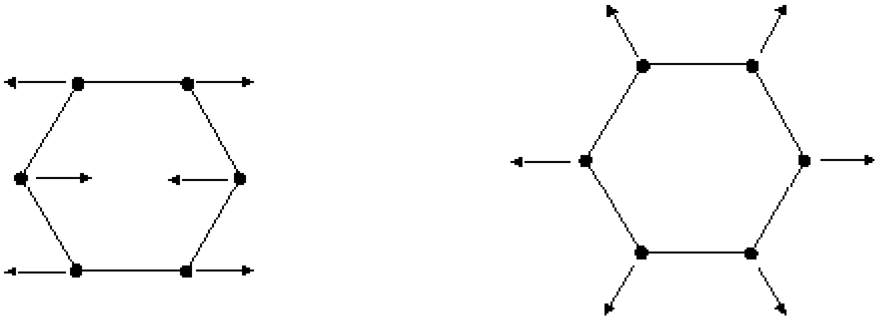
- Organic composition in the form of Maceral group analyses (%)
- Proportions of abnormal conditions including weathering (%)
- Forms and proportions of coke, char and other heat-affect products (porous structure, wall texture, reflectance %)
- Rank determinations by light reflectance on vitrinite (RoV minimum, random and maximum%, standard deviations, ranges of reflectance and blend proportions)

2.2.3 Raman Spectroscopy

Raman spectroscopy is a non-destructive, light scattering technique yielding information about atomic ordering in a material. In the measurement process, light from a laser source interacts with the vibrations (phonons) within a solid material. A small proportion of the light is scattered at a frequency different from that of the incident light (Raman process). This difference in the frequencies of the incident and scattered light corresponds to the frequencies of the vibrations in the solid. As these frequencies are characteristic of the structure and order in the solid, the peaks in the so-called Raman spectrum yield valuable information about the nature and structure of the material.

The unit of the Raman spectrum is that of reciprocal centimetres (cm^{-1}), and is always measured relative to the laser line (i.e. the laser line is always at 0 cm^{-1}). In the case of carbonaceous materials, there are two prominent peaks in the Raman spectrum. The so-called *G* peak around 1580 cm^{-1} corresponds to the in-plane bond-stretching motion of pairs of carbon sp^2 atoms (see Figure 1 below). It occurs at all sp^2 sites, not only at those in rings. In other words, the G factor reflects the extent to which a material has achieved levels of 2-dimensional planar bonding similar to that found in graphite lamellae. The more ordered the material under investigation, the closer to the ultimate lamellate structure of graphite it will be. Whilst lateral bonding within the planes becomes strong, the inter-lamella or third dimensional “vertical” bond remains weak. The ultimate form of pure lamellate graphitisation will be reached when the peak of the spectrum is sharp and narrow and reaches 1580 cm^{-1}.

The *D* peak around 1355 cm^{-1} is a symmetric breathing mode associated with six fold rings (see Figure 1 below) and is only active in the presence of disorder. In this case the D factor reflects groupings of carbon atoms with 3 dimensional bonding similar to the aromatic structure of inertinitic materials in coal. Such structures may be randomly distributed in small disordered carbon clusters within a matrix thereby giving a wide base to the D peak, but with increasing cluster size, namely with larger groupings of tightly bonded carbon atoms, higher levels of 3-dimensional carbon clustering will be achieved which will be reflected in a narrowing of the D peak within the spectrum until it approaches the ultimate sharp peak indicative of large bonded but disordered clusters of atoms at 1355 cm^{-1}.



Vibrations giving rise to G peak

Vibrations giving rise to D peak

Figure 1. Carbon motion in the G and D modes. Note that the G mode is just due to relative motion of sp2 carbon atoms and can be found in chains as well.

Raman spectra were collected using the micro-Raman attachment of a T64000 Jobin-Yvon Raman spectrograph operated in single spectrograph mode, with a liquid-nitrogen cooled CCD detector. The microscope objective was 20x, yielding a spot size on the sample of 1-2 μm in diameter. The excitation source was the 514.5 nm line from an argon ion laser, and the spectrograph was calibrated using the green emission from a Hg lamp. Power at the sample was <1 mW, and care was taken not to heat or burn the sample with the laser beam during measurement. Several spots (n = 4 to 6) on each sample were measured, and the peaks fitted to a linear combination of a Gaussian line shape and a Lorentzian line shape to extract the peak parameters. The data reported below are the average of the data for the different spots, and the error bars represent one standard deviation.

2.2.4 Surface Area

The surface areas of samples 1, 2, 3, 5, 7 and 8 were measured, namely, the feed anthracite, carbon residue samples used in the test case under review and other selected samples for comparative purposes. These included a bright Bituminous coal (Sample 1), a dull Bituminous coal (Sample 2), a second anthracite (Sample 5) and a coke (Sample 7). Surface area is measured in square metres per gram. The BET surface areas were measured in a Micromeritics ASAP 2010 using nitrogen as the adsorbing gas. Each sample was degassed at 120^{o}C prior to measurement.

2.2.5 Reactivity Analysis

The reactivity of some of the carbon samples under investigation in this preliminary study was measured by means of thermogravimetry. The measurements were conducted at 1500^{o}C in CO-CO_2 atmospheres ranging from pure CO to pure CO_2. The duration of tests varied from 1 to 6 hours. Reactivity was defined by the rate of mass loss as indicated by the gradient at any point on the thermogravimetric (TG) curves. This measure was taken to reflect the inherent property of each specific material.

3. RESULTS AND DISCUSSIONS

3.1 Assessment of the Feed Anthracite supplied to the Test Case Electric Arc Furnace and its Carbon Residue

The anthracite supplied to the submerged arc furnace in the test case was unusual in that it contained a low volatile matter content (9,4% air dried) but a high ash content (22,1% air dried) and a relatively high inherent moisture content (4,4%) compared to other anthracitic products in South Africa. All other specifications including phosphorus and sulphur contents appeared to be within specification.

Investigation of the freeze line slag and its entrapped carbon material was undertaken by petrographic analysis using cut sections and particle analysis. Plate 1 illustrates the distribution, size ranges and forms of the carbon material as seen optically. Plates 2 and 3 illustrate the microscopic forms of the materials encountered. To the naked eye, the sample falls into three physically distinct zones. Zone A marks the outer unconsolidated section containing the bulk of the trapped carbon pieces; Zone B, the pale grey, foamy mid section with some carbon pieces entrained, and Zone C, the innermost visibly homogeneous darker layer in which no visible pieces of carbon were visible to the naked eye. Microscopic examination of each zone was then undertaken.

Zone A was found to contain high proportions of unconsumed carbon in the form of anthracite (see Plate 2). This material was predominantly comprised of massive bands of inertinite (77%) with some narrow bands of clean vitrinite. Some particles of anthracite have clearly undergone a high degree of graphitisation with over 60% of the material exhibiting reflectance ranges consistent with those known to exist in the graphite range of rank. Many particles also exhibit a form of granulation similar to one that manifests following calcination at temperatures considerably higher than 2000^{o}C. Virtually all anthracite particles in this zone exhibited strong thermal stress cracks parallel to the stratification (the layering of the coally material). Incipient carbon consumption was observed along some of these cracks, but in almost all cases, the carbon particles exhibited clean, unconsumed margins, in many cases not fused to the slag. No further examples of such “granulation” or thermal stress fracturing were encountered in the other zones in the slag.

These observations indicate that the unreacted carbon material found in the slag was highly graphitised, granulated and thermally stressed. The inference is that this material may have been exposed to excessively high temperatures and therefore rendered unreactive *prior* to its introduction into the test case furnace. An alternative scenario could be that such temperatures as would be required to induce such conditions in this anthracite may have been derived from the passage of electricity across the surface of the molten bath during feeding into the furnace. It is beyond the capacity of this investigation to explore this matter further.

Zone B was found to contain some rare elements of some anthracitic material, but in general these materials were only reactive (i.e., showed slight increases in porosity and interaction with mineral phases) on their outer margins. Other chars of a more porous nature exhibited a relatively higher degree of devolatilisation, and partial consumption and common mineral interaction (See Plate 3). Also observed were viscous phases of a highly reflecting metallic mineral with diffusion into some of the large, less-porous organic particles in this zone. Many particles of carbon exhibit unwetted surfaces adjacent to the slag.

Zone C exhibits a high proportion of almost fully consumed, fragmented and porous chars, most of which are well-embedded (“glued”) within the slag matrix. These char forms differ from those in the upper two zones in that they are characterised by far more porous structures and heterogeneous textures, and as such, are consistent with those derived from lower ranges of bituminous coals. In addition, what would appear to be nucleation and crystallographic growth, or replacement of the organic materials, are now encountered within the char matrices, either replacing the carbon matter or consuming it (note white crystalline structures in Figures 3c, 3d, 3e and 3f). Minor proportions of porous chars that have achieved a modest level of graphitisation were also observed. There is no evidence of anthracitic material in this zone.

In summary, the observations outlined above expose the problem that the carbon residue material encountered at the surface of the freeze line slag is considerably different to that encountered within the slag. It is clearly unreactive in nature and anthracitic in origin, relative to the more reactive, bituminous-derived material encountered within the slag. Given that the feed material was said to be an anthracite, further investigations were called for.

3.2 Comparative Analyses between three Commercial Anthracites Supplied to the Metallurgical Industry

Comparative analyses between two other anthracites, Samples 4 and 5, and the test case feed anthracite, Sample 3, revealed that all three coals exhibit low ranges of volatile matter, namely, 2 and 10,5% air dried, with the test case anthracite 9,4% air dried. On a dry ash free basis (daf %), the analyses of the test case anthracite (Sample 3) and anthracite (Sample 5) are similar, whereas anthracite (Sample 4) exhibits lower volatiles, namely:

	Test Anthracite (Sample 3)	Sample 5	Sample 4
Volatile matter content daf %	12,8	12,0	2,2
Fixed Carbon content daf %	87,2	88,0	97,8

Petrographic analyses were undertaken to confirm the similarities between samples 3 and 5, and account for the difference in sample 4. Results were surprising and not consistent with the chemical assessment.

Sample 3, the test anthracite, was found to be a blend of low rank bituminous coal (5%), devolatilised bituminous coal and incipient char (15%), and fully developed highly porous and highly reflecting char (73%). The last two processed carbons point to a derivation from reactive coals of bituminous rank. Minor proportions of anthracitic material, some graphitised or granulated (presumably calcined), were also included in this blend (7%). This result is consistent with the variety of carbon materials observed microscopically within the slag.

From these observations and from the differentiation of carbon forms encountered in the layered zones, one may infer that a significant proportion of, if not virtually all, the bituminous coals and the chars derived from coals in these lower ranges of rank were likely to have been successfully consumed (or be on route to being consumed) within the reduction process in the furnace. The source of the problematic carbon residues on the surface of the slag is anthracitic material which was added to the blended feed material called “anthracite”. As it was suspected that this material may have been calcined and rendered unreactive prior to use, further examination was needed to confirm both the level of graphitisation and degree of unreactivity of these materials.

By way of contrast, the anthracite in Sample 5 is revealed petrographically to be a simple, single-seam, high-grade, moderate-ash, semi-anthracite (Anthracite C) product, rich in vitrinite (70%), with a mean reflectance reading of Rr 2,44% and range in rank from Rr 1,8 to 3,5 %. Sample 4, by way of further contrast, is a blend made up of higher rank anthracitic material much of which appears to have been graphitised or granulated, as may be expected when such material passes through the process of calcination at very high temperatures (>2500^{o}C). [NB: Anthracites are non-graphitisable below this temperature (Pinheiro, pers comm)]. Such observations provide the reason for the very low volatile matter content (2,2%daf) and very high fixed carbon content (97,8%daf) in this latter sample.

In summary, and based upon the results above, it must be stated that anthracites are highly variable in composition, rank and levels of graphitisation, thus when selecting products for specific technological performance, the assessment, of such materials, when drawn from different sources, should not be based solely on simple chemical parameters. The same principle applies to the selection of other carbon-rich reductant materials including chars, cokes and blends of different reductant materials.

3.3 Full Assessment of a Range of Coal and Carbon Materials

In order to assess the reasons for the varying reactivities of the above materials, and to establish the validity of some of the above observations, several additional coal and carbon materials were introduced into the next phase of testing. The materials included in this phase were bituminous coals (Samples 1 and 2), cokes (Samples 6 and 7, and pure graphite (Samples 9 and 10).

3.3.1 Surface Area

The surface areas of samples are listed in Table 1. The reasons for these values are evident in Plate 4. The bituminous coals (both samples of which are close to the sub-bituminous levels of maturity) exhibit low surface areas relative to the other samples, namely 0,27 m^2/g for the bright coal and 0,78 m^2/g for the dull coal compared to the ranges 1,23 m^2/g to 32,3 m^2/g in the other samples. The anthracites vary significantly and exhibit unexpected differences: Sample 3 is 26 times that of Sample 5, the test case feed anthracite. The surface area of one of the coke samples (Sample 7) is approximately half that of carbon residue from the test case furnace. These considerable differences require explanation.

Table 1. BET Surface areas of coal and carbon products.

SAMPLE	**m^2/g**	**Error ±- m^2/g**
Bituminous coal – bright : Sample 1	0,27	0,02
Bituminous coal – dull : Sample 2	0,78	0,01
Anthracite : Sample 5	1,23	0,01
Anthracite test case : Sample 3	32,3	0,7
Coke : Sample 7	3,86	0,07
Carbon in slag : Sample 8	7,25	0,04

Nevertheless, from these results it will be noted that there is a consistent and almost linear increase in surface area from the bituminous coals (0,27 and 0,78 m^2/g) to one of the anthracite samples (Sample 5, with 1,23 m^2/g) and the process heat-treated materials (coke and carbon in slag). This series excludes the anomalous feed anthracite (Sample 3).

Petrographic analysis of the samples explains the pattern of surface areas described above.

The bright bituminous coal comprises predominantly the hardened, gelified, relatively homogeneously-structured Maceral vitrinite in which there are very few pores to be seen. The closest analogy to this material would be a sheet of glass. In contrast, the dull bituminous coal contains a higher proportion of more fibrous woody material with inherent botanical cells evident, most of which are filled by clay and carbonate minerals. This material may be likened to a piece of tree-trunk in which most of the botanical cells are filled with resin.

The comparative anthracite (Sample 5), on the other hand, with double the surface area of the dull bituminous coal, has a considerably higher proportion of empty-celled porous woody material (i.e. nearly one third of its organic constituents is comprised of inertinitic granular or fibrous material with generally empty botanical cellular cavities (lumens)). The high surface area of anomalous feed anthracite, sample 3, by way of contrast, derives from a highly porous structure formed in the charring of highly reactive bituminous coals.

The coke material, the surface area of which is three times that of the comparative anthracite (Sample 5), is seen microscopically to be comprised of relatively large pores with walls of varying thickness, all of which have arisen through the heating process at 600 to 800^{o}C. At these temperatures the vitrinitic materials in coking coals (i.e. those encountered in the mid bituminous range in rank) soften and devolatilise. In so doing, they release some volatiles to the process environment whilst also retaining gases within the body of the coally particles, namely, gases that cannot diffuse out of the particle. These gases then create pores (holes) developing within the body of each particle. As the released gases within the pores increase in volume and quantity, the softening walls expand and stretch, the pores become more numerous and grow bigger and more complex, sometimes coalescing, and the whole particles increase in size until a point is reached on the temperature scale (as determined by the rank of the coal) where the material hardens. It may even shrink slightly, thereby creating minor cracks. In this process the surface areas of the coal-coke particles increase accordingly.

The surface area of carbon pieces within the slag is double that of the coke sample. This may be explained in part by the release of volatiles concomitant with heating to temperatures as high as 1750°C, such volatiles that, in anthracites and inertinitic materials, are only generated at temperatures of 1400°C and above. Thus, whilst the material identified in the carbon residue in the slag is in fact an anthracite with a high level of inertinitic constituents (77% inertinite), the presence of naturally occurring empty cells observed in many of the woody fibrous inertinite bands (58% of the material) *and* the development of numerous small pores arising from devolatilisation of gases which were observed in the more gelified semi-inertinite and vitrinitic material at these elevated temperatures, more than adequately explains the larger porosity of this sample with respect to that of the coke material.

Thus, the extent of surface area exhibited by a coal or carbon material has been shown to be influenced by (a) the presence of natural, cellular structures within the organic constituents (primary porosity), (b) the rank of the coal which controls the proportions of volatile matter arising from the organic constituents and the conditions under which they can be released, and (c) the temperature levels to which the coal is heated which influences the quantity of volatile matter released and therefore a second form of porosity. These factors are likely to play an enormous role in controlling the process of diffusion in direct reduction processes. NB: Such factors do not, however, control the levels of reactivity alone. Reactivity is a factor that needs to be associated more to the proportions of active chemical sites on the surfaces of a carbon particle than just surface area alone. This aspect will be investigated further in future.

3.3.2 Raman Spectrocopy

The data are examined in terms of the positions and widths of the *G* and *D* peaks of the different samples. Figure 2 shows as an example of raw materials a Raman spectrum of bituminous bright coal (Sample 2, listed as Bitbright) and as an example of processed material a Raman spectrum of the carbon nodules from the slag in the furnace (listed as C nodules). As the *D* peak is present in all the spectra (not just those in Figure 2), it indicates that some degree of disorder is present in all the samples[1].

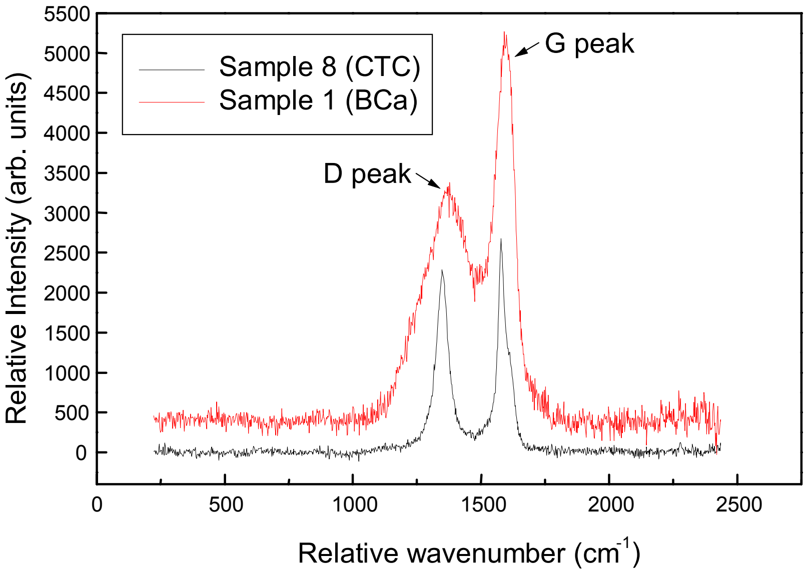


Figure 2. Raman spectra of carbon nodules and bituminous bright coal, illustrating differences in the characteristic spectra. The spectra have been offset for clarity.

Figure 3 shows a scatter plot of the width and peak position data of the *G* peak for the different samples. Two clear, broad groupings are visible: the raw materials (coke, anthracite and bituminous bright coal) are grouped in the upper right corner of the graph, whereas the processed materials (carbon nodules and graphite materials) are grouped in the lower left corner. The raw materials are characterised by relatively larger values of peak position and peak width. Both the movement of the peak position to lower values and the narrowing of the peak width indicate an ordering taking place in the material associated with processing. Processing moves peak position towards that of pure graphite; a narrower peak reflects a structure that is more ordered than in the raw materials.

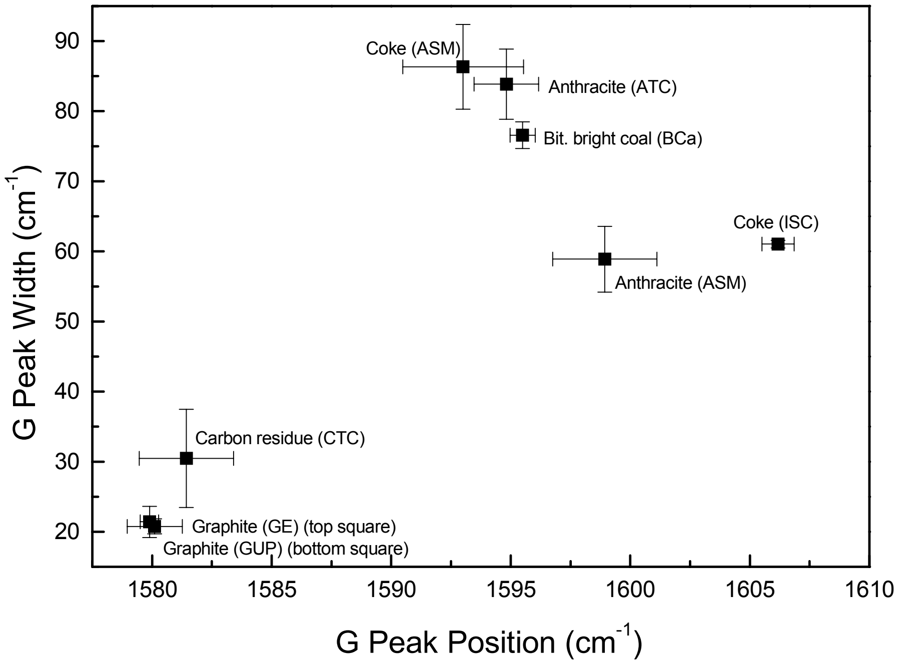


Figure 3. Scatter plot of peak width versus peak position for the *G* peak of the materials investigated. NB: The bars indicate the range of values for each sample with a mean value at the cross point.

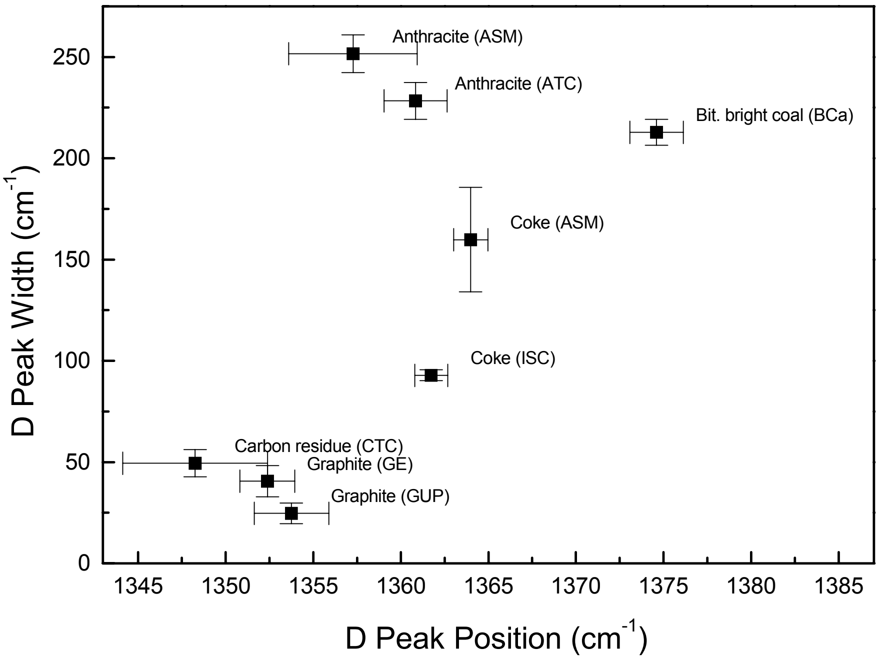


Figure 4. Scatter plot of peak width versus peak position for the D peak of the materials investigated.

A similar trend, although not as clear, is displayed in Figure 4, where the data for the *D* peak are plotted in a scatter graph. The processed materials are again grouped towards the lower left corner, and the strongest trend is the narrowing of the peak width from raw to processed materials.

In coal, the material typically reflective of aromatic disordered 3-dimensional clusters of carbon atoms is inertinite. In low to medium rank coals, this maceral group is composed of various small clusters of randomly distributed aromatic carbon atoms tightly bonded to some extent with oxygen. With increasing rank, some re-ordering takes place, resulting in an increase in the sizes of the 3-dimensional aromatic clusters. Little or no graphite-like lamellae formation occurs. Thus the progression from a broad peak base to a narrow one approaching the ultimate level of 1355 cm^{-1} reflects changes due to increasing rank and maturity found in typically aromatic forms of inertinite macerals. Thus whenever coal or its carbon derivatives contain this material, a D peak may be expected in the Raman spectrum. This is indeed the case in the current set of analyses, and petrographic analyses can once more confirm the existence of such structures and levels of disordering in the carbon material from the furnace slag sample and the graphite samples.

A better understanding of the relationship is therefore now apparent between the Raman results, which infer the chemical structure of coal, and the petrographic composition (maceral type) and rank of coal. Key physical changes may now be linked closely to temperature-related process conditions. In coal, the ultimate graphitic structure of the G peak is only likely to be found when vitrinite, a highly aliphatic carbon material with small aromatic nuclei, increases in rank and maturity to anthracite and then to natural graphite due to intense pressure from depth of burial and overlying rocks. During this process, the aliphatic chains of lighter and heavier hydrocarbons break off and are released as gases and heavier hydrocarbon materials at various stages in the maturing process thereby releasing the remaining small carbon nuclei and causing them to re-goup into increasingly larger clusters of lamellate chains which, with increasing pressure and temperature, straighten and flatten out into the pancake-like ordered layers of graphite. These changes in structure and form may be induced by geological or geothermal temperature increases and by heating in industrial processes. The latter will artificially induce graphitisation, the level and purity of which is likely to be subject to the initial rank of the coal and the conditions prevalent during the heating process. Thus the ultimate G peak may only be found in coal or its derivatives when such extreme conditions have been applied to vitrinite, the specific constituent in coal that will yield to such conditions.

From these observations it is clear that Raman spectroscopy is a powerful tool in the suite of techniques available for the analysis of carbonaceous materials. The results and discussions presented here focus only on the prominent aspects from a first round of investigations. More detailed analysis, also of secondary peaks not discussed above, will yield more information on the structure of the materials under investigation. Interpretations on an even finer scale are already possible by means of cross-referencing one analytical tool with the others in this exercise. Space, however, precludes further detail at this time.

3.3.3 Reactivity Analysis

Only two materials were tested in the laboratory, viz the comparative coke (Sample 7) and the comparative anthracite (Sample 5). The results to date have been manifested by TG curves on time-temperature graphs. No kinetics or detailed calculations have as yet been produced. In the interests of space, the graphs have not been included in this paper. Suffice it to state that the TG curves of the two materials were shown to vary slightly but to be similar in general terms.

These preliminary results indicate that slight differences in reactivity, defined as the rate of mass loss as manifested by curve variations, are apparent between the coke and anthracite under the conditions tested. Of the two products, anthracite appears to be slightly more reactive, i.e. is the more rapidly consumed under CO and CO_2 conditions. Further test work is required before definitive answers can be achieved, but the indications are that reactivity is a function of both the inherent nature of the material and the composition of the gaseous environment. The effect of temperature has yet to be determined.

4. SUMMARISING CONCEPT – THE CARBON FRAMEWORK

Based upon the observations encountered above, and on supporting evidence reported in previous investigations [2][3][4], a close correlation between the petrographic characteristics of coal (type and rank) and its technological performance, in this case the reactivity of carbon as a reductant in a submerged arc furnace, has been found. However, this is not a simple correlation. A third major factor, namely that of temperature applied during the processing of the parent coal to its final carbon product, has been found to be equally important. Other conditions including gaseous environment, time and pressure have also been found to play a part in the final structure and behavioural characteristics of carbon materials, but these factors have not been found to be as relevant as those listed above in the first instance.

On the basis of these observations, a concept employing the use of the three prime factors listed above to create a three-dimensional framework is herein proposed. Known as the *3-D Carbon Framework*, this structure employs *coal type* (or the proportions of macerals) on the x axis, *coal rank* or the maturity of the parent coal on the y axis (as determined by vitrinite reflectance i.e. Rr%) and *temperature-related process conditions* on the vertical or y axis (temperature in ^{o}C).

Using this basic framework, Figure 5 illustrates how the vertical axis has been further divided into different temperature zones or "pancake" layers. At each layer, isocontours for a variety of technological properties, for example, swelling or coking capacities, ignition temperatures, burn-out capacities or CO_2 reactivities, can be established. These behavioural characteristics are known to change within different temperature ranges or on different "layers". Coal samples used in the current investigation lie on the lowest temperature level (0-50^{o}C) and range from lower rank bituminous coals to anthracite (Rr0,6 to 5,2%), and low to high proportions of reactive macerals (16 to 70% vitrinite). The coke products lie in the temperature range from 500 to 1000^{o}C whereas the calcined anthracite, carbon in the slag and graphite samples lie in the temperature ranges above 2 000^{o}C. Each of the latter products could be placed at a specific location on its pancake layer relative to its original parent coal type and rank. Based upon this location, each product can be linked to key performance characteristics and all can be located according to logical 3-D spatial resolution.

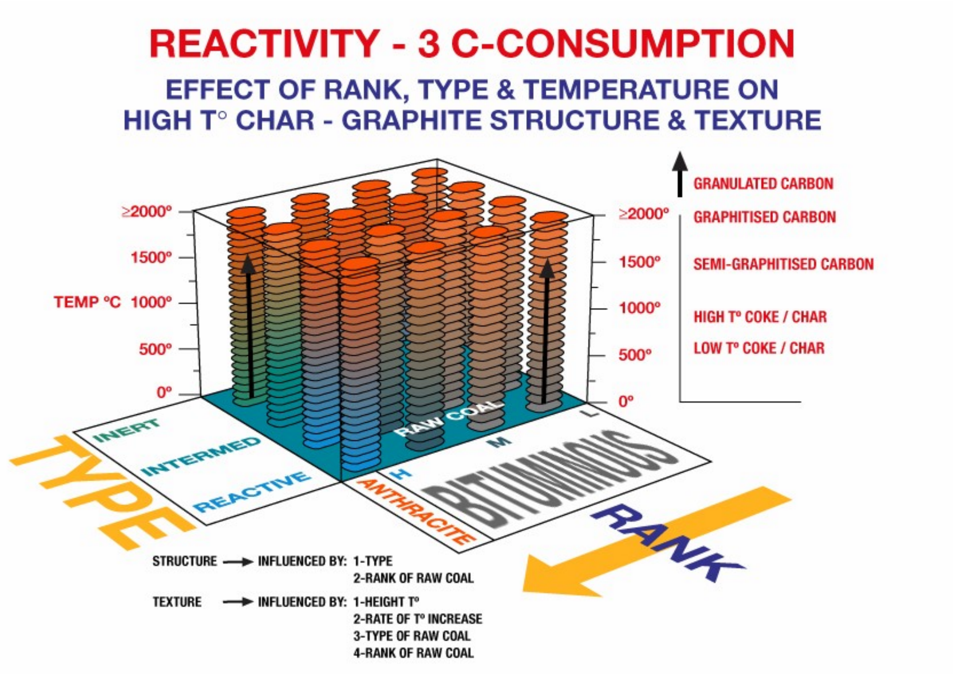


Figure 5. Carbon Framework based upon coal/carbon type (*x axis*), rank (*y axis*) and temperature-related process conditions (*vertical y axis*) "Pancake" format.

Figure 6 illustrates a different use of the *3-D Carbon Framework*, namely, the progressive change in structure and behaviour for each specific coal type encountered at each specific level of rank. Each vertical "pile" (each one equal to one organic form (type) of coal located at a specific level of rank) rises upwards through varying process conditions, i.e. a series of increasing temperatures in this diagram. In so doing, the specific parent or raw coal will undergo a continuum of change chemically, physically and optically which, in turn, will impact upon the technological properties specific to that coal and its ultimate carbon product. The final carbon product and its properties will be controlled by the highest level of temperature (or other process condition) to which that specific coal has been exposed.

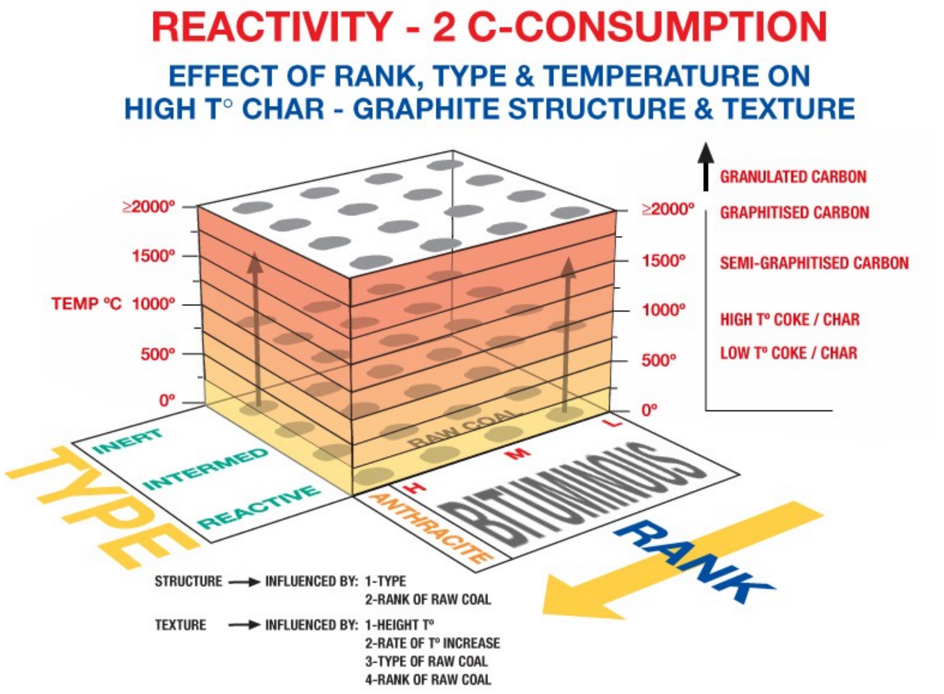


Figure 6. Carbon Framework based upon type, rank and process conditions "Pile" format.

The changes encountered in each coal-carbon sequence can also be tracked over time and with varying gaseous conditions, and linked to performance in practice. Furthermore, different coals and carbons can be associated with one another to create mutually acceptable blends, or to substitute effectively for one another.

In this manner, all coal and coal-derived carbon materials can be located within this framework. All key properties based upon the inherent nature of the coal and carbon materials can be superimposed and isocontours for such properties as reactivity may then be interpreted with greater degrees of confidence than has been the case in the past.

5. CONCLUSIONS

Based upon the above investigations the following conclusions have been reached:

- The anthracite feed to the test case furnace, whilst classified originally as an anthracite on the basis of conventional chemical specifications, was found on petrographic examination to be a blend. This was comprised predominantly of highly porous, thin-walled isotropic chars derived originally from bituminous coals. To this had been added minor proportions of normal bituminous coal some of which showed signs of devolatilisation leading to the formation of incipient chars. Highly reflecting anthracite, much of it graphitised, was also present in minor proportions. This latter material is consistent in form to that found after natural anthracites have been calcined at temperatures of 2000^{o}C and above.
- The test case freeze line slag, on detailed examination, was found to exhibit three major zones of reaction, all bearing carbon materials in different forms. Results based upon petrographic observation conducted on the innermost fine-grained homogenous zone (closest to the refractory wall) indicated that only fragments of the isotropic highly porous char materials were present in this zone. Where observed, these were in the process of being consumed or had largely been successfully consumed, many associated with metallic nucleation and metallisation. No anthracitic material was observed in this zone. In the mid zone of the slag, some anthracitic pieces were seen, a few exhibiting very small, evenly-distributed pores within their matrix with slightly more porous and partially reactive rims on their outer surfaces. In the outer unconsolidated zone of the slag, large anthracites pieces had accumulated none of which exhibited any significant reactivity at all. The only signs of change relative to their original state in the feed material were higher reflectance values and increased stress cracking parallel to stratification, as observed petrographically. Very rare signs of reaction in the form of narrow reaction rims were encountered along the margins of some of the stress cracks.

- The anthracite particles trapped in the outermost zone of the freeze line slag was examined in more detail and found to be predominantly inertinitic, high-reflecting, graphitised and in some cases highly granulated. The reason for the poor or limited carbon consumption rate or reactivity of this material appears to lie in the chemical, physical, structural and textural characteristics of the organic components comprising this material, all of which appear to have been a consequence of exposure to temperatures in excess of 2000 ^{o}C. This has resulted in a level of crystallographic order that appears to be resistant to further chemical reaction in the furnace. The relatively low density of this material relative to the molten bath is most likely to have resulted in its floating to the surface of the bath.
- The reactivity or carbon consumption rate of the feed "anthracite" introduced into the test case furnace was found to have varied considerably. This was attributed to the widely varying forms or heterogeneous parcels of carbon materials making up the "anthracite" blend. This appears to have resulted in different rates of reaction and possibly a separation of materials due to variations in density. This in turn, may have been the cause of layers of differentiation between carbon reductants within different sectors of the molten bath.
- Analytical comparisons between three commercial anthracites including the test case feed coal indicated that, whilst all three fall within the chemically defined class of anthracite, with two of the products exhibiting almost identical chemical analyses and the third moderately so on dry ash free bases, all were in fact significantly different from one another in terms of organic composition, rank, structure, texture and blend composition. These differences may be expected to result in considerably different technological performances when using these products.
- Based upon the above assessments, it was established that conventional chemical specifications (proximate analyses in particular) are insufficient to assess the value and potential performance of carbon reductants when drawn from a variety of sources for use in the metallurgical industry.
- Conclusions reached concerning the application of further advanced analyses used in the examination of the coals and carbons included in the current investigation are as follows:
- Organic petrography in association with char spectroscopy was found to provide important detailed information concerning the basic organic composition of all coal or carbon products. This included identifying type of coal (by identifying the organic constituents comprising a product, i.e. maceral proportions and associations), rank (by determining the levels of maturity of the organic matter within a product), the extent of blending (by identifying the proportions of different types and/or ranks of coals within a product), the nature and extent of the effect of process conditions on a coal (by determining levels of porosity, existence of other structures and material textures in the resulting heat-processed chars, cokes and graphitised products). These factors provide the basic framework for a simplified understanding of the physical, chemical and structural changes that occur in coal within the natural geological system and those carbon forms resulting from imposed technological processes.
- Surface area measurements provided relatively precise total internal area measurements for each coal and carbon tested. Results indicated that, with increasing rank and process temperature, internal surface area increased in significant orders of magnitude. The considerable and anomalous increase in surface area encountered in the test case feed anthracite was related petrographically to the presence of inordinately high proportions of very porous, thin walled chars. This technique has important implications for the physical accessibility required in chemical and technological processes. Further work would need to include the determination of the extent of chemically active sites on the surfaces exhibited by different coals and the carbon products produced under different process conditions.
- Raman spectroscopy provided valuable information concerning the nature and extent of chemical bonding and related structures within the coal and carbon products under review. Results indicated that with increasing geological rank and process-imposed temperatures, both graphitisation (G peak) and disordered crystallisation (D peak) in the coals, cokes, anthracites and graphitised products under review increased towards the levels classically found in graphite with certain specific variations between them. This technique promises to provide information of even greater significance in future, when results are correlated against a variety of coal and carbon products and the effects on them of a variety of process conditions to which they may be exposed.

In conclusion, this paper has sought to address some of the many issues open to question in the understanding and use of coals and carbon materials in metallurgical processes. It has attempted to open the door to multi-disciplinary collaboration and interpretation and, by these means, to assist in the longer-term understanding of the needs, problems and requirements of the South African metallurgical industry. Towards this end, the paper seeks to close on a simple and yet hopefully effective concept, that of incorporating all natural coal and processed carbon derivatives into one specific framework, one upon which the simple basic parameters of cause and effect can be established. It is proposed that this be termed the Carbon Framework and that it will be based upon the simple parameters of cause and effect, or in coal terms, type and rank, with process conditions determining the third dimension. The reader is referred to Figures 5 and 6 for further consideration. This matter will be developed further in the next phase of the overall programme currently under development.

6. REFERENCES

[1] Ferrari, A.C. and Robertson, J., “Interpretation of Raman spectra of disordered and amorphous carbon”, Physical Review B, vol 61, number 20, pp 14095-14107, 2000.

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[3] Beesting, M, Hartwell, R.R. and Wilkinson, H.C., “Coal rank and coke reactivity”, Fuel, vol 56, pp 319-324, 1977

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PLATE 1

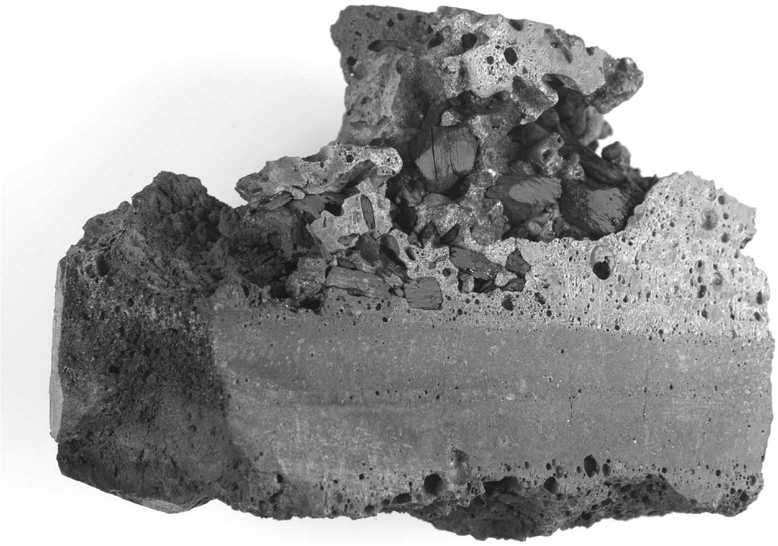


Plate 1a. A piece of freeze line slag taken from the refractory wall of an electric arc furnace. The upper most section with the freely trapped coal particles is termed Zone A, the white foamy slag section in the mid section is termed Zone B and the visibly homogeneous grey layer comprising the lower half of the total slag piece closest to the refractory wall is termed Zone C.

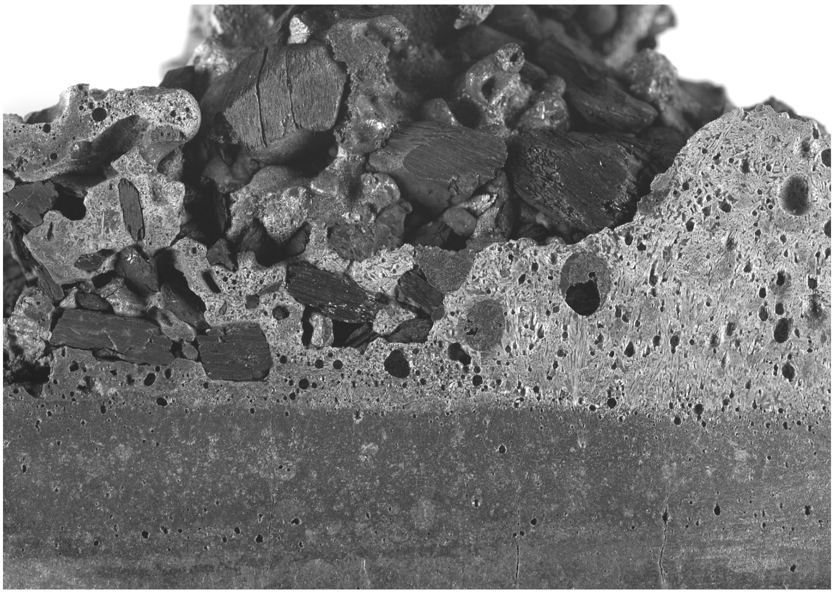


Plate 1b. An enlargement of Plate 1a. illustrating in greater detail the rectangular or slab-like forms of many of the carbon residue particles, the lateral or planar cracking along stratified planes and the lack of bonding or wettability on the margins of the carbon material relative to the host slag.

PLATE 2 – Forms of Carbon Residue from the Freeze line Slag (outer Zone A).
Scale: 1cm = 50 microns

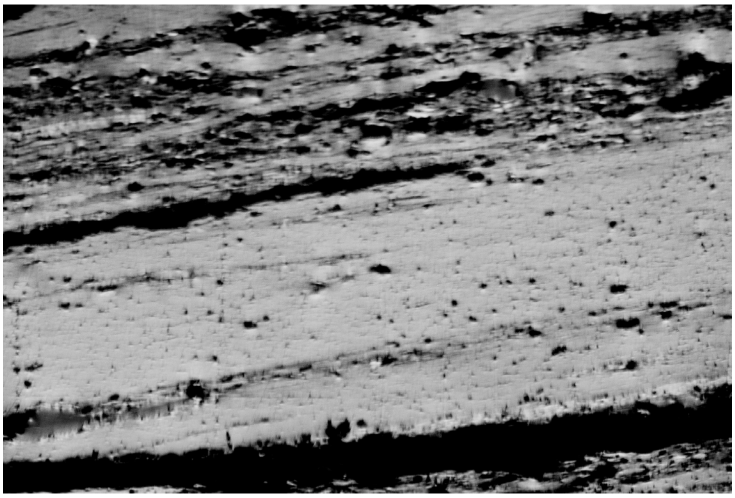


Plate 2a. Polished section of dense, highly reflecting, layered anthracite with stratified thermal cracks. From Zone A.

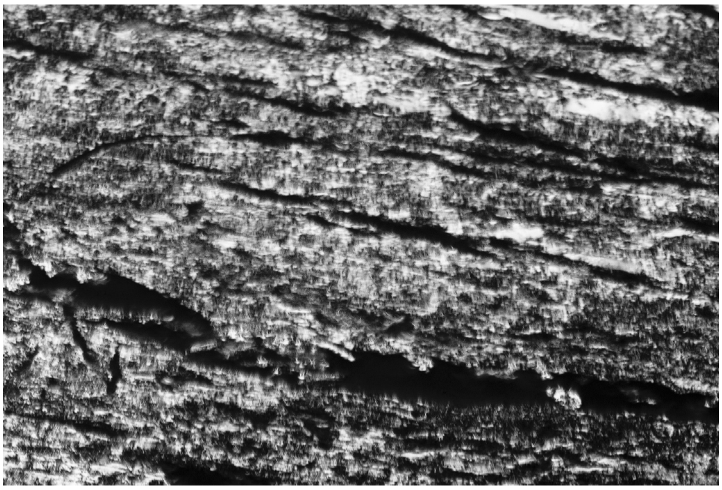


Plate 2b. Polished section of a piece of graphitised and granulated anthracite (presumably calcined) with stratified stress cracks.

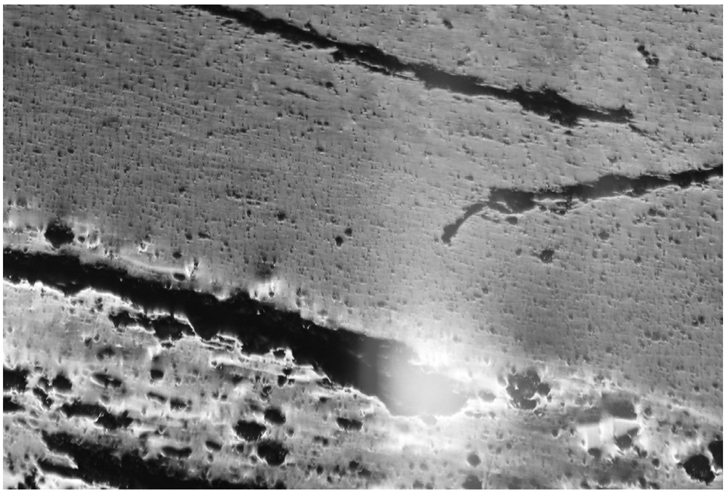


Plate 2c. Polished section of an anthracite particle with minute gas pores and partial reactivity along a thermal crack.

PLATE 3 – Forms of Carbon Residue from the Freeze line Slag (Mid Zone B and Inner Zone C)

Scale : 1cm = 50 microns

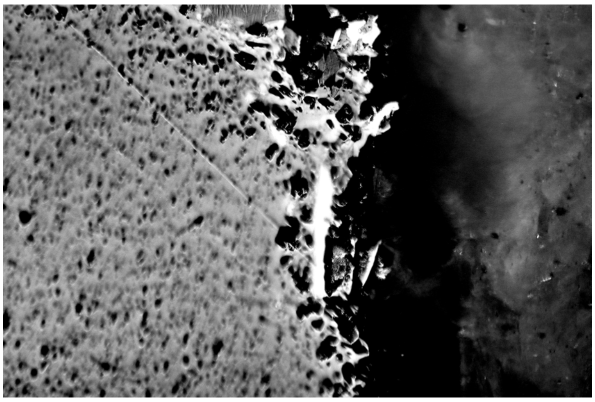


Plate 3a. Portion of an anthracite particle (left) with minute internal pores; replacement or nucleation of a liquid phase metal has taken place on the margin (white phase). Zone B.

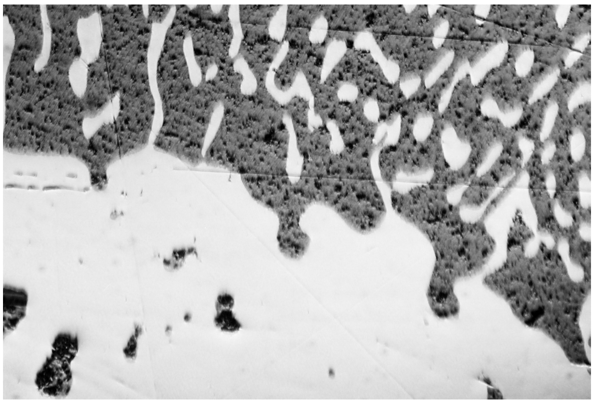
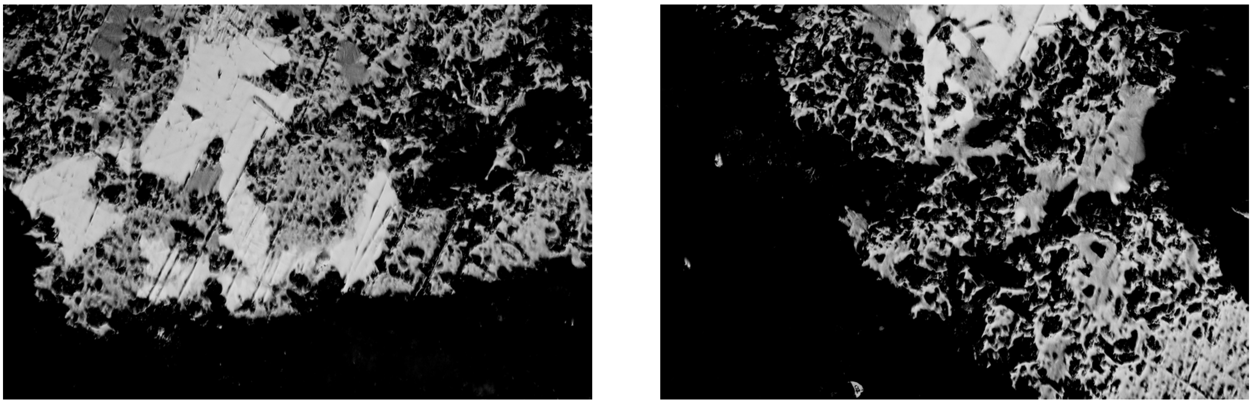
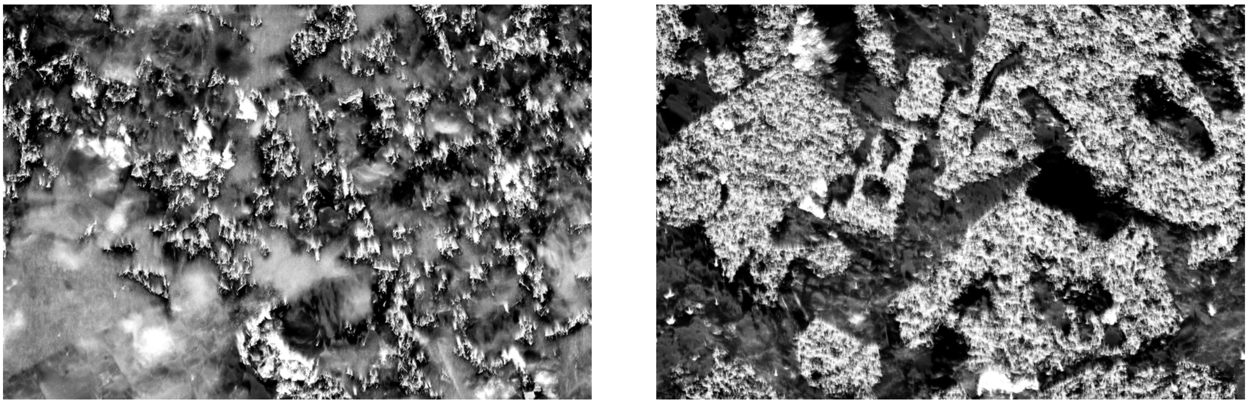


Plate 3b. Portion of an anthracite particle (grey, minutely porous in upper portion), with viscous phase metallic material (white) replacing or consuming the anthracite particle in the lower portion. Zone B.

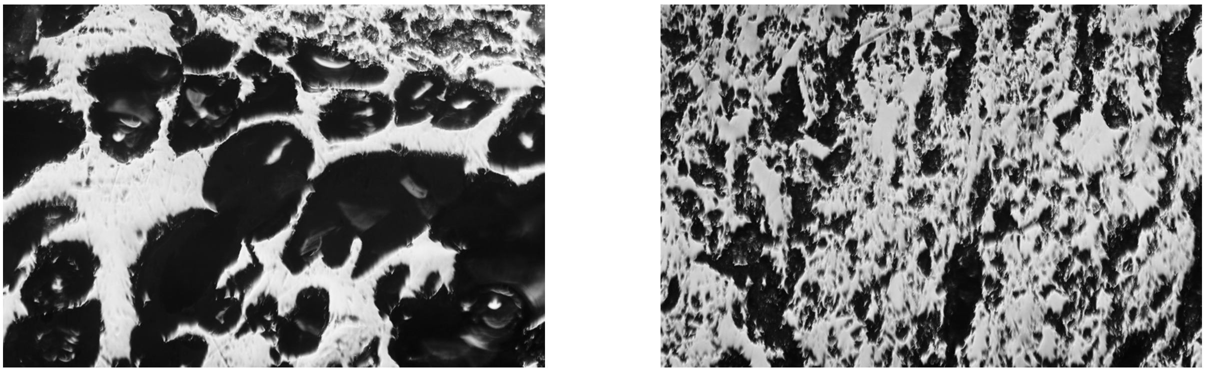


Plates 3c and 3d. Portion of partially consumed, porous chars derived from inertodetrinitic forms of lower rank bituminous coal. Replacement phases or the formation of crystalline metallic forms within the organic matrix are already well advanced (white angular forms within the char). Zone C.

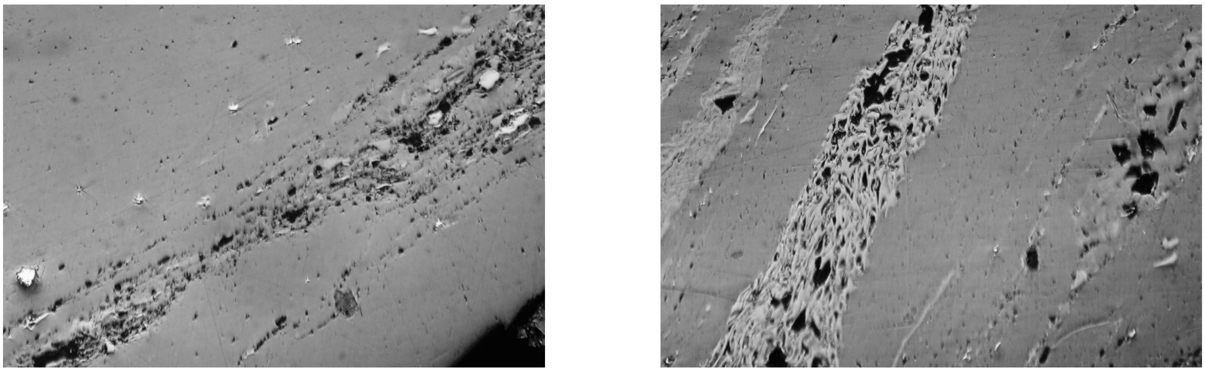


Plates 3e and 3f. Fragments of different forms of partially consumed chars embedded in the slag matrix encountered in Zone C, each associated with incipiently forming white metallic crystalline bodies. The highly porous char in Plate 3e is likely to have been derived from a bituminous C reactive coal whilst the less porous, fragmented and slightly graphitised char in Figure 3.f is likely to have been derived from a higher rank more inert coal. Zone C.

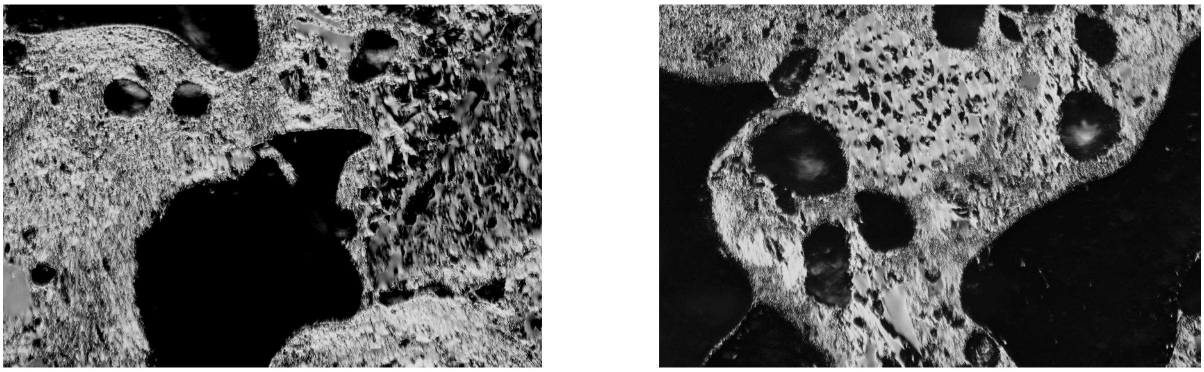
PLATE 4 – Typical Organic Constituents in the Feed Anthracite relative to other Selected Coke and Anthracite Samples.



Plates 4a and 4b. The dominant organic constituents encountered in the “Anthracite” supplied to the test case electric arc furnace (Sample 3). These are isotropic chars derived from lower rank bituminous C coals (73%). Plate 4a represents a highly porous, thin-walled isotropic char with large lumens derived from reactive-rich coals of bituminous rank. Plate 4b represents a more compact, unevenly walled porous char with smaller lumens but high internal surface area. The latter char is derived from inertodetrinitic coals of bituminous rank.



Plates 4c and 4d. The dominant organic constituents comprising an alternative metallurgical anthracite (Sample 5). The presence of high proportions of smooth, compact, homogeneous, gel-like vitrinite (darker grey matrix) is illustrated, which exhibits a mean random reflectance placing the sample in the rank category of Anthracite C (semi-anthracite). This maceral comprises 70% of the alternative anthracite product. Plate 4d illustrates the presence of bands of woody fibrous tissue (fusinite and semifusinite, white to pale grey) with empty botanical cells in some particles of this anthracite.



Plates 4e.and 4f. The dominant organic components of ASM coke (Sample 7), a product commonly used as a reductant by the metallurgical industry. Both Plate 4e and f illustrate the well-developed devolatilisation pores and thick, strong, anisotropically-textured walls. This metallurgical coke exhibits a high proportion of binder phase carbon material with fine to medium-sized circular anisotropic “crystallites”. These are derived from vitrinite and related reactive organic macerals from the mid-bituminous range of rank. Inertinite macerals are present as filler materials.