THE STRUCTURE AND REACTIVITY OF SOME METALLURGICAL CARBONS

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LONDON

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In collaboration with
British Steel Corporation
Teesside Laboratories

June, 1988
# The Structure and Reactivity of Some Metallurgical Carbons

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THE STRUCTURE AND REACTIVITY OF SOME METALLURGICAL CARBONS

By
Kenneth Edwin ADAMS

ABSTRACT

The reactivity and micro-structure of three coals and two cokes used in iron and steel manufacture have been studied by a variety of techniques, including gas sorption analysis, thermal analysis and microscopy.

Changes in surface areas and porosities of the coals and cokes during combustion have been determined by a gravimetric nitrogen sorption technique at 77K.

The cokes and coals have been studied by thermal analysis under isothermal and dynamic conditions in different gas atmospheres. Rates of reaction have been correlated with surface area changes. Attempts have been made to calculate activation energies from Kissinger plots of DTA data.

Microstructural changes in the cokes and coals during carbon burn-off have been investigated by electron microscopy. Relative porosities have been estimated by image analysis. Mechanical strengths of the cokes have been measured and correlated with porosity data.

Selected metals in the cokes and coals have been determined by flame photometry, atomic absorption spectroscopy and Mössbauer spectroscopy. The composition of residual mineral matter (ash) has been investigated by X-ray diffraction. The chemical compositions of the coal distillates have been characterised by IR/UV spectroscopy, NMR spectroscopy and by GC-MS techniques. Calorific values of the carbons have been determined.

Results are discussed in relation to previous work and to applications in blast furnace practice. In coal combustion the surface areas increase during the initial stages of carbon burn-off, reaching maximum at about 50% burn-off before decreasing. The increases are considerably higher at 400° and 500°C than at 300°C for all three coals. Hysteresis data from the sorption isotherms show that the coals develop full ranges of meso-porosity and some micro-porosity during burn-off at the higher temperatures.

However, the coal oxidation is only slightly accelerated, since most of the new surface is located in the micro- and meso- pores where access to atmospheric oxygen is restricted by slow diffusion, so that the earlier stages of oxidation are approximately linear with time. This improves our knowledge of current empirical industrial carbon solution tests.

There is comparatively little change in surface during the coking of the coals at 1000°C and only restricted sintering of the coal ashes at 300-500°C. In the combustion of the cokes in carbon dioxide at 1000°C the maxima in surface areas occur within 25% burn-off. However, one of the cokes shows a second maximum at later stages of burn-off, ascribed to the European component in the parent coal blend. This gives a more uniform rate of burn-off which is advantageous industrially.
Coke in a blast furnace has three roles i) as a chemical reductant, ii) as a fuel and iii) as a support refractory. The properties a good coke requires to fulfil its roles in a blast furnace are a narrow size range, optimum size and shape, high strength throughout the furnace temperature regime, low ash, sulphur, alkali and moisture contents, resistance to chemical attack and thermal degradation and perhaps most of all consistency.

Since there is a world shortage of prime coking coals which by themselves can be made into satisfactory metallurgical coke, the industrialised nations have been forced to blend coals to serve the purpose. Such blending has been found to be successful and this practice is being currently used in Britain by the British Steel Corporation.

1.1 ORIGINS OF COAL
Coal from which coke is made to fuel metallurgical processes results from the preservation of organic remains in anaerobic conditions of compacted mass of plant debris, the starting point for coal formation being usually peat or some similar accumulation of decaying vegetable material (Rastrick and Marshall, 1952; Gibson, 1979). By compaction and some moderate
heating during burial, peat is eventually converted into coal. Slow subsidence of the earth's surface giving rise to swamps, bogs and marshes are necessary environments for such a process. (Murchison and Westoll, 1968). The occurrence of warm humid climates have allowed, in the past, rapid vegetation growth which provided the very large accumulations of plant debris necessary to make thick coal seams (Scheiderman, 1980). Coal seams are interspersed with smaller quantities of inorganic material and the whole buried beneath inundating sediments. Eventually the familiar hard or bituminous coal is produced by the gradual elimination of the oxygen and hydrogen content (Gwen and Dickinson, 1975). This compacted material is not a pure form of carbon such as graphite or diamond that has associated with it various amounts of moisture and mineral matter (Karr, 1978).

The actual coalification process can be represented as shown in Table 1.1.

<table>
<thead>
<tr>
<th>Composition Wt % (dry mineral matter free)</th>
</tr>
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<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>Wood</td>
</tr>
<tr>
<td>Peat</td>
</tr>
<tr>
<td>Pressure and temperature</td>
</tr>
<tr>
<td>Lignite</td>
</tr>
<tr>
<td>Subbituminous</td>
</tr>
<tr>
<td>Bituminous</td>
</tr>
<tr>
<td>Anthracite</td>
</tr>
</tbody>
</table>

Table 1.1 Representation of the coalification process (Speight, 1983)
1.2 **COAL RANKING**

The 'rank' of a coal is defined as its position in the coalification series extending from peat at the lowest rank to anthracite which forms the highest rank. Essentially the rank of a fuel is determined by the degree of metamorphism to which it has been subjected. The process of coalification results in plant material being dehydrated, decarboxylated and demethanated (Francis, 1961).

High rank coals are classified according to their fixed carbon or volatile contents calculated on a dry mineral matter free (dmmf) basis. Low rank coals with carbon contents less than 69% dry mineral matter free are classified according to their calorific value calculated on a moist, mineral matter free basis (Williamson, 1967).

The rank series can be divided into four clear groups:

1. **Peat.** Partially decomposed plant material with a very large water content.

2. **Lignites and brown coals.** This defines an early stage of the transition to coal. Lignites contain some recognizable woody material but brown coals do not. Both forms have high water content and contain 40-55 per cent volatile matter. High moisture content causes disintegration on drying and gives a low calorific value. There is a liability to spontaneous combustion in air.
3. **Bituminous coals.** These coals are the most widely distributed of the solid fuels. They burn characteristically with a smokey flame and melt on heating in the absence of air. Bituminous coals with volatile contents of 30-45 per cent are required for steam-raising and general use, while those containing 19.6 to 32.0 per cent volatiles are the basis for the coke needed for the iron and steel industries. Coals of the bituminous type are characterized by bands of "bright" and "dull" constituents. The "bright" bands are derived principally from wood or bark material, while the "dull" bands arise from degraded plant material, which includes spores or pollen. A certain amount of inorganic material is inevitably present, which arises from the location upon which the original plants grew and from the mineral salts incorporated in their tissues and from minerals carried into the developing coal deposit by the ingress of water. This is in the main the ash component left after coal is burnt.

4. **Anthracites.** The change from bituminous coal to anthracite involves a progressive loss of coking properties due to the volatile content being reduced. Banding is almost completely missing in higher grade anthracites, which take on a metallic appearance and are hard. Anthracites comprise up to 95 per cent carbon and less than 5 per cent volatile material.
1.3 **COAL STRUCTURE**

By and large, coal is a material of non-uniform, polymeric structure, the components being normally of high molecular weight (Davidson, 1980; van Krevelen, 1961; Larsen, 1978). Carbon is the main constituent, which is present in a variety of molecules. These may be described in terms of several parameters such as size distribution, type and degree of crosslinking, aromaticity, number of hydroxyl groups, average size of condensed aromatic units and scissile bridging structure. In the process of coalification low molecular weight components like methane, phenolic compounds and aliphatic/aromatic hydrocarbons are produced early in the process and then are driven off. Coal structure also changes considerably. Most low rank coals have an open structure of randomly oriented small layers and a large pore system with an average pore diameter of about 50 nm. High-rank coals have highly orientated and large layers, an increased aromaticity and a much smaller pore system with an average pore diameter of 0.5-1.5 nm. Prime coking coals lie near the minimum in the rank vs porosity curve.

Coal molecules contain a number of heteroatoms. Hydrogen is present in a number of groupings such as -OH, -CH, -CH₂, -CH₃, -CHO and aromatic -CH, whilst oxygen is found in medium molecular weight compounds, particularly carbonyl or phenolic hydroxyl groups. Nitrogen and sulphur are also present and their oxidation in combustion products produces pollutants which are a major impediment to coal use.
Coal also contains a proportion of mineral matter which may be bonded into the organic matrix or which may be finely divided amongst them. This is mainly in the form of complex alumino-silicates, carbonates of Fe, Mg, Ca, sulphides, hydroxides and oxides of Fe; some free silica can also be present. The chemical composition of this ash controls the temperatures at which it softens and melts, this is known as the "ash softening point" which, if low, can make coal use difficult.

The porous nature of coal allows large quantities of moisture to be held particularly in the lower rank materials. Such inherent moisture reduces the calorific value of the coal by consuming heat energy to overcome its latent heat of evaporation (Zimmerman, 1979).

1.4 COAL CLASSIFICATION SYSTEMS

There is no agreed method for classifying coal. Some systems are based on rank and this is indicated by proximate analysis, which assesses moisture, volatile matter, ash and by difference, fixed carbon, or ultimate analysis where carbon, hydrogen, sulphur, nitrogen and ash are determined and oxygen estimated by difference. Reflectance is also used as an indicator of rank for pulverised coals (Williamson, 1967; Simeons, 1978).

For everyday use, coals need to be classified quickly and only a few aspects are taken into account (Karr, 1978).
American ASTM system uses the amount of fixed carbon and the calorific value on a dry (dmmf) and moist (mmmf) mineral matter free basis respectively. The European UNECE system uses dry ash free (daf) volatile matter content and the moist ash free (maf) calorific value to distinguish nine coal classes divided into sub-groups on the basis of their coking properties and with further sub-divisions based on caking properties (Speight, 1983). The outcome is expressed in a three digit code, with the first indicating class, the second caking behaviour and the third coking ability. The United Kingdom uses volatile matter content and coking properties, the latter parameter as ascertained by the Gray-King coke type test which is based on the appearance of a coke specimen prepared under standard conditions (Brame and King, 1967).

Classification of coals at present relies on limited and time consuming sampling techniques. This does not allow for variations in coal composition, which can occur within a few metres in the same seam, to be taken into account. Perhaps in the future continuous nuclear analysis (CONAC) might be employed to measure the elements in coal by gamma-ray frequencies which are emitted during neutron bombardment (EPRI Journal, 1980). Instantaneous readings would be given and it has been claimed that this method can be carried out on a large scale. Moisture content could also be ascertained by attenuation of microwaves passed through coal.
<table>
<thead>
<tr>
<th>Volatile Material (dmmf)</th>
<th>Coal type</th>
<th>Rank/Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Under 9.1% Anthracite</td>
<td>100</td>
<td>Gasification, domestic stoves and where no smoke is permitted</td>
</tr>
<tr>
<td>9.1 - 19.5% Low volatiles</td>
<td>200</td>
<td>Low volatile steam coal</td>
</tr>
<tr>
<td>Dry steam coal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coking steam coal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.6 - 32.0% Medium volatiles</td>
<td>300</td>
<td>Coking coals, gas coal, gasification</td>
</tr>
<tr>
<td>Prime coking medium/low</td>
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<tr>
<td>coking coal</td>
<td></td>
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</tr>
<tr>
<td>from over 32% High volatiles</td>
<td>400-400</td>
<td></td>
</tr>
<tr>
<td>to over 36% from very strongly coking</td>
<td>900</td>
<td>500 Coking/gas coals</td>
</tr>
<tr>
<td>coking to non-coking</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>700 General purposes</td>
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<tr>
<td>800/900 High volatile steam and house coals</td>
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</table>

(Chais & Peters, 1980).

Table 1.2. Outline of the classification system used by British coal.
Classification by rank (Table 1.2) fails to take note of the fact that coal arises by a number of metamorphic paths and is not invariably a satisfactory prediction of its technological properties. This has led to classification systems based on their maceral composition, particularly their vitrinite content, which does give such a guide. Eventually a system taking account of both rank and petrography might be developed.

1.5 COKING OF COAL

Steel will continue to be produced principally from pig-iron, and despite many experiments with other procedures, the blast furnace remains the main method of the industry; this needs the use of coke and the availability of the necessary tonnages of coking coals.

Coke is a residue arising from the destructive distillation of coking coal. Its main component is carbon but there is also some residual volatile material and some mineral matter present. Coke is normally produced in slot ovens although beehive or some other forms of non-recovery ovens are also in use.

During the carbonisation process at temperatures in the region of 350-500 °C, the coal softens and fuses into a solid mass i.e. semicoke. It is partially devolatilized at this point and further heating at temperatures up to 1000-1100 °C is required to lower the volatile matter to less than 1%. The character of
the coke produced very much depends on the softening and fusing process which occur during heating (Jasienko, 1978) and the subsequent contraction after semicoke formation.

Coals of CRC301 (Coal Research Station Classification), which are prime coking coals having volatile matter contents in the range of 19.6-32.0% dmmf, are used to make blast furnace coke. However, coals having an excess of 32% volatile matter of CRC400 and 500 have been used alone or in blends with prime coking coals and have been found also to be suitable (Grainger and Gibson, 1981).

In order to produce cokes having the desired properties, blending of two or more coals prior to carbonisation is usually required. High volatile coals of 32-38% volatile matter content are generally blended with low volatile coals of 15-20% volatile matter in mixes containing up to 20-40% low volatile coal. Some charges are a mixture of high, medium and low volatile coals and small additions of inert material such as coke breeze and anthracite are used as contraction modifiers. In general low volatile coal is normally added to enhance the physical properties of the coke, particularly its yield and strength (Horton and Freeman, 1979; Brown 1980).

Some consideration must also be given to the amount of ash and the sulphur contents and possibly also to the phosphorus levels of the coals used.
1.6 **REACTIONS IN THE BLAST FURNACE**

Eight chemical equations may be said to govern the reactions that occur in the operation of a blast furnace and each will be discussed in turn (Peacey and Davenport, 1979). The thermodynamic equations set out below apply since a comparison is being made of one state with another by the calculation of Gibbs free energy. For comparison, the thermodynamic functions are quoted for standard states. The relationship between changes in free energy and enthalpy is given by the Second Law of Thermodynamics.

\[ \Delta G = \Delta H - T \Delta S \]

A plot of standard free energy change versus temperature is known as an Ellingham diagram and is a convenient method of depicting reaction data (Ellingham, 1944).

If a reactant X will interact with oxygen in accordance with:

\[ X + \frac{1}{2} O_2 = XO \]  

(1)

and a metal M will react with oxygen in accordance with

\[ M + \frac{1}{2} O_2 = MO \]  

(2)

then if the metal oxide MO is mixed with the reactant X the following reaction will be favoured:

\[ MO + X = = M + XO \]  

(3)

provided that the free energy curve for (1) lies below that for (2) on the Ellingham diagram.

In a blast furnace X would equate to carbon or hydrogen both of which are capable of acting as reducing agents. Ellingham
diagrams of sulphides may be treated in exactly the same way as the oxide diagrams but sulphides tend to be less stable than their corresponding oxides.

In connection with the operation in a blast furnace

a) the stability of CO$_2$ remains virtually unchanged over the range of interest (because $\Delta S$ is nearly zero) but CO increases in stability with increasing temperature (because $\Delta S$ is positive)

b) Metallic oxides usually decrease in stability with increasing temperatures but Fe$_2$O$_3$ reverts to a more stable lower compound FeO on heating in the region of 500 K and does not decompose until a much higher temperature is reached.

The main supply of reducing gases and energy in a blast furnace comes from burning coke

$$2C(s) + O_2(g) = 2CO(g)$$

where C(s) is carbon in the form of solid coke

$$\Delta G^\circ = - 22400 - 176 \text{ } T \text{j mol}^{-1} \quad (1)$$

Oxygen is injected into the furnace as an air blast through the tuyeres and is entirely used up by reaction with the coke charge within the immediate vicinity of the tuyeres. If this blast contains moisture a reaction between coke and water vapour occurs to give both hydrogen and carbon monoxide-
\[
C(s) + H_2O (g) = CO(g) + H_2 (g) \quad (2)
\]
\[
\Delta G = +135000 - 142 \text{ T J mol}^{-1}
\]

It will be seen from the free energy equations for reactions (1) and (2) that while reaction (1) causes heating of the charge and temperatures of the order of 2300 K in front of the tuyeres (\(\Delta H^{\rightarrow} - \text{ve}\)) reaction (2) will have the effect of cooling this region in the furnace. Thus it becomes clear that the injection of steam in a blast furnace is a method that may be used to control the temperature of the lower regions of the furnace while producing reducing gases for use higher up the stack.

Another reaction that occurs within the blast furnace is the disproportionation of carbon monoxide:

\[
2CO (g) = C (s) + CO_2 (g) \quad (3)
\]
\[
\Delta G = -170000 + 174 \text{ T J mol}^{-1}
\]

This reaction (the reverse of the Boudouard reaction) entails the deposition of soot within the solid charge at temperatures of the order of 770 - 970 K. The carbon so deposited returns to the lower regions of the furnace as the burden moves down the column. Gas compositions at different levels in a blast furnace are set out in Table 1.3. Such compositions arise as the result of the gas reactions and the various reduction reactions which occur in the furnace.
Two paths of reduction of wustite (non-stoichiometric FeO) are known to occur in the blast furnace. These reactions given by equations (4) and (5) have been termed indirect (or gaseous) reduction and direct reduction respectively:

$$\text{FeO}(s) + \text{CO}(g) = \text{Fe}(s) + \text{CO}_2(g) \text{ (indirect reduction)}$$ (4)

$$\Delta G = -19000 + 22.5 T \text{ J mol}^{-1}$$

$$\text{FeO}(s) + \text{C}(s) = \text{Fe}(s) + \text{CO}(g) \text{ (direct reduction)}$$ (5)

$$\Delta G = +147600 - 150 T \text{ J mol}^{-1}$$

The latter reaction between two solids is kinetically unfavourable, but a two-stage reaction that would give the result in equation (5) would be

$$\text{FeO}(s) + \text{CO}(g) \rightarrow \text{Fe}(s) + \text{CO}_2(g)$$ (4)

$$\text{C}(s) + \text{CO}_2(g) \rightarrow 2\text{CO}(g)$$ (6)
Thus the net result of direct reduction also takes place via a gaseous reducing agent. Indirect (or gaseous) reduction occurs within the stack of the furnace whilst direct reduction is achieved in the bosh and tuyere regions. Reaction (6), the Boudouard reaction, is termed the solution loss reaction since it is the way in which loss of carbon can occur before it reaches the tuyere region of the furnace.

If hydrogen is produced either by the water gas reaction between water vapour and carbon in the tuyere region of the furnace, equation (2), or by the dissociation of hydrocarbons, it acts as a reducing gas within the stack of the furnace.

\[
\text{FeO}(s) + \frac{1}{2}\text{H}_2(g) = \text{Fe}(s) + \frac{1}{2}\text{H}_2\text{O}(g)
\]

\[
\Delta G = 10050 + 5.2 \text{ T J mol}^{-1}
\]

The decomposition of limestone occurs as follows:

\[
\text{CaCO}_3(s) = \text{CaO}(s) + \frac{1}{2}\text{CO}_2(g)
\]

The nitrogen, present in the air supply, is unchanged in its passage through the furnace.

1.7 ROLE OF COKE IN THE BLAST FURNACE

In a blast furnace the stack of the furnace widens downwards towards the hearth region which permits the burden to move downwards in a uniform manner. In the bosh region of the furnace the cross-sectional area is decreased by approximately 20% to allow for the decrease in volume caused by the melting of the ferruginous components in the charge while still

- 15 -
supporting the upper volume of the charge. The coke combustion zones are situated at the base of the bosh in front of the tuyeres, through which air for combustion is blown.

Beneath the bosh is the hearth of the furnace which is the collecting region for liquid metal and slag. There are two types of reaction to be considered in the blast furnace. In the stack region gas reactions between carbon dioxide and coke carbon and reduction of iron ores by CO and H₂ prevail. In the hearth region slag metal reactions take place with the coke. Both types of reaction occur in the bosh which separates these two regions.

The greatest temperatures are found directly in front of the tuyeres, where oxygen in the air blast reacts with the coke to give temperatures in the immediate vicinity of about 2280 K.

In practice the distribution of the thermochemical zones is more complete and can be controlled by the burden distribution pattern adopted. Common types of distribution are:

a) the V-type
b) the inverted V-type
c) the M-type.

In the inverted V-type larger materials are found in the centre of the furnace and so the gas velocity is greatest in the
centre of the furnace. In the V-type, the larger lumps occur around the shell of the furnace and so the gas flow is greatest in this part of the furnace. The M-type pattern is a combination of the V-types such that the gas flow is concentrated both at the walls and at the centre of the furnace leaving a zone of lower gas passage between the wall and furnace.

1.8 COKE REACTIVITY

Coke reactivity has been discussed by Carter (1983). Interaction between coke and carbon dioxide can occur in the blast furnace giving rise to carbon monoxide. This phenomenon known as "solution loss" is undesirable, if extensive, as it reduces the quantity of coke available for the reduction of iron ore, hence a coke with a low reactivity to carbon dioxide is a preferred requirement (Mott & Wheeler, 1939).

Coke reactivity is usually understood to refer to the rate at which coke reacts with oxidising gases. As coke descends through the blast furnace the temperature, porosity, topography, mineral matter etc. are constantly changing. Thus "reactivity" is a changing multidependent parameter, being not so much an intrinsic property of the coke, but an implied behavioural property.

Interest in coke reactivity is of long standing. In a study of American blast furnaces Howland (1916-17) stated in 1916 "the
The most desirable thing about a coke is that quality in the carbon which will allow of its being instantaneously burnt to carbon monoxide. The application of reactivity testing up to 1945 is reviewed by Mayers (1945) who reserves the term "reactivity" for tests in which the oxidising gas is CO₂, and "combustibility" for tests using air or oxygen in which extent of reaction was determined by weighing or gas analysis and "ignition point" for tests using air or oxygen in which extent of reaction was determined by temperature measurement. This latter test is related to the "critical air blast test" (see later) developed by the Northern Coke Research Committee. Coke reactivity is also reviewed by Blayden (1958).

Although great disparity exists between laboratory test and blast furnace conditions, importance is placed industrially on the measurement of reactivity to assess coke quality and to predict blast furnace performance. The test can indicate to what extent the Boudouard reaction will proceed, without the influence of alkalis in the upper part of the furnace shaft, i.e. to what extent carbon will be lost before it takes part in the reduction of metal oxides.

Many tests have been developed to measure reactivity. These vary in detail but in principle measure the rate of conversion of CO₂ to CO by granular coke in the temperature range 950 to 1100 °C. Extent of reaction may be determined by weight loss of the coke or CO/CO₂ ratio of the effluent gas. Although
Mayers states "...all the methods mentioned (i.e. reactivity, combustibility, ignition point) are simply different devices for measuring the same property", when a series of similar cokes are compared by different reactivity tests they are not necessarily placed in the same order by all of them. Physical factors which are not evaluated must play some part in effective reaction rate.

Indirect methods such as measurement of electrical conductivity, and measurement of strength after reaction have also been investigated by Brown (1980).

The E.C.E. test (1965) for measurement of reactivity of metallurgical coke was published in 1965 to standardise tests for the chemical reactivity of cokes. Dry coke (7-10 g) of 1 to 3 mm particle size is reacted with CO$_2$ at 1000 °C, under standard flow conditions, and the effluent gas sampled after a set time. The CO content of the reaction gas is determined by infra-red spectroscopy, thermal conductivity or absorbing the CO$_2$ in KOH solution. A coefficient of reaction speed $K_m$ is calculated from the conversion of CO$_2$ per second and the sample mass. Many laboratories use their own standard test.

The method used to measure reactivity is obviously chosen with the intended use of the coke in mind and the limitations of it being a routine comparative test. The presence of alkalis in the coke increase reactivity. Methods of evaluating coke reactivity are summarised by Carter (1983).
Reactivity of coke to air is assessed by the "critical blast test" - (CAB) as set out in B.S. 1016, Part 13, revised 1980. In brief, the CAB test consists of electrically igniting a bed of graded coke in a standard combustion chamber, with dry air passing through the bed at a rate of 4.25 l min\(^{-1}\). When the coke is fully ignited the air rate is reduced to a pre-selected value for 20 min and then raised to the original value to attempt resuscitation. This procedure is repeated with fresh portions of the coke and with other rates of air flow until the critical value is found.

The CAB value is calculated using the formula

\[
\text{CAB} = \frac{11.53 \, P \, V}{(273.15 + T) \, d} \times 10^3
\]

where 
- \(d\) = the diameter of combustion chamber, in mm
- \(P\) = the atmospheric pressure in bar
- \(V\) = the air blast rate at which resuscitation occurs in litres/min of dry air as measured using a flowmeter
- \(T\) = the air temperature, in °C.

The more reactive the fuel the lower is its CAB e.g.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CAB (litres/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low temperature coke</td>
<td>0.42</td>
</tr>
<tr>
<td>High temperature coke</td>
<td>1.84</td>
</tr>
</tbody>
</table>
Brame and King (1967) have implied that this British Standard test for determining the reactivity of coke is somewhat general in that it has been used to calculate values for boiler firing, domestic stoves and open fires. However, the Nippon Steel Corporation in preparing a specification of coke requirements for their large capacity blast furnaces developed a coke reactivity test and associated with this test a post-reaction strength (PRS) test. Both tests have been adopted in the U.K.

Basically, the tests consist of:

i) exposing a 200 g sample of coke which has been prepared to a size of 20 ± 1 mm square aperture screen to carbon dioxide attack at 1100 °C in a reaction vessel for 2 h and determining weight loss, which expressed as a percentage of the changed weight gives the reactivity.

ii) rotating the residual coke from test (i) at 20 rpm in a tubular test drum 0.7 m long and 0.13 m in diameter for 600 revolutions. The +10 mm material after testing, expressed as a percentage of residual coke charged to the drum gives the post-reaction strength.

The Japanese minimum quality requirement was set for reactivity to be <35 and post-reaction strength > 48.0, but the more successful operators such as Oita in 1977 were using a reactivity figure of 26.7 and a PRS figure of 60.4.
Brown (1978) reported linear relationships between (a) reactivity and post-reaction strength, (b) reactivity and maximum reflectance, (c) PRS and maximum reflectance; also (d) reactivity values for individual coals had been shown to be additive when examining the reactivities of blends, allowing blend reactivities to be predicted with some certainty from reactivity values of cokes made from individual coals, which simplified blend formulation. (e) Preheating had a negative effect upon reactivity reducing the value by three to five percent as opposed to charging wet. (f) Reactivity and post-reaction strength were strongly rank dependent and bimodal blends were more prone to carbon solution and breakdown than were blends with unimodal reflectograms. (g) Reactivity was not affected appreciably by variations in carbonizing conditions.

There is also the important point that circulating alkali loads have adverse affects on reactivity in a blast furnace. The adverse effect of alkalis on coke properties and blast furnace operation are well known. Test details, comments and difficulties encountered with alkali problems have been reported over a number of years in the Coke Oven Managers' Yearbooks, particularly by Monson (1979), Brown (1980) and Hyslop (1981) who include appropriate references to work reported on in this area by Japanese researchers.
Coke reactivity is considered to be an important coke property which has been related to coke degradation in the blast furnace and in blast furnace operation. While it is true that coke reactivity can be related to coal blend rank, coke structure and ash chemistry, in practice little is known about the nature of the structural changes occurring during the carbon solution process or the role of the component coke materials.

The aims of this research are therefore as follows:

1. To study the changes in the surface areas of high and low reactivity cokes during the carbon solution and oxidation processes over a range of temperatures in CO₂ and O₂ atmospheres, using gas sorption techniques.

2. To attempt to determine the role of the three component coals used in the production of the low reactivity coke, using gas sorption.

3. To study differences in structure, chemistry and mineralogy of high and low reactivity cokes and relate them to coke reactivity.

Two cokes, one of low reactivity and the other of high reactivity were supplied by BSC. Their compositions are given in Table 1.3. The English, European and Australian coals used
in the low reactivity coke were also supplied for study.

Table 1.4 Coke compositions

<table>
<thead>
<tr>
<th>Coke 1</th>
<th>Coke 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>60% Yorkshire (HV)</td>
<td>50% English (HV) (Coal A)</td>
</tr>
<tr>
<td>25% Nottingham (HV)</td>
<td>30% European (MV) (Coal B)</td>
</tr>
<tr>
<td>15% S Wales or Kent (LV)</td>
<td>20% Australian (LV) (Coal C)</td>
</tr>
<tr>
<td>producing a coke with high reactivity</td>
<td>producing a coke with low reactivity</td>
</tr>
</tbody>
</table>

HV = high volatile  
MV = medium volatile  
LV = low volatile

The current research was directed towards the examination of these cokes together with the three coals which are used to prepare Coke 2.
REFERENCES

CHAPTER 1


Scheiderman, S J. Thick and steep seam mining, World Coal, 6, 1980.


Chapter 2

GAS SORPTION ANALYSIS STUDIES

The reactivity of a solid material towards gases is governed, inter alia, by its active surface area. Thus measurements of specific surface areas at various stages of reaction may provide useful information about the reactivity of a material.

In this research surface area changes during carbon burn-off have been monitored for a selection of metallurgical carbons. This chapter describes such studies by gas adsorption on three coals and two cokes made therefrom.

2.1 INTRODUCTION

Previous studies on surface area measurements of carbons have been summarised by Carter (1983). Such measurements can highlight the wide variations in the reactivities of different industrial carbons (Carter, Glasson and Jayaweera, 1981).

The variations in reactivity of three metallurgical cokes used in the zinc-lead blast furnace have been studied by Carter et al. (1982, 1984). These studies showed also the effect on reactivity of doping the cokes with boric oxide. Reduced reactivity at high temperature is ascribed to the physical blocking of pores in the cokes by the additive.
The results of some of the present research has been published already (Adams, Glasson and Jayaweera, 1983, 1985, 1986 and 1987).

2.2 GAS SORPTION ANALYSIS

2.2.1 Principles

This method of analysis relies on the fact that when a solid is exposed in a confined space to a gas at a definite pressure, the solid will commence to adsorb the gas. Adsorption takes place because surface atoms have no like atoms above the surface plane with which to form chemical bonds. Since a surface atom is capable of forming a similar number of bonds to those in the body of the solid, it attracts fluid molecules in order to satisfy bonding capacity. This situation exists at all interfaces.

Gases and vapours are adsorbed by solids in different ways, which may be distinguished according to the type of force holding the molecule to the surface: (a) van der Waals adsorption, which is physical, where the adsorbed molecules are held by residual forces round the molecules (such adsorption is reversible), (b) chemisorption, where the adsorbed layer is combined chemically by covalent forces to the solid, and (c) electrostatic adsorption, where the adsorbed layer is held by electrovalent forces. All these adsorptions are exothermic, and the mass adsorbed decreases with increasing temperature.
For a gas-solid system at constant temperature the amount adsorbed is related to the gas pressure by an adsorption isotherm. The Freundlich (1909) adsorption isotherm is of the form:

\[ x = kc^n \]

where \( x \) = the amount adsorbed  
\( c \) = the concentration  
\( k \) & \( n \) = constants, where \( n > 1 \)

This equation does not allow for saturation of the surface. The amount adsorbed increases as \( c \) increases. If the equation applies, a plot of log \( x \) against log \( c \) will give a straight line of slope \( n \).

Langmuir (1916) suggested that adsorption is an equilibrium between condensation of molecules on the surface from a gas and evaporation of molecules from the surface, disregarding the length of time involved. The equation he proposed can be written:

\[ \theta = \frac{kp}{V+kp} \]
where
\[ \Theta = \text{the fraction of the surface covered with a unimolecular layer} \]
\[ V = \text{a constant for the system} \]
\[ k = \text{a constant} \]
\[ p = \text{the gas pressure} \]

There are two special situations which arise: (a) when the surface is only partially covered (in this case \( \Theta \) would be small and the amount of gas adsorbed is proportional to the pressure), and (b) at high pressure when the surface is completely covered and the amount of gas adsorbed is independent of pressure. Between these limits the equation simplifies to the Freundlich isotherm.

Isotherms of the Langmuir type are founded on simplified assumptions, namely, (a) all sites of the surface area are considered to be the same, and (b) no interactions between adsorbed molecules occur. Systems to which these conditions apply are referred to as exhibiting "ideal adsorption" but in reality there is often deviation from the Langmuir equation. Difference may arise when the surface is not uniform; there may also be some interaction between adsorbed molecules, since a molecule on a surface might make it either more or less difficult for another molecule to be received at a nearby location.
The amount of gas adsorbed on a solid depends upon the pressure, \( p \), temperature, \( T \), the nature of the gas and the nature of the solid

\[ x = f(p, T, \text{gas, solid}) \]

where \( x \) is the amount of gas adsorbed, usually expressed in grammes of adsorbate per gramme of adsorbent. When the adsorbate is below its critical temperature, the form:

\[ x = f\left(\frac{p}{p_0}, T, \text{gas, solid}\right) \]

is more useful, where \( p_0 \) is the saturated vapour pressure of the adsorbate at temperature \( T \).

The majority of adsorption isotherms resulting from physical adsorption may be grouped for convenience into five classes - the five types of classification originally proposed by Brunauer, Deming, Deming and Teller (BDDT) (1940), nowadays commonly known as Brunauer, Emmett and Teller (BET) (1938) classification. The five types are illustrated in Figure 2.1. Type 4 possesses a hysteresis loop (dotted line), where the lower branch represents progressive addition of vapour to the system and the upper branch represents progressive withdrawal. It is possible to use isotherms of Type 2 and 4 to calculate specific surface and use Type 4 isotherms for making an estimate of porosity of the adsorbent.
Figure 2.1. The five types of adsorption isotherm in the BET classification.
Types 3 and 5 isotherms are relatively rare. Type 1 isotherms are typical of microporous materials.

Measurement of surface area by gas sorption depends on ascertaining the monolayer capacity ($x_m$). When the quantity $x_m$ is multiplied by the area occupied by a single adsorbed molecule ($A_m$) the surface area (in m$^2$ g$^{-1}$) is calculated from $S = x_m N A_m \times 10^{-20}$ where $A_m$ is in square Angstrom units, $N$ is the Avogadro constant, $M$ is the relative molar mass of adsorbate, and $x_m$ is in g adsorbate per g of solid. The assumption made is that the adsorbate molecules are close packed on the surface. Calculation of adsorbate cross sectional areas, from liquid density, critical constant data etc, has been discussed by Gregg and Sing (1967) and with respect to carbons by Sutherland (1967). A value of 16.2 Å$^2$ for N$_2$ at 77 K was used in the present work.

When characterising a solid by physical adsorption measurements, a model of the adsorption process has to be used. In Langmuir's original work a kinetic approach led to the isotherm, $x = x_mbP$ where $b$ is an adsorption coefficient and $x = \frac{x_m b P}{1 + bP}$ is the amount sorbed per g adsorbent at equilibrium pressure $P$. The same isotherm can be obtained on statistical mechanical grounds. Thus a graph of $\frac{P}{x}$ versus $P$ is linear and $x_m$ may be
calculated from the slope. Langmuir's equation would be applicable in the case where Type 1 isotherms are obtained. The equation could not be applied with success for non-porous or wide pore adsorbents due to multilayer formation and/or capillary condensation.

For the cokes studied in the current research where Type 2 isotherms were found, surface areas were estimated from the BET equation. Derivation and discussion of the BET equation is given by Gregg (1961) and Lowell (1979). The equation was used in the form

\[ \frac{p}{x(p_0-p)} = \frac{1}{x_mC} + \frac{c-1}{x_mC} \cdot \frac{p}{p_0} \]

where \( x \) is the amount sorbed per g adsorbent at equilibrium pressure \( p \), \( p_0 \) the SVP of the adsorbate and \( c \) is a constant equal to \( \exp \left( \frac{E_1-E_2}{RT} \right) \), \( E_1 \) being the heat of adsorption of the first layer and \( E_2 \) that of subsequent layers, and taken as the heat of liquefaction of the adsorbate.

Hence a plot of \( \frac{p}{x(p_0-p)} \) versus \( \frac{p}{p_0} \) should result in a straight line of slope \( \frac{c-1}{x_mC} \) and intercept \( \frac{1}{x_mC} \). The addition of slope and intercept gives \( \frac{1}{x_m} \).

Adsorption onto porous materials can give rise to hysteresis, where the desorption branch of the isotherm is different from that of the adsorption. Observation of a reproducible isotherm hysteresis loop can be associated with a form of porosity in
the adsorbent. The relationship between shape of hysteresis loop and pore geometry is classified by de Boer (1956). Pores are classified as macro \((r > 25\, \text{nm})\), meso \((r = 1\, \text{to} \, 25\, \text{nm})\) and micro \((r < 1\, \text{nm})\) where \(r\) is the pore radius.

Particle size may be estimated from the surface area value, \(S\). It is assumed that the particles have the same size and shape and the mean particle length \(l\) may be calculated from \(S = \frac{f \rho}{l}\) where \(\rho\) is the density of the material and \(f\) a parameter which is 6 for cubes and spheres, 4 for rods and cylinders and 2 for plates. The length \(l\) is then a mean minimum size of crystallites.

In this research, surface areas have been calculated from adsorption data by using the BET equation.

2.2.2 The Nitrogen Sorption Balance

Plate 2.1 shows the nitrogen sorption balance (Cl microforce balance Mark 2), for the determination of surface areas within the range 0.2 to 1000 m\(^2\) g\(^{-1}\) using samples of 0.25 g. The weighing part is contained in the balance head and connected by a multi-way cable to the electrical control cabinet.

The head unit contains an electronic bridge circuit maintained in continuous balance by a servo system. The balance arm carries a shutter interposed between a lamp and a pair of silicon photocells. With the arm central, the cells have equal
Plate 2.1. The Nitrogen Sorption Balance.

Key:
A  to vacuum pump
B  cold trap
C  manometers
D  system for independent flushing of reservoir and doser
E  doser of approximately 40 cm³ capacity
F  nitrogen reservoir
G  CI analogue control unit Mark 2B
H  reservoir manometer
J  balance head unit
K  sample
L  degassing furnace
M  to nitrogen cylinder
Plate 2.1. The Nitrogen Sorption Balance
resistance and no bridge current flows. A small displacement of the arm changes the relative illumination of the photocells causing a bridge current. This current passes through a movement coil and rapidly restores equilibrium. Thus the head unit electromagnetically balances the torque produced by the sample weight. The vacuum head has 824 glass fittings and is designed to work at pressures down to $10^{-6}$ torr ($1.33 \times 10^{-4}$ Pa).

The generated weight-proportional current is monitored by the CI Mark 2 analogue control unit with five electrical weight ranges, selected by direct switching. Stabilised power supply and zero adjustment are provided. The Mark 2B has weight ranges $0 - 25$ µg, $0 - 250$ µg, $0 - 2.5$ mg, $0 - 10$ mg and $0 - 100$ mg. Ranges 2, 3 and 4 were those most frequently used.

2.2.3 Procedure

The sample was placed in an aluminium foil bucket suspended from the balance with a fine pyrex fibre (27 cm long). This enabled the sample to be at least 15 cm below the level of the liquid nitrogen contained in a Dewar flask, keeping the temperature to $-196.0 \pm 0.1 \, ^{\circ}C$ as previously determined by Glasson (1956). In practice, the sample is about $1 \, ^{\circ}C$ warmer than the liquid nitrogen outside the balance limb (as determined by Glasson and Linstead-Smith (1973) using internal and external thermocouples).
The balance head was coupled by the taps and glass tubing to a two-stage rotary pump (enabling the pressure to be reduced to $10^{-3}$ torr), and to a nitrogen reservoir and gauges, the nitrogen pressure being measured by the mercury manometers.

The cold trap was immersed in a Dewar flask of liquid nitrogen in order to aid outgassing of the sample and to reduce the effects of thermal transpiration.

The system was evacuated and the sample degassed at room temperature or by heating to 200 °C for at least 30 min. True sample weight (i.e. less adsorbed moisture and volatiles) was noted, the balance zero then set and the balance limb containing the sample immersed in liquid nitrogen.

A pressure of 30 - 50 mmHg (4000 - 6670 Pa) of nitrogen was introduced and the system allowed to attain equilibrium (30 min), when the nitrogen pressure and uptake were recorded. Six or seven readings were taken in the BET range (0.05 to 0.30 relative pressure). Thereafter pressures of 70 - 80 mmHg (9.33 - 10.66 kPa) of nitrogen were introduced, giving another seven readings up to the maximum relative pressure obtainable (0.96).

Desorption points were determined by pumping out to similar pressures of nitrogen. Weight corrections for buoyancy effects of the sample, container and suspension were applied to the uptake readings.
2.3 COKE SURFACE AREAS

Changes in surface areas, porosity and rate of oxidation were investigated for the two cokes.

Samples of the cokes (consisting of approximately 5 mm diameter lumps) were burnt off in a Stanton Redcroft Mass Flow balance at 1000 °C in flowing carbon dioxide (35.2 cm³ min⁻¹) for different lengths of time. The extent of burn-off was determined by weighing each sample before and after reaction. Some samples were burnt off in static air.

The adsorption (and desorption) isotherms of the burnt-off samples were determined on the CI Electronics Mark IIB vacuum microbalance using up to 200 mg samples and with nitrogen as the adsorbate at 77 K.

The apparent density of some samples were determined by nitrogen gas displacement on the vacuum microbalance.

2.3.1. Results

Figures 2.2 and 2.3 show the extent of carbon burn-off with time at 1000 °C in carbon dioxide for Coke 1 and the Coke 2 respectively. The rate of burn-off (expressed as a percentage of the mass of original carbon) is almost linear for Coke 2 up to about 90% burn-off. For Coke 1, the curve is sigmoidal, with the rate of burn off increasing in the first hour and then decreasing gradually.
Fig 2.2. Coke No. 1
Oxidation in CO₂ at 1000°C.
Fig. 2.3. Coke No. 2
Oxidation in CO₂ at 1000°C
The variations in surface area during oxidation in carbon dioxide at 1000 °C are shown in Figure 2.4 for Coke 1 and in Figure 2.5 for Coke 2. The graphs show the variations in the specific surface area, $S$, of the residual material and the surface area, $S'$, of the residue from one gram of original material, with time and with per cent burn-off.

The adsorption (and desorption) isotherm for the 22.6% burn-off sample of Coke 1 in carbon dioxide at 1000 °C is shown in Figure 2.6. Figure 2.7 shows the isotherm for the 16.8% burn-off sample of Coke 2 in air at 1000 °C (time of burn-off is 30 minutes). It was found that all the materials gave isotherms characteristic of Type I and/or II on the BDDT classification (Brunauer et al., 1940). The data fitted into linear BET plots (Brunauer, Emmett and Teller, 1938) from which specific surface areas were calculated.
Figure 2.4 Oxidation of British Steel coke No. 1 in carbon dioxide at 1000 °C.
Indigenous: 60% Yorkshire,
25% Northants,
15% S. Wales (or Kent).
Figure 2.5 Oxidation of British Steel coke No. 2 in carbon dioxide at 1000 °C.
50% British (Durham),
30% European,
20% Australian.
Fig. 2.6. Adsorption of $N_2$ on coke No.1 oxidised 22.6% in $CO_2$ at $1000^\circ C$. 
Fig: 2.7. Coke No. 2 burnt at 1000°C in air (16.8%) burn-off Adsorption of N₂ at -196°C.
Table 2.1 Porosity data for cokes

<table>
<thead>
<tr>
<th>Coke</th>
<th>Coke 1</th>
<th>Coke 2</th>
<th>Nantgarw</th>
<th>Polish</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>apparent density/gcm⁻³</td>
<td>closed pore volume/cm³g⁻¹</td>
<td>mean maximum pore radius/nm</td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coke 1</td>
<td>1.27</td>
<td>0.346</td>
<td>0.261</td>
<td>15.5</td>
</tr>
<tr>
<td>Coke 2</td>
<td>1.34</td>
<td>0.305</td>
<td>0.220</td>
<td>32.4</td>
</tr>
<tr>
<td>Nantgarw</td>
<td>1.48</td>
<td>0.232</td>
<td>0.150</td>
<td>33.4</td>
</tr>
<tr>
<td>Cwm</td>
<td>1.40</td>
<td>0.273</td>
<td>0.188</td>
<td>15.8</td>
</tr>
<tr>
<td>Polish</td>
<td>1.40</td>
<td>0.273</td>
<td>0.188</td>
<td>15.3</td>
</tr>
</tbody>
</table>

Closed pore volumes were calculated for the two cokes from apparent density measurements. The calculations were made using "true" densities as ascertained by helium penetration Williamson (1967) (and specific volumes) corresponding to (a) the X-ray density of graphite and (b) the "true" density of cokes carbonised at 1000 - 1100 °C. Results are shown in Table 2.1 and compared with the values for Nantgarw, Polish and Cwm cokes used in the zinc-lead blast furnace Carter (1983). These figures represent a mean of up to ten measurements.
2.3.2 Discussion

At lower percentage carbon burn-off, both cokes showed considerable increases in specific surface areas, $S$, reaching maxima within 25% burn-off. This is ascribed to the formation of pores at the coke surface, including opening of initially closed pores as the oxidation proceeds. Thus although the original cokes have only macroporosity, yet they develop full ranges of mesoporosity (pore diameters 2 - 50 nm) (Robens, 1980) in the earlier stages of carbon burn-off in carbon dioxide and in air, as shown by the hysteresis in the isotherms in the relative pressure range 0.37 upwards.

The surface areas, $S'$, of material derived from 1 g samples of original cokes after carbon burn-off showed similar changes to specific surface areas. These results are similar to those obtained for cokes used in the zinc-lead blast furnace (Carter, Glasson and Jayaweera, 1984).

Coke 2 coke shows a second maximum in the surface area curves at about 40 - 50% carbon burn-off. This is ascribed to the presence of the European component in the blend, see Section 1.9. The Polish coke used in the zinc-lead blast furnace also shows maximum surface area at 40 - 50% carbon burn-off, compared with the cokes prepared from indigenous South Wales coals (Nantgarw and Cwm) which also show maxima but at 10 - 25% carbon burn-off (Carter, Glasson and Jayaweera, 1984).
The decrease in surface area of Coke 1 following the maximum is ascribed to the sintering of the increasing proportion of ash present. The European component helps Coke 2 to retain its reactivity.

The kinetics of Coke 1 burn-off follows an approximate two-thirds order reaction, fitting into a contracting sphere model, Figure 2.8. Deviations from linearity of the two-thirds order plot, becoming concave upwards, are ascribed to impeding of the reaction by solid mineral matter.

Apparent densities (Table 2.1) and surface area changes can be used to obtain information on the development of porosity of the material during carbon burn-off. Using values for maximum surface areas on the burn-off curves, the mean maximum pore radius can be calculated as follows.

When 1 g of Coke 2 burns-off 16.8% carbon in air at 1000°C (corresponding to a weight loss of 15.1%), its surface area, $S'$, increases from 0.8 to 6.9 m$^2$. If the material and its burn-off product were non-porous, the change in surface area can be calculated on the basis of a contracting sphere model. This gives a calculated value of $0.8 \times (\text{fractional weight left})^{2/3} = 0.8 \times (1 - 0.151)^{2/3} = 0.72$ m$^2$ for the surface area of the product. Thus 6.2 m$^2$ of surface was developed in burning off 0.151 g or 0.0795 cm$^3$ of carbon (taking the "true" density of the coke as 1.90 g/cm$^3$), compared with a pore volume
Fig. 2.8. Two-thirds order kinetics plot for oxidation of coke No.1 in CO₂ at 1000°C.
opened 51 x 0.220 = 0.0332 cm³. Since the pores opened are mainly macropores (> about 100 nm diameter), the surface of the opened pores can be estimated from the formula

\[ \frac{4}{3}r = \frac{V}{S} \]  

............... (1)

(assuming the pores are cylindrical in shape), where

\[ r = \text{radius of cross-section of pore} \]
\[ V = \text{pore volume} = 0.220 \text{ cm}^3 \]
\[ S = \text{surface of opened pores} \]

Since \( r > 50 \text{ nm} \) for macropores (Robens, 1980), this gives a maximum value for the surface area of 8.8 m² per g of original coke, or 1.3 m² for 0.15 g of coke. Thus most of the increase in surface is due to the formation of new pores. If the volume of carbon lost on burn-off to maximum specific surface area is taken to be equal to the pore volume developed, the mean maximum pore radius (for cylindrical pores) can be calculated using equation (1), where,

\[ V = \text{volume of carbon burn-off} = 0.0795 \text{ cm}^3 \]
\[ S = \text{increase in surface due to new pores} = 6.2 - 1.3 \text{ m}^2 \]
\[ = 4.9 \text{ m}^2 \]
This gives a value of 32.4 nm for the mean maximum pore radius of Coke 2, the actual figure depending on how much of oxidation forms new pores. There will be direct burn-off from the external surface but some oxidation can form new pores or open and enlarge macropores. Accordingly the hysteresis loop of the nitrogen adsorption isotherm (Figure 2.7) indicates pore size across the whole of the mesopore range (20 - 50 nm), the commonest size (at the widest part of the loop) being about 7 nm.

Similar calculations for Coke 1 give a development of surface of 16.5 m² for 22.6% burn-off of 1 g sample (corresponding to maximum in surface area curve), compared with <2.2 m² for opened macropores. This leads to a value of 15.5 nm for the mean maximum radius of newly-formed pores. Again the hysteresis loop of the nitrogen adsorption isotherm indicates pore sizes over the whole mesopore range, the commonest being 5 nm.

Porosity data for the above two cokes are compared in Table 2.1 with those used in zinc-lead manufacture (Carter, Glasson and Jayaweera, 1984). The greater reactivity of Coke 1 (as confirmed by thermal analysis data, see Chapter 3) is attributed to its higher porosity and surface area developed compared with Coke 2. However, the latter coke retains its
surface area at high burn-off (because of its European component). This explains its linear kinetics, in contrast to Coke 1.

An estimate of how much of the oxidation contributes to formation of new pores can be made by measuring the uptake of nitrogen during the filling and emptying of the mesopores from the adsorption isotherms (Figures 2.6 and 2.7). This is approximately the difference between the highest and lowest weight readings of the hysteresis loop, using a value of 34.67 cm$^3$ for the volume of a mole of liquid nitrogen at -196 °C. These calculations indicate that only about 2.6% of the oxidation of Coke 2 in air and 2.5% of Coke 1 in carbon dioxide forms mesopores, so that the appreciable increases in surface area are associated with only a small proportion of the oxidation and the new surface is located in mesopores, giving it poor access to air or carbon dioxide. Hence, any increase in oxidation rate due to a new surface being formed will be comparatively small, but could tend to make a two-thirds order rate become approximately linear during the earlier stages of oxidation, as is often encountered in coke reactivity tests.

2.4 COAL SURFACE AREAS

The three coals were studied by gas sorption analysis for changes in their surface areas and porosity.
The techniques and procedures applied were similar to those used for the study of cokes as described in Section 2.4. The coals were burnt-off isothermally at 300, 400 and 500 °C using 5 mm diameter lump samples in a furnace in static air. Adsorption (and desorption) isotherms were recorded for the burnt-off products at 77 K using nitrogen as the adsorbate on the Cl Electronics Mark IIB microbalance.

For the English coal, surface areas changes were investigated also during sintering of the coal ash.

The coking behaviour of European coal was studied by heating samples thereof in a horizontal tube furnace in flowing nitrogen at 1000 °C. After 1 hour (during which most of the volatile matter was lost), the coke formed was oxidised in flowing carbon dioxide at the same temperature for times ranging up to 10 hours to give complete carbon burn-off. Other samples of the coal were coked in nitrogen at 1000 °C for up to 24 hours.

2.4.1 Results

Figures 2.9, 2.10 and 2.11 show the rate of carbon burn-off for the three coals at 300, 400 and 500 °C in static air.

Figure 2.12 shows the variations in surface areas with time and with percent burn-off for English and European coals at 500 and 400 °C respectively in static air. Figure 2.13 shows similar
Figure 2.9. Coal A burnt in air at 300, 400 and 500 °C burn-off.
Figure 2.10. Coal B burnt in air at 300, 400 and 500 °C burn-off.
Figure 2.11. Coal C burns in air at 300, 400 and 500 °C burn-off.
Fig. 2.12. Combustion of European coals in air.
Slow burning of coal in air.

**Fig 2.13.** Combustion of coal A in air
data for English coal at 300 °C, and Figure 2.14 for European coal at 300 °C. Corresponding data for Australian coal are presented in Figure 2.15 and 2.16. All the graphs show variations in the specific surface areas, \( S \), of the burnt-off products and the surface areas, \( S' \), of material from original 1 g samples of coal as functions of both time and percent carbon burn-offs.

Figure 2.17 shows the effect of sintering on the specific surface area of English coal ash at each of the three temperatures.

Figure 2.18 shows the nitrogen adsorption (and desorption) isotherms on English coal, and Figure 2.19 for the 31.5% burn-off material at 400 °C (corresponding to a specific surface area of approximately half of the maximum on burn-off curve). Figure 2.20a shows the nitrogen sorption isotherms on approximately half-burnt European coal at 400 and 500 °C. The materials correspond to those having surface areas approximately to maxima on the burn-off curves. Figure 2.20b shows the isotherms for European coal ash at 500 °C curve (i) being that of ash formed when coal combustion is just complete at 500 °C (in 2 h), and curve (ii) for ash that has been sintered at the same temperature for a further 8 hours. Figure 2.21 shows similar data for Australian coal. Again the isotherms of the partially burnt coals at 400 and 500 °C correspond to approximately half-burnt material when the
Fig 2.14. Combustion of coal B in air
Fig 2.15. Combustion of coal C in air
Fig. 2.16. Combustion of coal C in air
Fig. 2.17 Sintering of coal A ash
Figure 2.18. Adsorption of nitrogen on coal A
Figure 2.19. Adsorption of nitrogen on coal A oxidised at 400 °C in air (31.5% burn-off)
Fig 2.20 Nitrogen adsorption isotherms on (a) partly-burnt coal B (b) coal B ash
Fig 2.21 Nitrogen adsorption isotherms on
(a) partly-burnt coal C
(b) coal C ash
surface areas reach near maximum values (Figure 2.21a); and the coal ash isotherms are those of (i) coal where combustion is just complete at 500 °C in 2 h, and (ii) of ash which has been sintered for a further 8 h at the same temperature (Fig. 2.21b).

Figure 2.22 shows the variation of burn-off with time for European coal in carbon dioxide at 1000 °C. Figure 2.23 shows the changes in surface areas of the products. Nitrogen sorption isotherms are shown in Figure 2.24 for (a) the coal coked in nitrogen for 1 hour at 1000 °C during which time most of the volatile matter is lost and for (b) the coke residue after about 33% burn-off in carbon dioxide at 1000 °C. The latter sample corresponds to development of maximum surface area (see Figure 2.23).

2.4.2 Discussion

The English coal burns more rapidly than the Australian coal at all temperatures, Figures 2.9 and 2.11. This is consistent with its higher volatile matter content. The burn-off rate and volatile matter content of the European coal is intermediate, Figure 2.10.
Fig. 2.22. Oxidation of coked coal B in carbon dioxide at 1000 °C
Fig. 2.23. Oxidation of coked coal B in carbon dioxide at 1000 °C
Fig 2.24. Nitrogen adsorption isotherms on
(a) coked coal B,
(b) coke residue after 33 % burn-off
in carbon dioxide at 1000 °C.
2.4.2.1 Surface areas

As the oxidation of the coals proceed at 400 and 500 °C, their specific surface areas, $S$, increase, reaching maxima in the later stages of burn-off, before decreasing, Figures 2.12 and 2.15. This behaviour is similar to that observed with the cokes, Section 2.4, but the maxima occur at higher burn-offs. This may be ascribed to the coals (a) having more volatile matter and (b) burning at lower temperatures.

At 300 °C the maximum specific surface areas, $S$, of the English and European coals occur when burn-off is almost complete, Figures 2.13 and 2.14. However, the maximum for the Australian coal occurs at about 90% burn-off, Figure 2.16.

Similar maxima are shown for changes in the surface areas, $S'$, of residue from initial 1 g samples of the three coals at all three temperatures. However, the maxima all occur at about 50% burn-off.

The increases in surface area are considerably greater for the more rapid burn-offs at 400 and 500 °C than for the slow burn-offs at 300 °C. Thus $S'$ rises to 152 m$^2$ at 400 °C and to 93 m$^2$ at 500 °C for the European coal compared with 125 and 83 m$^2$ for the British coal and 170 and 125 m$^2$ for the Australian coal respectively. The smaller increases at 500 °C compared with those at 400 °C are ascribed to the tendency of the coal residues to form small "globules", suggesting that the rates of
energy transfer were insufficient to maintain an even temperature and leading to the formation of "hot spots". (See also Section 4.8.6 for electron microscopic studies). The temperature of 500 °C is well above the softening temperatures of the coals (346 °C for English 366 °C for European and 406 °C for Australian coal) facilitating the loss of volatiles, and is just above the resolidification temperatures (449, 472 and 487 °C respectively).

In contrast at 300 °C (a temperature below the softening point) the increases in surface areas, $S'$, are much smaller, Figures 2.13, 2.14 and 2.16. The maximum is much greater for the Australian coal (11.1 m$^2$) than for the English and European coals (5.6 and 3.5 m$^2$ respectively), for practically equal oxidation rates during the first half of the burn-offs. Initially the Australian coal is more compact ($S = 0.5$ m$^2$/g) than the English and European coals ($S = 2.0$ and 0.7 m$^2$/g respectively), and evidently is subjected to greater strain during the loss of its volatile matter (19.6 - 27.5% dry mineral matter free) compared with English and European coals (32.1 - 36.0 and 27.6 - 32.0% dry mineral matter free). The Australian coal tends to flake on combustion, thereby forming more new surface than the European coals, which have been formed under very different geological conditions (Section 2.3).
2.4.2.2 Porosity

There is development of porosity, including opening of initially closed pores, as the oxidation of the coals proceed. Thus, although the original coals have mainly macroporosity and some mesoporosity, Figure 2.18, they develop full ranges of mesoporosity (2-50 nm pore diameter) and some microporosity (< 2 nm pore diameter) (Robens, 1980) during the burn-offs. This is shown by the hysteresis in the nitrogen sorption isotherms on the partly burnt coals at 400 and 500 °C. The European coal develops microporosity during burn-off at both 400 and 500 °C, Figure 2.20a. However, the porosity of the partly-burned Australian coal extends down to micropore range only at 400 °C, Figure 2.21a. At 400 °C, the English coal also develops microporosity, Figure 2.19. (Hysteresis may be due also to pore shape).

An estimate of how much of the oxidation at 400 °C of English coal formed new pores may be made by measuring the uptake of nitrogen during the filling and emptying of pores from the adsorption isotherms. This is approximately the difference between the highest and lowest weight readings of the hysteresis loop in Figure 2.19, i.e. 9 mg per g of residue or 6.3 mg in the 0.7 g residue after 31.5% burn-off. The 6.3 mg corresponds to a pore volume of 0.0078 cm³, using 34.67 cm³ as the molar volume of liquid nitrogen at 77 K. This compares with 0.3 g of carbon burnt off, which has a volume of 0.13 cm³ (using a figure of 2.27 g/cm³ for the density of carbon); i.e. less than 6% of the coal oxidation resulted in formation of
micropores or mesopores. Thus the appreciable increases in surface are associated with only a small proportion of the oxidation. These results are analogous to those found for the oxidation of metallurgical cokes, where less than 5% of the oxidation formed micro- or meso-pores, Section 2.4.

2.4.2.3 Kinetics

Because the new surface developed during oxidation is located in the micropores and mesopores, the access of oxygen thereto is restricted by slow diffusion. Thus the large increases in the oxidations expected from plots of $S'$ against time, Figures 2.12 - 2.16, are not observed (where $S'$ is proportional to oxidation rate and oxidation-time curves should be acceleratory and sigmoidal). However, it is observed experimentally that the oxidations are only slightly accelerated, Figures 2.9, 2.10 and 2.11 so that the diminution in oxidation rate based on a contracting sphere model, is just compensated enough to make the earlier stages of oxidation approximately linear with time (cf. oxidation of Coke 2, Section 2.3). The burn-off data for English coal at 300 °C fit into a two-thirds order plot, Figure 2.25.

2.4.2.4 Coal ash

The ashes prepared from English coal at the three temperatures had similar surface areas, in spite of the different surface area changes and combustion rates during oxidation. The same observation was made for European and Australian coal ashes.
Figure 2.25. Kinetic analysis of coal A burn-off at 300 °C.
The specific surface area of the newly-formed European coal ash was 66 m²/g about double the values for English and Australian coals (25 m²/g and 30 m²/g respectively).

The main components of the coal ashes, as identified by X-ray powder diffraction (see Chapter 5), are silica, alumina, or alumino-silicates, and iron oxides, Fe₂O₃ and Fe₃O₄. The European coal ash contained up to 14% iron oxides, English coal ash contain 9-10% and the Australian coal ash some 4-5%.

Figure 2.17 shows the effect of sintering on Coal A ash. As expected sintering is more extensive at higher temperatures. Since the Tammann temperatures (half melting point in Kelvin) correspond to 890 °C for alumina, 730 °C for silica and 650 °C for iron(III) oxide, sintering by crystal lattice diffusion is not possible at the ashing temperatures used in this work. Thus, sintering is possible only by surface diffusion; this becomes appreciable at temperatures above one third melting point in Kelvin, i.e. 500 °C for alumina, 400 °C for silica and 340 °C for iron(III) oxide. Since only the lower mechanism is available, sintering is restricted; this results in some initial loss of surface, as illustrated in Figure 2.17 for English coal ash.

The nitrogen sorption isotherms on English coal ashes indicate some mesoporosity and no microporosity. This is also observed with European and Australian coal ashes, Figures 2.20b and
2.21b. The isotherms are of the Type II classification (Section 2.2.1) in contrast with those for partly-burnt coals, which are of Type I.

2.4.2.5 Coking of coal
When samples of European coal were coked in flowing nitrogen at 1000 °C, most of the volatile matter was lost within one hour (see also thermal analysis results Chapter 3); and there was some increase in surface area from 0.7 m²/g to give a coke of about 8 m²/g surface area. On further coking up to 24 h, the surface area decreased to about 4 m²/g, becoming comparable with metallurgical cokes (Section 2.4 and Carter, Glasson and Jayaweera, 1984).

When the newly-formed coke (S = 8 m²/g) from European coal was oxidised in carbon dioxide at 1000 °C, the specific surface area increased to a maximum of about 80 m²/g at about one third burn-off and then decreased, Figure 2.23. Similar changes were observed for the surface area, S', of initial 1 g samples of the coke, as was observed with European coal (Section 2.5.1). However, the increase in S is not as large as those during the fast burning of the coal in air at lower temperatures, where S increased up to 320 m²/g at just over half burn-off. Corresponding maximum changes in surface areas, S', of initial 1 g samples of coke and coal range from 8 to 42 m²/g and 0.7 to 152 m² for about one-third and one-half burn-offs respectively.
The ten-fold increase in specific surface area, $S$, for the coke oxidation is similar to those for commercial metallurgical cokes (Carter, Glasson and Jayaweera, 1984 and Section 2.3).

The oxidation of the newly-formed European coke gave approximately linear kinetics in the earlier stages of burn-off, Figure 2.22, similar to those of the commercial cokes. This is similar to the kinetics of the European coal oxidation in air, Section 2.5.2.3. There is also considerable development of porosity as the coke oxidises, as shown in the nitrogen sorption isotherms, Figure 2.24. Again, most of the new surface is located in the micropores and mesopores developed, where access to carbon dioxide is restricted by slow diffusion. Similarly large increases in oxidation rate suggested by plots of $S'$ versus time are not obtained and the coke oxidation is only slightly accelerated. Likewise, the diminution in the oxidation rate according to the two-thirds order law (based on contracting sphere model) is just compensated enough to make the earlier stages of oxidation approximately linear.
REFERENCES

CHAPTER 2


3.1 REVIEW AND INTRODUCTION

Thermal analysis is defined as a group of techniques whereby a physico-chemical property of a substance is measured as a function of temperature during which the sample is subjected to a controlled temperature programme (Wendlandt, 1986).

The temperature programme may be (a) isothermal, where the temperature would be kept constant at a given value and the selected physical property is measured as a function of time or (b) dynamic, where the material under examination is heated/ cooled at a constant heating/cooling rate.

The principal techniques of thermal analysis are Thermogravimetry (TG) (Keattch and Dollimore, 1969) and Differential Thermal Analysis (DTA) (Pope and Judd, 1977).

Thermogravimetry involves the measurement of the weight of a material as it is heated or cooled at a controlled rate and it therefore provides quantitative information on all processes taking place which may occur in connection with a change in weight and this information enables the stoichiometry of a reaction to be followed directly.
Differential Thermal Analysis gives information on the enthalpy of a substance subjected to a controlled temperature programme. When employing this technique the measurement is made by continuous monitoring of the temperature difference ($\Delta T$) between a sample and a thermally inert reference material, usually achieved by having an opposed thermocouple system, suitably amplified.

Equipment for thermal analysis has been developed extensively and high-quality, precision, commercially available thermobalances became widely used in the early 1960s. The possibilities offered by such methods in the investigation of both physical and chemical phenomena have ensured that these methods have found application in almost all of the natural sciences.

In common with any instrumental technique there are a number of factors which influence the nature, precision and accuracy of the experimental results. TG and DTA have a large number of variables because of the dynamic nature of the temperature change of the sample and the factors that can influence results for both techniques fall into two categories viz, instrumental factors or those relating to sample characteristics.

Many factors such as sample-holder geometry, recording speed, balance sensitivity and sample-container air buoyancy are fixed with any given thermobalance and correlations cannot be easily
made with other types of instruments. In addition, some factors which are variable and difficult to reproduce are involved, such as - sample-particle size, packing, the solubility of evolved gases in the sample, furnace convection currents and electrostatic effects. Comparison and criticisms of various methods is given by Blažek (1973).

Basic principles of DTA, apparatus and applications are given by Pope and Judd (1977). A critical review of the meaningful parameters for DTA has been made by Sharp (1972) and the effect of kinetic factors on the shape of the DTA curve has been examined by Kissinger (1957).

As a fuel in general use, coal has been the subject of extensive thermal analysis studies.

Weltner (1965) studied various coals using a combination of TG and DTA in the derivatograph. He was able to devise a method for determining the volatile matter and fixed carbon contents and the DTA measurement also enabled the rank of coal to be ascertained. A general evaluation of coal samples was obtained from a study of the weight change and the rate of weight change.

Using TG, Serageldin and Pan (1983) described the reaction kinetics of the thermal decomposition of coal.
Rajeshwar (1983) and van Krevelen (1961) have reviewed what has been achieved on coal. Van Krevelen and Schuyer (1957) have comprehensively dealt with similar topics concerning the coking of coal.

Further applications of thermal analysis to carbons have been summarised by Carter (1983). Extensive studies on the kinetics of carbon-gas reactions are cited in the literature and have been reviewed by Carter (1983).

3.2 INSTRUMENTATION

3.2.1 The Stanton Redcroft STA 781 Thermal Analyser

The Stanton Redcroft STA 780 series of thermal analysers consist of a range of equipment for TG and simultaneous TG/DTA. The STA 781 is the TG/DTG/DTA model working over the temperature range ambient to 1500 °C, figure 3.1.

A 5 g capacity electronic microbalance is used with a digital control unit incorporating a microprocessor. Any desired weight range from 2 to 200 mg full scale deflection can be selected with a resolution of 1 μg in the range 2-20 mg and 10 μg in the range 2-200 mg. This facility makes it easy to display a selected percentage of the sample weight as full scale. Full digital taring, multiple inject and DTG facilities are incorporated.
Figure 3.1. Schematic Diagram of STA 781 Thermal Analyser.
Thermocouple connections are taken from the balance beam to measuring circuits using very fine wires made of the thermocouple materials. The $\Delta T$ signal is amplified by a low noise DC amplifier giving a maximum sensitivity of 10 $\mu$V full scale. Cold junction compensation and temperature linearisation are available for the sample temperature output.

The design of the gas-flow system, in conjunction with the water-cooled finger, enables runs to be carried out in flowing atmospheres without having to make a large weight correction, the magnitude of the latter generally being below 0.1 mg. Typical flow rates are normally in the range 25-75 cm$^3$/min, with the flow meter calibrated for air discharging at atmospheric pressure. With other gases at the same outlet pressure, the velocity varies inversely as the square root of the gas density relative to air. Thus taking the densities of air and CO$_2$ as 1.2929 g l$^{-1}$ and 1.9769 g l$^{-1}$ respectively at STP (Dodd and Robinson, 1954), the flow rate of CO$_2$ was calculated as $0.81 \times$ (air flow rate). Flow meter reading of 100% corresponded to 87 cm$^3$ min$^{-1}$ of air.

Figure 3.2 shows the apparatus set up for TG/DTA. Sample and reference materials are housed in flat bottomed crucibles 5 mm diameter and 4 mm high.

Full calibration weighing procedure was carried out from time to time as described in the manufacturer's handbook.
Figure 3.2. STA 781 Thermal Balance. Cross Section of Furnace with TG/DTA Hangdown in Position.

Key:

- D are 5 mm diameter Pt crucibles supported by plate-type Pt v Pt 13% Rh thermocouples giving T and ΔT by a similar circuit to that shown in Figure 3.4.

- For work above 1000 °C 0.1 mm alumina discs P are inserted between crucibles and thermocouples.

- The head assembly supported by a four-bore alumina rod R and surrounded by thin walled ceramic tube G, hung within an alumina cup A, which has been electrically shielded for high temperature work. The cup seats against baffles B ensuring even heat distribution and good atmosphere control around the sample as the desired gas is passed in an upwards direction through the cup.

- The sample is heated by a water cooled furnace F, wound non-inductively with a Pt/Rh alloy W.

- The furnace is motor-driven and sealed against the water cooled finger C. Furnace temperature is monitored on the UTP from thermocouple T, accurately positioned against the alumina tube and winding. There is an air space between the furnace winding and the water-cooled metal body.

- S is a gas inlet side arm which allows direct linkage to gas chromatograph or mass spectrometer.
3.2.2 The Stanton-Redcroft MF-H5 Mass Flow Balance

This instrument was used with a Stanton Redcroft Eurotherm linear temperature programmer model CA with programmed heating rates between 2 to 40 °C min⁻¹ and Leeds Northrup "Speedomax W" chart recorder. A schematic diagram of the balance and ancillary equipment is given in Figure 3.3.

The thermobalance design incorporates two beams, one inside the chamber and the other outside, the two being coupled by a magnetic link. Changes in weight occurring on the inner beam are transferred to the outer beam, detected electronically and indicated by an arm with a full-beam deflection of 20 mg and sensitivity of 0.2 mg.

A schematic cross-section of the balance chamber is shown in Figure 3.4. The balance chamber is a 10-gauge copper tube 178 mm diameter, silver brazed and epoxy-resin coated with doors 10 mm thick sealed with "O" rings. A water-cooled silicone "O" ring seals the mullite reaction tube to the chamber. There are four gas entry or outlet ports, two to the reaction tube and two to the main balance chamber. It is possible to keep a nitrogen atmosphere in the balance chamber and pass air containing corrosive gases over the sample. By means of the vacuum attachment, the system can be easily flushed out and known atmospheres introduced. The air for the oxidations under a flowing atmosphere was obtained from a pressurised cylinder and introduced via the two upper gas entry/exit ports, first
Figure 3.3 Massflow Thermobalance and Ancillary Equipment.

Key: 1. Chart recorder for $T$ and $\Delta T$
2. Signal switching unit for $\Delta T$ and/or $T$
3. D.C. amplifier 20-1000 $\mu$V range
4. Thermocouple of DTA head
5. Ice pot
6. Furnace
7. Thermobalance
8. TG record
9. Temperature programmer
10. Control thermocouple between furnace wall and mullite tube
11. Furnace load.
Figure 3.4
Gas circuit of the Stanton-Redcroft Massflow Balance MF-H5
passing through a rotameter where the rate of flow could be set. For the static air oxidations one of the entry ports was left open and the others closed.

Automatic electric weight loading increases the range of the instrument to the equivalent of ten full beam deflections of gain or loss without a decrease in sensitivity. This enables weight gains or losses of up to 200 mg to be followed.

During operation the balance automatically arrests and releases itself every 5 min to check that it is not sticking and to improve the sensitivity with very small weight changes.

The sample holder consists of an alumina block 20 mm in diameter and 13 mm in depth with two wells each 6.5 mm diameter and 10 mm in depth to take the crucibles. The alumina head is coupled to the internal balance by alumina and silica rods joined by an aluminium chuck containing three adjustable screws by which the head is kept vertical.

Two matched (0.8 g) platinum crucibles with dimples are used to contain the sample and reference material, as shown in Figure 3.5. The crucibles are placed in the 6.5 mm wells of the alumina head with the thermocouples sitting in the dimples and are thus surrounded by the sample. This leads to high sensitivity for the differential thermal output.
Figure 3.5 Massflow Thermobalance Sample Head.

Figure 3.6 Thermocouple arrangement of Sample Head.
Two Pt/13%Rh-Pt thermocouples are employed to detect the temperature difference between sample and reference, $\Delta T$, and sample temperature, $T$, as shown in Figure 3.6. The signal from the thermocouples is passed from the alumina head down the inside of the alumina and silica rods to the outside by 0.025 mm compensated platinum wires, which have a very small damping effect on the balance. Further compensated leads are employed to connect the signal with the DC amplifier and constant-reference-temperature ice-bath. The DC amplifier has seven pre-set ranges from 20-1000 $\mu$V; normally the 100 $\mu$V sensitivity setting is used. A single channel Leeds Northrup Speedomax W chart recorder is used with a switching unit enabling the differential output to be recorded for 4 min 55 s and then the temperature recorded for 5 s.

Calcined alumina was used as the thermally inert reference material. For isothermal work a shallow alumina crucible 24 mm diameter and 5 mm height was placed on the head and the switching unit used to record sample temperature, $T$, only.

The platinum-rhodium bifilar wound furnace has a 50 mm bore and is closed at the top with a 100 mm deep alumina plug filled with alpha-alumina powder.

The temperature is controlled by a Stanton-Redcroft Eurotherm temperature controller with the sensing Pt/13%Rh-Pt thermocouple trapped between the mullite reaction tube and the
furnace wall. The controller enables the heating rate to be continuously varied from 2-20 °C min⁻¹ with the maximum temperature (up to 1100 °C) pre-selected and subsequently held constant indefinitely (isothermal conditions).

Calibration curves were recorded, in static and flowing air, to determine the buoyancy effect in TG and baseline drift in DTA, using alumina in both crucibles and a heating rate of 5 °C min⁻¹. The apparent weight increase was 1.5 to 2 mg and negligible after 200 °C. Buoyancy effect was also determined for isothermal TG using alumina in the shallow dish and preheating the furnace to 500, 700 and 900 °C. The effect was greater, although of shorter duration, the higher the furnace temperature. Correction for buoyancy was applied to all the TG work.

3.3 ISOTHERMAL TG

Isothermal TG allows an oxidation to be continuously monitored up to conclusion of burn-off. Where weight loss curves can be utilized to calculate a rate constant then its variation with temperature may be given in the form of an Arrhenius plot, permitting the kinetic parameters $A$ and $E_A$ to be assessed from the intercept and slope.
Oxidations of two cokes were carried out initially on the Stanton Redcroft Massflow balance MF-H5 in static air, moving air and carbon dioxide atmospheres. However, there is a restriction on this apparatus in that the temperature limit of the furnace is approximately 1000 °C.

With the acquisition of a Stanton Redcroft STA 781 thermal analyser, air and carbon dioxide oxidations of the cokes and coals at higher temperatures were studied and an appropriate number of the lower temperature runs on the cokes were repeated.

3.3.1 Experimental

The work was carried out on the two thermal balances described in the section dealing with techniques. Cokes and coal samples were sieved from bulk samples. Air oxidations under static conditions of the cokes were first performed on the Massflow balance with the sample container in a shallow alumina crucible, 24 mm diameter and 5 mm in depth, resting on the ceramic TG/DTA block. The crucibles within the block were too small to take very substantial lump coke samples. Approximately 120 to 100 mg of each coke in the form of one or two lumps, ~3 mm lump size, were used.

With the furnace raised the TG pen was positioned on the scale by the addition of suitable counterweights to the balance pan. The furnace was heated rapidly (40 °C per minute) and when it
had reached the set temperature it was lowered carefully over the mullite tube. Environment temperature was constantly recorded on the Leeds Northrup recorder with the DTA signal switched off. The buoyancy correction for the appropriate conditions was applied to the data. Results were obtained for coke oxidations up to approximately 950 °C.

In addition, samples of the cokes were oxidised in air in the Stanton-Redcroft 781 thermal analyser. The small volume of the furnace and sample environment might have meant that reactions in static air were prevented by reactant starvation, so runs in air flowing at 43.5 cm³ min⁻¹ were also arranged. By choosing a suitable range on the balance control module of the STA 781, the percentage weight losses could be directly recorded on the TG trace. The cokes were examined isothermally also in CO₂ flowing atmospheres.

Samples of the three coals were examined similarly on the STA 781 under static air conditions, moving air, oxygen, nitrogen and carbon dioxide atmospheres.

All results presented in the graphs for the cokes and the coals relate to data acquired from the experiment runs conducted on the STA 781 which gives assurance of consistency of data.
3.3.2 Results for cokes

Figures 3.7 and 3.8 show the isothermal TG plots for Coke 1 and Coke 2 respectively in flowing carbon dioxide. The cokes were heated in flowing nitrogen (44.4 cm$^3$ min$^{-1}$) at 40 °C to the pre-set furnace temperature, and the gas flow then switched to carbon dioxide (35.2 cm$^3$ min$^{-1}$).

3.3.3 Discussion of cokes

The limiting percentage weight losses for the two cokes (after 1.25 h in flowing CO$_2$) at different temperatures are summarised in Table 3.1. The results show that Coke 1 is more reactive than Coke 2. This is consistent with interpretations on gas sorption data reported in Chapter 2, Section 2.3.

Table 3.1 Limiting percentage weight losses in carbon dioxide

<table>
<thead>
<tr>
<th>Temp/°C</th>
<th>Coke 1</th>
<th>Coke 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>5.7</td>
<td>4.7</td>
</tr>
<tr>
<td>1100</td>
<td>44.4</td>
<td>41.5</td>
</tr>
<tr>
<td>1150</td>
<td>65.0</td>
<td>61.8</td>
</tr>
<tr>
<td>1200</td>
<td>90.6</td>
<td>84.8</td>
</tr>
<tr>
<td>1300</td>
<td>92.3</td>
<td>91.2</td>
</tr>
<tr>
<td>1400</td>
<td>94.3</td>
<td>93.6</td>
</tr>
</tbody>
</table>

The above figures represent a mean of up to about twenty measurements.
In flowing nitrogen (44.4 cm³ min⁻¹) to 1000, 1100, 1150, 1200, 1300 and 1400 °C at 40 °C per minute then in flowing carbon dioxide (35.2 cm³ min⁻¹).
In flowing nitrogen (44.4 cm$^3$ min$^{-1}$) to 1000, 1100, 1150, 1200, 1300 and 1400 °C at 40 °C per minute then in flowing carbon dioxide (35.2 cm$^3$ min$^{-1}$).
The reactions of both cokes are slow at 1000 °C, but their rates increase rapidly by 1100 °C.

The determination of activation energies for the isothermal TG data of the cokes is reported in Section 3.5.

3.3.4 Results for coals

Figures 3.9, 3.10 and 3.11 are the isothermal TG plots in flowing air for Coal A, Coal B and Coal C respectively. The coals were heated in flowing nitrogen (44.4 cm³ min⁻¹) at 40 °C per minute to the required temperature and the gas flow was then switched to flowing air (43.5 °C min⁻¹).

Figures 3.12, 3.13 and 3.14 show the isothermal TG curves for the three coals in flowing carbon dioxide (35.2 cm³ min⁻¹). Again the samples were heated at 40 °C min⁻¹ from ambient to indicated temperature in flowing nitrogen, before switching the gas to carbon dioxide. (Crushed coal samples were used)

3.3.5 Discussion of coals

The percentage total weight losses of the three coals during 3/4 hour in flowing air and flowing carbon dioxide are summarised in Tables 3.2 and 3.3 respectively.
Figure 3.9 TG traces for coal A heated in flowing nitrogen (44.4 cm$^3$ min$^{-1}$) and then in flowing air (43.5 cm$^3$ min$^{-1}$). Sample heated at 40 °C per min to indicated temperatures in nitrogen. Atmosphere was then switched to flowing air.
Figure 3.10 TG traces for coal B heated in flowing nitrogen (44.4 cm$^3$ min$^{-1}$) and then in flowing air (43.5 cm$^3$ min$^{-1}$). Sample heated at 40 °C per min to indicated temperatures in nitrogen. Atmosphere was then switched to flowing air.
Figure 3.11 TG traces for coal C heated in flowing nitrogen (44.4 cm$^3$ min$^{-1}$) and then in flowing air (43.5 cm$^3$ min$^{-1}$). Sample heated at 40 °C per min to indicated temperatures in nitrogen. Atmosphere was then switched to flowing air.
Figure 3.12 Isothermal TG traces for coal A heated in flowing nitrogen (44.4 cm$^3$ min$^{-1}$) and then flowing carbon dioxide (35.2 cm$^3$ min$^{-1}$). Samples heated at 40 °C per min to indicated temperatures in nitrogen. Atmosphere then switched (O) to flowing carbon dioxide.
Figure 3.12 Isothermal TG traces for coal B heated in flowing nitrogen (44.4 cm$^3$ min$^{-1}$) and then flowing carbon dioxide (35.2 cm$^3$ min$^{-1}$). Samples heated at 40 °C per min to indicated temperatures in nitrogen. Atmosphere then switched (0) to flowing carbon dioxide.
Figure 3.14 Isothermal TG traces for coal C heated in flowing nitrogen (44.4 cm$^3$ min$^{-1}$) and then flowing carbon dioxide (35.2 cm$^3$ min$^{-1}$). Samples heated at 40 °C per min to indicated temperatures in nitrogen. Atmosphere then switched (0) to flowing carbon dioxide.
Clearly the coals react faster in air atmospheres than in carbon dioxide. In both gases, Coal A has the greatest weight losses and Coal C the least. This is consistent with their rank.

In flowing air the reactions at 400 °C are very sluggish for all three coals, Figures 3.9, 3.10 and 3.11. At 600 °C and above the reactions are fast and the weight losses reach their limiting values rapidly. The initial weight losses in nitrogen are due to loss of volatile matter.

In flowing carbon dioxide, at temperatures up to and including 600 °C the weight losses reach limiting values. At 800 °C and higher the reactions are rapid, Figures 3.12, 3.13 and 3.14.

Table 3.2 Percentage weight loss of coals in flowing air during 45 minutes

<table>
<thead>
<tr>
<th>Temp/°C</th>
<th>Coal A</th>
<th>Coal B</th>
<th>Coal C</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>6.2</td>
<td>3.3</td>
<td>3.0</td>
</tr>
<tr>
<td>500</td>
<td>90.5</td>
<td>75.7</td>
<td>47.0</td>
</tr>
<tr>
<td>600</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>92.9</td>
<td>92.0</td>
<td>89.4</td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Table 3.3 Percentage weight loss of coals in flowing carbon dioxide during 45 minutes

<table>
<thead>
<tr>
<th>Temp/°C</th>
<th>Coal A</th>
<th>Coal B</th>
<th>Coal C</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>5.5</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>500</td>
<td>20.7</td>
<td>4.9</td>
<td>8.3</td>
</tr>
<tr>
<td>600</td>
<td>37.5</td>
<td>20.7</td>
<td>13.3</td>
</tr>
<tr>
<td>800</td>
<td>50.5</td>
<td>42.6</td>
<td>29.8</td>
</tr>
<tr>
<td>1000</td>
<td>64.5</td>
<td>48.5</td>
<td>37.0</td>
</tr>
<tr>
<td>1200</td>
<td>75.0</td>
<td>59.9</td>
<td>37.9</td>
</tr>
</tbody>
</table>

3.3.6 Proximate analysis of coals by TG

Thermogravimetry was employed also to provide what in effect were proximate analyses of the three coals. Such an analysis is the most direct method of illustrating the general characteristics of a coal. The usual procedure (British Standard 1016 Part 3, 1973) is commonly used for the commercial assessment of coals and involves the determination of the relative percentage of moisture, volatile matter, ash and fixed carbon present.

The moisture content is calculated from the loss of weight which occurs when a coal is oven dried in vacuo or in nitrogen at 105-110 °C. A knowledge of the moisture content is
important for commercial purposes since heat is lost on its evaporation and thus the efficiency of the coal as a fuel is lowered.

For the determination of the volatile matter content, one gramme of the coal is heated for 7 minutes at 900 ± 5 °C out of contact with air. The loss in weight, less that already calculated for the moisture, is expressed as a percentage of the initial weight of the sample. Thus an indication is given of gas and tar yields.

The ash content is represented by the incombustible residue remaining after a coal has been incinerated to a constant weight. Ash is a deleterious constituent having adverse effects upon the fuel values and combustion characteristics.

The fixed carbon content is calculated by subtracting the moisture, volatile and ash percentages from 100. Since the percentage of fixed carbon increases with the rank of a coal, it forms the basis of several classification systems, but since fixed carbon, as determined in a proximate analysis, also includes small amounts of oxygen, nitrogen and sulphur, it does not accurately express the percentage of true combustible carbon in a coal.

The present work examined the three coals in the Stanton Redcroft 781 Thermal Analyser in which 15 mg samples were used.
Each coal was:

i) heated to 110 °C under flowing nitrogen and held for 5 minutes to allow moisture loss followed by,

ii) dynamic heating of the sample at 40 °C/min to 950 °C, and held isothermally until all volatile material had been liberated then,

iii) the purge gas was switched to oxygen which permitted the determination of fixed carbon in the coal, the remaining weight being ash. The purge gas was then switched back to nitrogen.

Figure 3.15 is an idealised representation of the procedure.

The procedures were repeated for each of the three coals and the results are as follows:

Table 3.4 Proximate analyses of coals

<table>
<thead>
<tr>
<th></th>
<th>Coal A</th>
<th>Coal B</th>
<th>Coal C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Moisture</td>
<td>9.10</td>
<td>9.50</td>
<td>8.70</td>
</tr>
<tr>
<td>Volatiles</td>
<td>34.60</td>
<td>29.10</td>
<td>20.60</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>49.20</td>
<td>53.88</td>
<td>62.24</td>
</tr>
<tr>
<td>Ash</td>
<td>7.10</td>
<td>7.52</td>
<td>8.46</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Figure 3.15 Proximate analysis of a coal
The normal industrial method to meet the requirements of BS 1016 Part 3, 1973 as previously described was carried out also, in duplicate for each coal, and the results were found to be in close agreement with TG results. The volatile matter content values obtained are not unexpected for the respective NCB coal ranking, i.e., Coal A is a high volatile strongly caking coal, NCB Coal Rank Code 501. Coal B is a prime coking coal, NCB Coal Rank Code 301b. Coal C is a prime coking coal, NCB Coal Rank Code 301a.

3.4 DYNAMIC TG/DTA STUDIES

In industrial use metallurgical coke is subject to a time-dependent temperature regime and a gas composition variation during its descent in the blast furnace. Hence, it is more realistic to use dynamic thermal analysis methods in examining the reactions experienced.

With dynamic methods a whole temperature range can be studied quickly and continuously. With a sensitive thermal balance the sample size can be small and heating rate slow, reducing thermal gradients in the sample. Simultaneous TG/DTA was carried out initially on the Massflow balance for air oxidations of the carbons. The higher furnace temperature capability of the STA 781 thermal analyser allowed an
investigation of air and CO\textsubscript{2} oxidation of the materials and it
gave also simultaneous DTG data. On the grounds of consistency
all work was redone in the STA 781 and only these latter
results are reported here. There have been somewhat fewer
applications of dynamic methods to the oxidation of coke or the
coals from which they have been derived in contrast with the
large number of isothermal studies that have been undertaken.

A DTA peak is normally characterised by the temperature of the
"start" of a change (which is the temperature of the point of
intersection of the baseline with the extended straight line of
the ascending side), the temperature at the maximum rate of
reaction and the temperature at the "end" of the change. As
such these are complex functions, as described by Blažek
(1973). Kinetic factors are known to affect the form of a DTA
peak. Variations in activation energy and frequency factor
change the position and size of a peak but have little effect
on shape. Change in order of reaction greatly alters the shape
of the DTA curve, the higher the order the broader and more
symmetrical the peak.

For first order reactions Kissinger (1956) proposed a method
for obtaining kinetic parameters from the variation in peak
temperature with heating rate and later extended this method to
reactions of any order, provided the latter does not change
during the course of the reaction. (Kissinger, 1957).
In the present work a number of DTA curves for the two cokes were recorded at the same sensitivity and sample weight but at different heating rates. Peak temperatures were recorded and graphs plotted of \( \ln \left( \frac{dT}{dt}/T_m^2 \right) \) versus \( \frac{1}{T_m} \) where \( \frac{dT}{dt}/T_m^2 \) and \( T_m \) relate to the temperature at which the rate of reaction is greatest, a temperature which Kissinger took to be the peak temperature of the DTA curve. Straight line graphs were obtained of which the slopes were \(-\frac{E_A}{R}\).

The assumption that the DTA peak temperature coincides always with the maximum rate of reaction is incorrect and the foregoing method has been criticised by Sharp (1972). Nevertheless, the simultaneous TG/DTG/DTA functions of the STA 781 thermal balance showed that in the oxidations of the cokes under examination, these temperatures were very close. Isothermal work had shown that diffusion was not rate limiting for the CO\(_2\)/coke reaction to 1400 °C so an unchanging order of reaction was assumed. Isothermal studies rely on determination of the amount of material burnt off. The DTA curve makes no assumptions as to degree of burn off and does not yield such information.
3.4.1 Experimental

Some air oxidations were carried out on the Massflow balance applying appropriate buoyancy correction to the TG curve, which had been ascertained by finding the apparent weight gain at various heating rates using Al₂O₃ in the reference and sample crucibles. A TG chart speed of 12 inches h⁻¹ was used and the weight loss calculated and reported. The chart full width was set at 20 mg and a sensitivity of 0.1 mg could be achieved. Silica crucibles were used with calcined Al₂O₃ as DTA reference material. The DTA amplifier sensitivity was 100 μV full scale. The DTA baseline was made as linear as possible by adjusting three screws of the ceramic head containing the crucibles and the DTA chart was set to run at 3 inches h⁻¹. Flowing air was introduced from the lower inlet port after passing through a rotameter, adjusting the flow to 1 litre min⁻¹.

Air and CO₂ oxidations were carried out at a later date on the newly acquired STA thermal analyser. Pt/Rh crucibles were used with calcined Al₂O₃ as DTA reference material. The TG buoyancy effect was negligible. The DTA baseline was set by adjusting the feet of the balance unit and the gas flow was adjusted on the integral flow meter. CO₂ was first dried by passage through MgClO₄. Recorder chart speeds of 100 and 200 mm h⁻¹ were found to be satisfactory. DTA amplifier range and DTG range had to be found by trial and error, before a set of experiments.
For the investigation of the coals, material was crushed and sieved fractions taken. Coke sample of smaller particle size (< 180 μm) were used but the crucibles limited the coke lump size to about 3 mm diameter.

3.4.2 TG/DTA results for cokes

Figure 3.16 shows the TG curves for Coke 1 and Coke 2 in flowing nitrogen (44.4 cm³ min⁻¹) at a heating rate of 10 °C min⁻¹. Figure 3.17 represents the TG curves for the two cokes in static air at the same heating rate. The curves in flowing air (43.5 cm³ min⁻¹), flowing oxygen (41.3 cm³ min⁻¹) and in flowing carbon dioxide (35.2 cm³ min⁻¹) at 10 °C min⁻¹ are shown in Figures 3.18, 3.19 and 3.20 respectively.

Figures 3.21 and 3.22 show the weight losses in flowing carbon dioxide at different heating rates for the two cokes in the temperature range 1000 - 1400 °C. The samples were heated at 40 °C per minutes in flowing nitrogen (44.3 cm³ min⁻¹) up to 1000 °C, when the gas was switched to carbon dioxide (32.2 cm³ min⁻¹). Figure 3.23 compares the two cokes at the heating rate of 12 °C per minute.

Figures 3.24 and 3.25 show the DTA curves of the two cokes at different heating rates in flowing carbon dioxide in the temperature range 1000 - 1400 °C. As before, the initial temperature was reached by heating the samples in flowing nitrogen at 40 °C per minute.

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Figure 3.16 TG traces of 2 coke in flowing nitrogen (44.4 cm³ min⁻¹) at 10°C min⁻¹ to 1450°C
Figure 3.17  TG traces of 2 cokes in static air at 10°C min⁻¹ to 1450°C
Figure 3.18 T.G traces of 2 cookes in moving air (43.5 cm$^3$ min$^{-1}$) at 10$^\circ$C min$^{-1}$ to 1450$^\circ$C
Figure 3.19 TG traces of 2 coals in flowing oxygen (41.3 cm³ min⁻¹) at 10°C min⁻¹ to 1450°C
Figure 3.20: Tmt. loss of 2 coke in carbon dioxide (35.2 cm$^3$ min$^{-1}$) at 10$^\circ$C min$^{-1}$ to 1650$^\circ$C.
Figure 3.21  Coke No.1

40 °C per minute to 1000 °C in flowing nitrogen (44.4 cm³ min⁻¹) then to 1400 °C at 8, 10, 12, 14 and 16 °C per min in flowing carbon dioxide (35.2 cm³ min⁻¹).

% Wt losses were as follows:-

<table>
<thead>
<tr>
<th>°C</th>
<th>% Wt loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>92.0</td>
</tr>
<tr>
<td>10</td>
<td>89.0</td>
</tr>
<tr>
<td>12</td>
<td>84.3</td>
</tr>
<tr>
<td>14</td>
<td>77.0</td>
</tr>
<tr>
<td>16</td>
<td>73.0</td>
</tr>
</tbody>
</table>
Figure 3.22 Coke No. 2

40 °C per minute to 1000 °C in flowing nitrogen (44.4 cm$^3$ min$^{-1}$) then to
1400 °C at 8, 10, 12, 14 and 16 °C per min
in flowing carbon dioxide (35.2 cm$^3$ min$^{-1}$).

% Wt losses were as follows:

<table>
<thead>
<tr>
<th>°C</th>
<th>% Wt loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>91.41</td>
</tr>
<tr>
<td>10</td>
<td>87.37</td>
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<tr>
<td>12</td>
<td>76.50</td>
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<tr>
<td>14</td>
<td>68.18</td>
</tr>
<tr>
<td>16</td>
<td>60.61</td>
</tr>
</tbody>
</table>
Figure 3.23 Cokes Nos. 1 and 2

40 °C per minute to 1000 °C in flowing nitrogen (44.4 cm$^3$ min$^{-1}$) then to 1400 °C at 8, 10, 12, 14 and 16 °C per min in flowing carbon dioxide (35.2 cm$^3$ min$^{-1}$).

% Wt losses were as follows:

- Coke No. 2 76.5%
- Coke No. 1 84.3%
Figure 3.24
DTA of coke No.1 under five temperature programmes
(°C min⁻¹) CO₂ oxidation
Figure 3.25
DTA of coke No. 2 under five temperature programmes ('C min$^{-1}$) CO$_2$ oxidation
3.4.3 Discussion of cokes

Comparison of the TG curves in flowing nitrogen for the two cokes (Figure 3.16) shows that Coke 1 loses more weight due to its greater residual volatile matter. Thus in oxidising atmospheres (air, oxygen, carbon dioxide), Coke 1 has greater weight losses at a given temperature (Figures 3.17 - 3.20). The limiting weight losses for Coke 1 in oxidising atmospheres, however, are less than for Coke 2, indicating a higher mineral matter content for the former. (The initial mineral matter governs the residual ash).

As expected, from all the TG curves, with slower heating rates carbon burn off is greater at lower temperatures (Figures 3.21 and 3.22). Comparison of the two cokes show that at any given heating rate, Coke 1 is more reactive than Coke 2 (Figure 3.23).

The DTA curves for the two cokes (Figures 3.24 and 3.25) also highlight the greater reactivity of Coke 1, whose DTA peaks occur at lower temperatures, especially at the higher heating rates. The higher reactivity of the Coke 1 is attributed to its greater porosity, thus presenting a larger surface area available for reaction to occur (Chapter 2).

The determination of activation energies for the coke reactions by the Kissinger method is reported in Section 3.5.
3.4.4 TG/DTA results for coals

Figures 3.26 - 3.29 show the TG curves for the three coals in flowing nitrogen, static air, flowing air and flowing oxygen at 12 °C per minute heating rate.

Figure 3.30 shows the DTA curves for the three coals. The materials were heated in flowing nitrogen (44.4 cm³ min⁻¹) at 40 °C per minute until a temperature of 900 °C was reached. The gas flow was then switched to carbon dioxide (35.2 cm³ min⁻¹) and the heating rate to 12 °C per minute.

3.4.5 Discussion of coals

Under all conditions, Coal A reacts fastest and Coal C slowest. For all the coals, significant weight losses commenced at about 550 °C. As expected the oxidation was slowest in static air (Figure 3.27) and fastest in flowing oxygen (Figure 3.29). Also, under any given atmosphere Coal A had the highest weight loss and Coal C the least. These observations are similar to those found under isothermal conditions of reaction (Section 3.3.5).

The DTA curves (Figure 3.30) recorded under precisely the same conditions showed three quite different patterns for the loss of volatile material.
Figure 3.26 TG traces of 3 coals in nitrogen (44.4 cm$^3$ min$^{-1}$) at 12°C min$^{-1}$ to 1100°C
Figure 3.27 TG traces of 3 coals in static air at 12°C min\(^{-1}\) to 750°C
Figure 3.28 TG traces of 3 coals in moving air (43.5 cm$^3$ min$^{-1}$) at 12 cm min$^{-1}$ to 750°C
Figure 3.29 TG traces of 3 coals in flowing oxygen (41.3 cm$^3$ min$^{-1}$) at 12°C min$^{-1}$ to 55°C
Figure 3.30
DTA TRACES FOR 3 COALS

Arrows indicate change of heating rate

HEATING RATE 290°C to 900°C
THEN 12°C to 1400°C
CHART SPEED 300 mm min
SENSITIVITY mV/°C
ATMOSPHERE CO
FLOW RATE 100 cm³ s
REFERENCE Pt
HOLDER Pt

Coal A
Coal B
Coal C
Coal A loses volatile material at a lower temperature than the other two coals and a broad DTA peak is observed, followed by a small sharp peak. Coal B's volatile material is released at a somewhat higher temperature and the DTA curve shows a pair of sharper peaks, the first one larger than the second. The Coal C's DTA pattern records a single peak for loss of volatile matter, which occurs at a still higher temperature. These patterns of volatile matter release were maintained under other different atmospheric conditions (nitrogen, oxygen, static and flowing air).

The DTA traces of the three coals show clear differences which distinguish each coal from the others.

3.5 ACTIVATION ENERGIES

Thermal analysis data on the cokes and coals have been used to deduce activation energies.

The gradient of an isothermal TG curve showing variation of weight loss vs time is a measure of the rate of reaction. From a series of isothermal TG curves at different temperatures, it is possible to obtain kinetic data for an Arrhenius plot.

Figure 3.31 shows an Arrhenius plot for reaction of the two cokes in flowing air. The reaction rates were measured from the initial gradients of the isothermal TG weight loss curves. The activation energies were calculated to be 151 kJ mol$^{-1}$ for
Figure 3.31 Variation of reaction rate constant with temperature for Cokes Nos. 1 and 2 in flowing air.

- Coke No. 2
- Coke No. 1
Coke 2 and 140 kJ mol\(^{-1}\) for Coke 1. These values are comparable with those for cokes used in the zinc-lead blast furnace (Carter, 1983). It is noted that Coke 1 has a lower activation energy than Coke 2.

It is noted also that at higher temperatures, the Arrhenius plot changes gradient. This is because, whereas at lower temperatures the rate of reaction is controlled by the chemical rate (Walker, et al. 1959), above 700 °C the rate of reaction is determined by the thickness of the gas layer at the carbon surface, i.e. diffusion from boundary layer is rate controlling.

Figure 3.32 shows the Arrhenius plot for the Boudouard reaction of the two cokes. The calculated energy of activation is 182 kJ mol\(^{-1}\) for Coke 2 and 144 kJ mol\(^{-1}\) for Coke 1. Again the figure is higher for Coke 2 and is comparable with that for the Boudouard reaction of cokes used in the zinc-lead blast furnace (Carter, 1983).

The Arrhenius plot of the Boudouard reactions show a single linear region up to relatively high temperatures (1400 °C). This is because gaseous diffusion is not becoming rate-limiting until such high temperatures are reached.
Figure 3.32 Variation of reaction rate constant with temperature for Coke No.1 and Coke No.2 in flowing carbon dioxide.
Figure 3.33 shows the Arrhenius plot for the reaction of the three coals in flowing air. Again the reaction rates were estimated from the gradients of the isothermal TG curves. The activation energy of the reaction is 106 kJ mol\(^{-1}\) for Coal A, 125 kJ mol\(^{-1}\) for Coal B, and 128 kJ mol\(^{-1}\) for Coal C. These figures are somewhat less than those for typical metallurgical cokes.

Figure 3.34 is a Kissinger plot of the DTA data of the Boudouard reaction of two cokes. The activation energies deduced from the data indicate a lower value for Coke 1 (141 kJ mol\(^{-1}\)) than for Coke 2 (155 kJ mol\(^{-1}\)), consistent with the differences observed in values obtained by the Arrhenius method. The larger difference in value by the two methods for Coke 2 is of the same order as those for cokes used in the zinc-lead blast furnace (Carter, Glasson and Jayaweera, 1984). Agreement is much better for Coke 1 for values obtained from the two methods. The differences can be attributed to the incorrect assumption made in the theory underlying the Kissinger method, namely, that the DTA peak temperature corresponds to the temperature of maximum rate of reaction (Sharp, 1972).

Attempts to apply the Kissinger method to DTA data of the coals proved unsuccessful. This probably due to the complexity of the reactions taking place during coal oxidations e.g.
Figure 3.33 Variation of reaction constant with temperature for three coals.
Figure 3.34 Variation of peak minimum temperature $T_m$ with heating rate for two cokes in the Boudouard Reaction.
combination of loss of volatile matter and oxidation of carbon. Indeed for the Boudouard reaction it is difficult to carry out even Arrhenius plots on the TG data.
REFERENCES

CHAPTER 3


Chapter 4

OPTICAL AND ELECTRON MICROSCOPY

Coke microscopy has a history of more than fifty years. Beilby (1922) discussed the structure, origin and development of coke and Ramdohr (1928) reviewed those of cokes and graphites. There were difficulties experienced with these early works because microscopical techniques had not been developed satisfactorily. Marshall (1936) used polished sections to examine some metamorphosed coals using reflected light but this was difficult because of the high optical absorption of cokes. Others worked with ultra thin sections (0.4 µm) and then used transmitted light microscopy (Uejii, 1932; Marshall, 1945).

Oil immersion objectives were successfully constructed for use in reflected light by Ernst Leitz (Wetzlar), a German firm in the 1940's; continued development has transformed the technique for the study of highly absorbing substances. Arising from this a formidable post-war literature exists concerning industrial, natural and laboratory-made cokes; a high proportion of this literature has been descriptive and qualitative.

More recently it has become necessary to comprehend factors underlying the formation of coke and enhancement of quality for industrial purposes. This has resulted in an increasing number
of quantitative microscopical studies which attempt to define coke properties more clearly.

Some optical phenomena observed in relation to the changes in coals during carbonization are reviewed briefly now.

4.1 COAL CARBONIZATION

High temperature metallurgical coke manufacture requires non-oxygen environment with a temperature rising to 1050 °C, leaving the product of nearly elementary carbon. During the heating process there is the progressive loss of non-carbon elements with rising temperature. Such elements are lost as gaseous compounds, normally compounds of carbon, and this occurs concurrently with the remaining carbon material developing into condensed aromatic systems.

Three overlapping phases can be discerned in the carbonization process. Boundaries between phases depend on temperatures which vary with the nature of the coals undergoing carbonization. Unless the original material is very low or very high in carbon each of the three phases will occur.

The first phase between about 150-400 °C can be identified as the precarbonization time. Here some molecular rearrangements occur; also early condensation reactions and molecular stripping take place but there is very little change to be observed in the optical properties of the material.
The second phase which is that of active decomposition, from 400 - 650 °C, involves considerable devolatilization and condensation reactions leading to a residual carbon deposit (Berkowitz, 1967 and Blayden, 1969).

If three-dimensional bonding results early in aromatic condensation, the structure is disordered. However, if aromatic condensation occurs without cross-linking then the product will manifest very clear ordering due to development and progressive alignment of aromatic layers or lamellae in groups which form crystallites.

Thus it is during the second phase that softening or formation of liquid from the starting material accompanies the pyrolysis, leading to enhanced molecular mobility, which is required for a high degree of ordering to occur. A number of changes of state take place and can be seen as variations in the pattern of optical properties. When the organic matter is in the fluid state an optically anisotropic mesophase can form from the isotropic melt. Taylor (1961) gave the first description of the mesophase - droplets with lamellar development arise in the isotropic liquid. As the temperature increases, the droplets get bigger maintaining a characteristic optical anisotropy, then they coalesce and deformation takes place producing a mosaic texture with a greater complexity of optical anisotropy than that displayed by the droplets. Development of mosaic textures in coal is dependent on rank and type. Coals below

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bituminous rank, heavily oxidized material and inert constituents do not show mosaic textures and would form chars; bituminous coals display some mosaic textures and will form cokes; anthracites would give graphitic carbon with no coke.

The third phase of carbonization occurs between 650 - 1050 °C. This is the resolidification stage when shrinking takes place. Volatile products from this third stage are simple molecules with hydrogen the predominant product. However despite the fact that the microscopical appearance of the coke displays little change, its properties, including its optical properties, alter dramatically. The changes all point to a progressive lateral growth of aromatic systems although there is evidence for structural disorganization and reorganization taking place early in the phase.

The constituents of coals known as macerals, a term introduced by Stopes (1935), have been classified into three groups namely, vitrinite, exinite and inertinite. Their properties and sub-classes are shown in Table 4.1 and the expression microlithotype suggested by Seyler (1954) denotes the association of these macerals; the nature and the relative amounts of each determine the macroscopic appearance of the coal. The three principal microlithotypes are seen normally viz: vitrite (vitrinite mainly), clarite (vitrinite and exinite) and durite (exinite and inertinite). Vitrite can be seen by the naked eye as bright coal, clarite as silky in
<table>
<thead>
<tr>
<th>Maceral group and symbol</th>
<th>Appearance of maceral</th>
<th>Individual macerals in group</th>
<th>Microlithotype</th>
<th>Principal group of constituent macerals in the microlithotypes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in incident light</td>
<td>in transmitted light</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vitrinite (Vt)</td>
<td>dark grey to white</td>
<td>yellow, orange, red, brown, opaque as rank increases</td>
<td>Collinite Telinite</td>
<td>Vitrinite Vt</td>
</tr>
<tr>
<td>Inertinite (I)</td>
<td>bright</td>
<td>opaque</td>
<td>Micrinite Semifusinite Fusinite Scherotinite</td>
<td>Vitrinite Vt + I (micrinite dominant) I (except micrinite)</td>
</tr>
<tr>
<td>Exinite (E)</td>
<td>light and dark grey to grey</td>
<td>light to dark yellow</td>
<td>Cutinite Resinite Sporinite Alginate</td>
<td>Sporite E Clarite Durite Duroclarite Clarodurite</td>
</tr>
</tbody>
</table>

**TABLE 4.1: A SUMMARY OF NOMENCLATURE USED IN COAL PETROLOGY**
appearance and with a less brilliant lustre than vitrite and durite as dull material.

Microscopy shows that up to 350 - 370 °C, vitrinite grains retain sharp outlines indicating an absence of surface softening; then slight rounding begins to occur heralding the onset of coal softening. Between 380 - 400 °C small pores can be observed forming in the vitrinite indicating volatile evolution. With a few degrees increase in temperature clear signs of flow can be seen and in the region of 420 °C highly fluid conditions exist. Surfaces of reactive material grains are convex which means that it is still non-wetting at this juncture. By about 450 °C anisotropy is substantially developed and anisotropic reactive fluid is wetting organic inerts with the reactive material displaying a concave boundary. Maximum porosity occurs here.

As the temperature is raised further an increase in coke anisotropy takes place with the development of coarse mosaic units coupled with a decrease in porosity caused by the resolidification of the reactive material.

Vitrinite is usually the major petrographic constituent of British coals and the most consistent in its properties. It can be collected, without too much difficulty by density separation and hand selection. Vitrinite usually constitutes 70-80% of any seam, it rarely falls below 50% but this can
occur with some Gondwanaland coals. Much of the work on coal structure therefore has been on vitrinite. This has been preferred to working with a series of whole coals, which will differ amongst themselves in maceral group composition. Nonetheless, other macerals cannot be ignored; some coals particularly those from the Southern Hemisphere contain less vitrinite and have properties in some respects quite different from those coals from Britain and other Northern Hemisphere countries.

For microscopic studies of coal normally it is difficult to make thin sections, and impossible to do so from crushed material. The usual practice is to mount the coal particles in epoxy resin blocks and polish a flat surface across the material. In the portions of the particles thus exposed the macerals can be distinguished and their amounts can be ascertained by a point counting method.

4.2 **OPTICAL PROPERTIES**

Four optical properties are of interest in the study of carbonised vitrinites, viz., reflectance, bireflectance, refractive index and absorption index.

4.2.1 Reflectance

Reflectance of a coal is the measure of incident light reflected from a polished surface of the sample. It is ascertained by microscopic examination under oil immersion of
the vitrinite macerals in reflected light. A photocell or microphotometer is used as the measuring instrument. The optical work is done at a wavelength of 546 nm and a non-drying immersion oil of refractive index 1.518 is needed.

The properties of coal macerals alter with increasing metamorphism and for hard coals it has been found convenient to use just the one property - the reflectance of vitrinite - as a measure of coal rank or the degree of metamorphism. This means that coal rank can be determined independently of maceral composition and that it is possible to distinguish between single seam coals and coal blends, which is normally impossible by conventional analysis.

Smith (1973) used proportion of vitrinite reflectance classes to calculate Micum 40 indices of cokes from coals or blends used by NCB. Okuyama et al (1970) used reflectance and Gieseler fluidity to investigate blending of coals used in coking operations. Acceptable coking coal blends have a mean reflectance of about 1.2% and Gieseler fluidity of about 60-1000 dial divisions per minute. Lower mean reflectance of blends gives a weak coke; too high fluidity renders coke liable to cracking, if fluidity is too low adhesion between particles would be poor. In addition to coke strengths, important carbonization properties have been related to reflectance. Pressure above 2 psi have damaged coke oven walls and it has been shown (Benedict and Thompson, 1976) that peak pressure
exerted varies with reflectance of reactive vitrinite, but to counter this increased inert contents can be used to lower coking pressures. Graphical data has related reflectance to coking pressure and some data has related reflectance to coke reactivity (Thompson and Benedict, 1975; Okuyama et al., 1970). The reflectance of coke has been shown to be an important factor in considering coke strength and Patrick, Sims and Stacey (1977) developed a method whereby relevant detail of texture were ascertained from the microscopic examination of polished coke mounted in resin using a Quantimet 720 image analyser. The current work tackled the question of coke strength by a different approach which is reported in Section 4.7.4. Since reflectance increases continuously with coal rank its determination is a rapid method of quantitatively arriving at the carbon content and other chemical characteristics of a coal.

Reflectance has the additional use in that it is related to the refractive index and thus the molar refraction, which is an additive property of the structured units in the material. The reflectance of most coals varies with direction relative to the bedding plane of the deposit and this would show the influence of pressure during the coalification process. The degree of anisotropy is small in low rank coals but increases through medium rank coals and becomes marked in anthracites. Interestingly as reflectance is apparently unaffected by weathering, unlike other properties, the reflectance of an
outcrop sample could be used, as an indication of the normal chemical and physical properties of the coal at depth (Chandra, 1962).

The reflectance of an unknown sample is ascertained by comparison against a standard of known optical properties. It would be considered normal to measure the reflectance of at least fifty particles on a polished block to obtain the mean reflectance of a sample. Oil immersion objectives would generally be used but objectives designed for use in other media are necessary if refractive and absorption indices are to be determined from reflectance measurements.

4.2.2 Bireflectance and other properties

Bireflectance, defined as the difference between the mean maximum and minimum reflectance, \( R(\text{max}) - R(\text{min}) \), is a variable of significance when studying carbonized coals which estimates the anisotropy of samples. Increasing bireflectance of vitrinites with rising coalification indicates the progressive alignment of the crystallites; these are formed from groups of aromatic layers which occurs as aromatic condensation proceeds.

Most vitrinite of bituminous rank display a minimum bireflectance in the region of 400 °C; then molecular structure breaks down when vitrinite softens in the plastic stage of phase 2 of carbonization. Beyond this region the molecular structure begins to reorder itself and the crystallites attain
a higher degree of ordering than that possessed by the original material. Molecular reorganisations during phase 3 of the carbonization process are often interrupted in this temperature region and it appears that the rate of ordering of the molecular structure is related to this interruption.

The two indirectly determined variables, refractive index and absorption index provide information on the changes that take place in molecular structure during carbonization.

Despite the fact that reflectance is the most used, directly measured experimental parameter in microscopical studies of coals and cokes, it is not a fundamental property of organic matter; however, like other optical properties it responds to thermal and other influences. The reflectance ($R_s$) of an optically absorbing material is related to its refractive index ($n_s$) and absorption index ($k_s$), as well as to the refractive index ($n_m$) of the medium in which the measurement is made, by Beer's equation where:

$$R_s = \frac{(n_s - n_m)^2 + n_s^2 k_s^2}{(n_s + n_m)^2 + n_s^2 k_s^2}$$

4.3 **ANALYSIS OF SPORES**

Spores differ in a number of significant respects from other kinds of fossils. All land vascular plants produce at some stage in their life cycle the reproductive spore bodies, which
also include the pollen arising from seed plants. Until the appearance of insect pollinated flowering plants in the Cretaceous period (135-65 million years ago), all land plants from Silurian times (430-395 million years ago) onwards relied on air currents for dispersal (Anemophilous). Spores accumulating in the coal itself would largely be derived from the coal swamp vegetation which was presumably of considerable lateral extent.

Of Carboniferous plants, two types of spores are found, miospores which include microspores and isospores with maximum dimensions less than 0.2 mm and megaspores which are larger forms. The latter may be seen clearly in thin or polished coal sections as bright orange or yellow, elongated compressed masses. Miospores cannot be easily examined and have to be separated by oxidation techniques from the associated sediment or coal. In the past the various spore forms were identified by letter codes and numbers, which were considered to be suitable to express an arbitrary form of classification; this did not infer a definite affinity between various types (Raistrick and Simpson, 1933). Now a binominal classification, more in keeping with standard palaeontological nomenclature, is used.

As with some other palaeobotanical studies uncertainty exists as to exact affinities between certain spore types; some even have been shown to be merely juvenile forms of apparently
distinct adult spores (Moore, 1946). However, a great deal of evidence has accrued in recent years concerning the types of spores derived from particular plant types (Smith, 1962).

Spores are classified according to their shape, symmetry, size, internal structure and surface ornamentation. Uncompressed spores are often spherical or oval in shape and consist of two principal layers, an outer exine containing the intine. The relative dimensions of the layers are significant and some coals are recognized by the predominance of miospores with either thick or thin exines. The outer surfaces of exines are commonly spinose, ridged, granular, nodose or pitted. Some exines separate into a number of layers, thereby forming bladders which in the living material could have been filled with air enabling the free dispersion of the spores. In many spores, intines are portioned by sutures forming two or three nearly equal parts in the monolete and trilete forms. Alete forms are those in which no suture occurs.

Since spores occur within the coals, material for spore analysis can be collected from the coal face and does not depend on interseam sections which are used for the collection of other fossil groups. Both the larger megaspores and the smaller miospores have been used for correlation work, the frequencies of the different species normally varying in a vertical sequence. Despite the fact that the total spore
assemblages of two seams may be similar, their vertical distribution within the seams may be very different. Nevertheless the spore content of a seam can change laterally particularly when lithological changes take place. Hence spore analysis is reliable only for short range correlations with a limit of a few miles between sampling points.

The megaspore content of coals is ascertained from an appraisal of thin or polished sections forming an overlapping series throughout the total seam thickness. In this way Slater (1932) and several contemporary workers determined a series of spore types at that time numerically identified and analysed concentrations at particular horizons. Graphical representation by means of spindle diagrams were used which clearly demonstrated the application of the method to correlation. Subsequent work has supported those early conclusions but nowadays the accent is on the use of the miospores extracted from the coal seams. The early studies of miospore distribution were made by Thiessen in America (Stach 1968) and a lot of the subsequent work has been carried out in Europe.

The current study has covered the palaeontological examination of samples of British, European and Australian coals for fossil spores. It was reasoned that the two coals of Europe, laid down in tropical conditions in Carboniferous times (345-280 million years ago), would exhibit different characteristics in
this respect from those of the Australian coal, which as a Gondwanaland coal was laid down in Permian times (280-225 million years ago) and as such had never experienced a tropical climate.

4.4 POROSITY OF COKE

Coke is not only a source of heat and a reductant but acts as a refractory column supporting the burden in the blast furnace. It must survive in the melting zone to give an acceptable degree of permeability which implies that it must not only have sufficient physical strength to support the weight of the burden but also be capable of resisting serious degradation in its descent of the furnace shaft.

The relationship of strength to porosity of metallurgical cokes has been undertaken by a number of workers, a matter which was first investigated by Rose in 1924.

Density measurements have been one approach to assessing strength/porosity but pore sizes range from microspores of less than 1 nm involved in gas adsorption to macropores of several millimetres across and no single determination is able to cover such a range. However, for industrial purposes it would be unusual for a complete measure of porosity to be made and normally porosity is ascertained from the ratio of the apparent and true relevant densities or from mercury penetration of the material or by microscopic examination. Microporosity in the
range from 1 nm can be assessed from the capillary condensation of nitrogen. Volume porosity is calculated from true and apparent relative densities from the equation:

\[
\% \text{ porosity} = 100 \left( 1 - \frac{\text{apparent density}}{\text{true density}} \right)
\]

and this method is set out as a British standard (B.S. 1016, Part 13).

The technique of mercury porosimetry requires that mercury be forced under pressure into the pores and recording the volume of liquid penetrating the pores as a function of pressure applied. An assumption is made that pores are all of circular cross section and a calculation is made using the equation:

\[
r = \frac{75,000}{p}
\]

where \(r\) is the pore radius in \(\text{Å}\) and \(p\) is the applied pressure in \(\text{kg/cm}^2\). This method is suitable for the range of pore radii from 200 Å to 0.25 mm and is applicable only to the open porosity of the coke.

Lineal analysis or point counting is used in the determination of coke porosity from microscopic examination of polished resin mounted coke sections. Lineal analysis relies on the method used by Abramski and Mackowsky (1952) where values for five
different pore sizes are recorded and then an average porosity is calculated whereas in point counting the transverse of the sample is stepwise at a series of regular intervals. Both these methods can be labour intensive if automatic counting arrangements are not available apart from the necessity of selecting representative samples with porous structure undamaged in the preparation of polished sections.

A Quantimet 720 image analyzer based on a Vickers microscope for analysis of those properties of the porous structure of coke which influences its strength was used by Patrick et al., (1976). With such an apparatus a count of a very large number of points is possible.

In the current work an effective optical image-analysing system was devised utilizing what is now standard laboratory equipment and the results compared with data obtained from the application of scanning electron microscopy.

In representative samples of the two cokes it was apparent that the pores of coke 1 are larger than those of coke 2. It was found that the strength of coke 1, as ascertained by compression testing was less than found in the case of coke 2. The detail of the strength tests are included later in this section. Plate 4.1 (page 185) shows scanning electron micrographs of sample fracture surfaces of both cokes tested. Additional work to cross check these findings utilizing a
metallurgical microscope linked with a video, computer and printer was also undertaken and appears later in this section.

Most normal metallurgical cokes are composed of reacted components showing mosaic structures, the mosaic sizes varying from $0.3 \mu m$ up to $> 24 \mu m$. Mosaic size is modified by heating rate.

It is considered that more work could be done in this area since it has been found in practice that a good metallurgical coke performs satisfactorily in the blast furnace if its porosity lies between 50-55% but clearly such exploratory procedures as outlined here would not be practical for the purposes of everyday quality control.

Apart from the work on the cokes, microscopical examination of the three coals took the form of observing the differences on reaction both in air and in carbon dioxide at different temperatures. This was conducted in connection with sorption balance work and the samples selected for electron microscopic studies were the initial material, 50%, 70% and 100% burn-offs of the material.

4.5 STRENGTH OF COKE

Coke strength rather than the strength of the original coals is the important parameter in blast furnace technology. Thus, it
was not considered relevant to measure strength of the coals from which the cokes were made. Tensile strength of coals have been measured with some difficulty but compressive strengths within the range of $5 \times 10^3 - 7 \times 10^4$ kN/m$^2$ have been reported (Speight 1983). One property that can be related to strength measurements for coals is grindability based on the Hardgrove index (Grainger and Gibson, 1981).

British coals with volatile material contents of 15-30% are the easiest to grind, having Hardgrove indices of about 100—the higher the index the easier it is to grind. Coals with lower volatile content could be anthracites with a Hardgrove index in the region of 50 and coals with high volatile matter up to about 40% are also harder.

### 4.6 MICROSCOPIC TECHNIQUES AND APPARATUS

The resolving power of a microscope depends largely on the wavelengths of radiation employed, the optical microscope having a maximum resolution of between 200 and 300 nm. Optical microscopy can reveal surface defects, grain boundaries and gross morphology of solids, but much greater detail became possible with the advent of electron microscopy.

The three different arrangements employed for image formation in optical microscopy, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are shown in Figure 4.1.
Fig. 4.1 Image formation
4.6.1 Electron Microscopy

The basis of the operation of an electron microscope rests on the wave-particle duality of electrons as expressed in the de Broglie equation:

\[ \lambda = \frac{h}{m_e v} \]

where \( m_e \) is the mass of the electron, \( v \) its velocity, \( \lambda \) the associated wavelength, and \( h \) Planck's constant.

When an electron is accelerated through a potential difference of \( V \) volts the energy imparted is \( eV \), where \( e \) is the charge on the electron. This is equated to the kinetic energy \( \frac{m_e v^2}{2} \), so

\[ m_e v^2/2 = eV. \]

hence

\[ \lambda = \frac{h}{(2m_e eV)^{\frac{1}{2}}} \]

and if the appropriate values of constants are inserted in this equation a good approximation is

\[ \lambda = \left(\frac{1.5}{V}\right)^{\frac{1}{2}} \text{ nm} \]

Due to the high electron velocity, relativistic corrections are necessary for some uses, usually when acceleration potentials are in excess of 100 kV, thus \( m_e \) should be replaced by \( m_e \left(1 - v^2/c^2\right)^{-\frac{1}{2}} \) and the expression becomes:

\[ \lambda = \frac{1.5}{V \left(1 + 10^{-6}V\right)}^{\frac{1}{2}} \]

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The wavelength of electrons accelerated by a potential difference of 80 kV is 0.0043 nm (4.3 pm), so by the use of an electron beam and a thin (1 μm) specimen a much greater resolving power is possible. However, artefacts may be present, which could be caused by electron beam irradiation and the effect of high vacuum on the specimen. The theoretical limit of resolution (1 pm) cannot be attained mainly because of lens aberrations caused by limitations in lens design and manufacture, material impurity, electron instabilities and contaminations in the microscope column.

The unavoidable interactions of electrons with matter limits the thickness of specimens used in TEM because of the excessive scattering of the beam experienced in passing through them. Thus, in most cases, the specimen must be thinner in the direction of the beam, less than 200 nm if internal structure is to be observed.

Theory and application of transmission electron microscopy to surface chemistry is given by Fryer (1979), with many references to carbon and graphite.

In scanning electron microscopy the image is formed by secondary electrons ejected from the sample surface. The limit on sample size and thickness thus depends only on the dimensions of the sample chamber. The range of magnifications overlap those of optical and transmission electron microscopy.
and maximum resolution lies around 20 nm. Principles and applications are described by Goldstein et al. (1980).

4.6.2 The PHILIPS EM300 transmission electron microscope (TEM)

The Philips EM300 is comprised essentially of an electron emission chamber followed by a six-lens electron optical system. Figure 4.2 shows a schematic layout of the system. The electron gun is a "triode" which has an emitting cathode filament, a bias or Wehnelt cylinder and a cylindrical anode.

The EM300 has a resolution of 0.5 - 1.0 nm and is fitted with the "LINK" system for element analysis.

Samples were mounted on a copper grid with carbon film and the specimen grid mounted in the holder and introduced to the microscope through the objective lens. A voltage of 80 kV was selected and the filament adjusted to saturation current. After alignment of the beam and correction for condenser lens astigmatism, the wide angle, low magnification specimen images mode was selected and the grid viewed for a suitable area of the specimen. When found, the instrument was set to the magnification mode and the appropriate magnification factor selected. The image was then carefully focused and photographed after adjusting the illumination and exposure time. 8 x 10 cm plates were employed to record the images or on occasions some work was recorded on 35 mm film.
Figure 4.2 Philips E. M. 300 Electron Microscope schematic layout
4.6.3 The JEOL scanning electron microscopes

In SEM an area to be examined is irradiated with a finely focused electron beam, which may be static, or swept in a raster across the surface of the specimen. This produces secondary electrons, back scattered electrons, Auger electrons, characteristic X-rays and photons of various energies. The secondary and backscattered electrons vary as a result of surface topography as the electron beam sweeps across the specimen. The microscope has a large depth of field (1 cm - 1 \( \mu m \)), giving the image the appearance of a three dimensional structure and detailed surface relief.

As the secondary electron emission comes only from a volume near the beam impact area the use of a finely focused beam results in a high resolution.

4.6.3.1 The JEOL JSM-T20 microscope

The JSM-T20 was developed for easy operation and maintenance with a resolution of 20 nm (200 Å) and magnifications 35 x to 10,000 x in 16 steps. Both secondary electron image and backscattered electron image modes can be selected. It has a joystick image shifter and a 9 inch CRT.

The electron optic system has an electron gun with accelerating voltage of 19 kV and a 3-stage reducing lens system (two condensers and one objective). On the console three scanning
mode buttons allow the selection of wave-form (suitable for adjusting gun filament and focusing image), Y modulated image or the secondary electron image. Three scanning speed buttons allow the selection of image size. "Contrast" and "brightness" controls determine the correct exposure for the camera attachment.

4.6.3.2 The JEOL JSM-35C microscope

The JEOL JSM-35C is a high performance SEM. It is fully automatic and compact. It consists of the console, pump box and the operation and display system. It has a minimum resolution about of 7 mm (secondary electron image), the probe current is $10^{-12} - 10^{-7}$ A and the accelerating voltage is 0 - 39 kV. The lens system is of the electromagnetic type, two stage-condenser lens and objective lens and the objective lens apertures are 0.1, 0.2 and 0.6 mm diameter which are selectable from outside the column. The working distance is either 15 or 39 mm and there is an indicator display showing the setting. The stigmator is electromagnetic, 8-pole. The vacuum operation system is fully automatic but it can also be operated manually. The working vacuum is $1 \times 10^{-5}$ torr or better. An ultra-high resolution CRT is incorporated in the instrument and a highly magnified image can be obtained; magnifications can range from 10 times to 100 - 200 thousand times.

Figure 4.3 shows a schematic diagram of a scanning electron microscope.
Figure 4.3 Schematic diagram of a scanning electron microscope column
The fine-beamed electron probe scans the specimen and an image is displayed on the cathode ray tube. The image magnification is determined by the ratio of scanning amplitude of CRT to that of the electron probe.

The beam from the electron gun passes through a series of lenses which demagnify the electron beam, the final lens focusing the beam on the specimen. The resolving power of the microscope cannot be less than the electron beam diameter. A set of scanning coils is mounted above the final lens, and within the bore of the lens is located a stigmator and a set of three movable apertures. These apertures determine the angular aperture subtended by the electron beam at the specimen surface. At the base of the lens column is a large specimen chamber. The whole system is evacuated by means of a pumping system.

The secondary electrons are detected by a scintillator/photomultiplier system, the resulting signal being further amplified and applied to the cathode ray display tube.

The supporting electronics of the microscope are arranged in a modular design and there are modules to supply the current for the lenses, the accelerating voltage, control systems for the cathode ray displays and ancillary equipment associated with signal detection and amplification.
Samples for examination by SEM are mounted usually on brass or aluminium stubs and gold coated to approximately 15 nm in a Polaron SEM coating unit E5100 to ensure electrical conductivity.

If energy dispersive micro-analysis is to be used then the support stub can be made of graphite and the specimen coated with a conductive layer of carbon.

4.6.3.3 Energy dispersion X-ray microscopic analysis
The spectrometer used was a "LINK SYSTEM" fully quantitative X-ray micro-analyser, incorporated with the JEOL JSM 35C scanning electron microscope. The JEOL microscope has a selected area facility for limiting the scanned area of the specimen from which X-rays are emitted and analysed. There is also a static facility for micro-analysis using a mini beam size approaching 10 nm, neglecting spatial resolution.

With this combined equipment at high magnification (up to X20,000) it is possible to focus and observe an area or inclusion on the surface of a specimen and obtain elemental analysis either by the variable selected area facility or by single electron probe.

In this instrument the design of the X-ray detector which is faced by a barium "window", the lower limit of detection occurs at atomic No. 11; thus organic material cannot be detected.
4.6.3.4 Optical Microscopes

A Zeiss Standard 14 optical microscope fitted with a Zeiss 35 camera taking 35 mm film was used in the spore analysis work. An Olympus Photomicrographic system model PM-10AD incorporating an Olympus Canox microscope fitted with an Olympus C-35AD camera with automatic exposure was used to examine coal, coke and ash samples.

The main disadvantage of the technique is the insufficient focal depth, 0.4 - 10 µm.

4.7 EXPERIMENTAL PROCEDURE

4.7.1 Reflectance measurement

The method of analysis requires the preparation of a block of crushed coal and a binder which is ground and polished to give a flat surface. Examination is then conducted using a reflected-light microscope. The necessary equipment to undertake this work during the current research was not available locally. Some improvised arrangements failed to achieve consistent results. Reflectance measurements were made at the University of Newcastle using a Leitz MPVI microscope and an EMI 6094B photomultiplier. The immersion oil had an e of 1.518 at 20°C, the magnification of the oil objective was x60 and the measuring area was 10 µm diameter.
4.7.2 Spore Analysis

The current work used miospore extraction techniques for spore analysis.

Powdered samples of the three coals were treated with Schutz solution (nitric acid to which potassium chlorate had been added) for 24 hours. The actual time taken for oxidation depends on the rank or type and, if from a surface outcrop, or the degree of weathering of the coal. The reaction can proceed quite strongly in the initial stages and therefore the container was placed in an ice bath in a fume cupboard. After washing and decantation with water, the residue consisting of spores, plant material and unaltered particles was treated with a 10% solution of potassium hydroxide and then washed again several times by decantation.

A small portion of the residue was transferred to a test tube partly filled with water and centrifuged. The larger fragments settle so that the suspension consists of the finer material including the miospores (if present). A drop of the suspension was placed on a slide together with a smear of melted glycerine jelly forming the mount and was then evaporated gently.

The miospores can then be identified and counted under high power magnification or, as in the present case, they can be photographically recorded. A Zeiss Standard 14 optical microscope fitted with a Zeiss 35 camera taking 35 mm film was used.
4.7.3 Coke porosity measurement

The current work examined the porosity of samples of the two cokes by microscopic techniques. Two methods were used.

The first method involved an improvised automated system whilst the second method relied on linear measurements of the pores and pore walls of samples utilizing enlarged prints of electron micrographs.

For the first method, the following apparatus was assembled consisting of:
1. Metallurgical microscope fitted with black and white video camera.
3. Hitachi video monitor.
4. Apple II computer
5. Twin floppy disc drive
6. Video camera monitor
7. Apple graphex tablet with interface card.

Figure 4.4 is a schematic diagram of the apparatus.

A random selection of a piece (+ 40 mm) of each of the cokes was mounted in "Spur" resin discs. When the resin was set, each disc was ground on a carborundum wheel so that one flattened surface of each specimen was exposed.
1. Metallurgical microscope fitted with black and white video camera
2. Paper "tiger" printer integral data system
3. Hitachi video monitor (shows surface being recorded by computer printer)
4. Apple II computer
5. Twin floppy disc drive
6. Video camera monitor (shows actual surface)
7. Apple graphex tablet with interface card
8. Power pack
9. Additional monitor (needed for precise area selection)

Figure 4.4 Sketch of layout of equipment used to assess porosity of coke samples
Initially there was some difficulty in getting the apparatus to differentiate between pores and the solid coke material. The problem was solved by simply rubbing each surface with talc powder which filled the pores and presented clearly defined white areas to the camera against the dark non-porous background. A computer programme was devised to sum the dark and light portions of each specimen selected to be what seemed representative of the specimen as a whole. The programme is attached at Appendix 1.

4.7.4 Coke strength measurements

The strength of the two cokes were examined using two Instron Universal testing instruments, the floor model (TT-D) and the table model 1026.

Direct and indirect tensile strength tests were undertaken and Young's modulus for both cokes were measured. Difficulties arose with the tensile strength tests due to breakage of samples.

4.7.4.1 Indirect tensile strength

Diametral compression tests were employed using the standard floor model Instron machine TT-D operated with a cross head speed of 0.5 mm per minute, a chart speed of 100 mm per minute and 200 kg full scale deflection. Figure 4.5 indicates how load was applied.
Figure 4.5 Diametral compression test

\[ P = \frac{2w}{\pi D t} \]
The procedure followed was that test pieces of coke were hand ground on a carborundum wheel to a diameter and thickness of 1 cm and mounted between the closed jaws of the machine. An increasing load was applied and the load at fracture recorded. The strength, \( P \), of the coke was then calculated using the formula:

\[
P = \frac{2W}{Dt}
\]

where \( W \) = the applied load in kg

\( D \) = the diameter of the test piece in mm

and \( t \) = the thickness of the test piece in mm.

4.7.4.2 Tensile strength (direct)

Work was undertaken using the table model Instron machine 1026 operated with a cross head speed of 5 mm per minute and a chart speed of 500 mm per minute. It was found that the floor mounted Instron machine was too bulky for the task and even so flexible mountings had to be devised to accommodate the stresses set up in the samples as they were being mounted in the smaller machine.

Samples of both cokes were hand ground on a carborundum wheel into circular sectioned pieces of varying diameter and thickness. These samples were individually mounted between two 2 inch lengths of 0.5 inch diameter mild steel bar which had been recessed to a depth of 2 mm at one end of each piece of
steel to allow mounting the coke sample in Araldite, high strength epoxy adhesive, and allowed to set for 24 hours. (5 minute epoxy Araldite 2002 was earlier found to be unsatisfactory). Figure 4.6 shows detail of the mounting.

Despite the fact that the smaller Instron machine was used there were difficulties experienced with fracturing of specimens in setting up and this was dealt with by arranging non-rigid mountings. Mild steel holders were recessed to take 24-hour Araldite epoxy resin as before, but they were shortened and drilled through the base to allow the shaft of a substantial headed steel rod to be put through the hole before the specimen was mounted as indicated in Figure 4.7 This provided the required flexibility.

Each sample was then subjected to a steadily increasing tensile force until the coke fractured. Plate 4.1 shows fracture surfaces.

4.7.4.3 Young's modulus

Data obtained whilst assessing tensile strength using the bench model Instron 1026 was utilized to calculate Young's modulus.

The processed print-out recording of each valid trial measurement on the two cokes was considered. The print-out is in effect a graph of the stress applied against the strain
Figure 4.6 (a) exploded diagram of test piece

- 183 -
Figure 4.7 Modified coke test piece holder
Plate 4.1

Fig: (a) Fracture surface of coke No.2.

100 μm

Fig: (b) Fracture surface of coke No.1.

100 μm
involved and Young's modulus is therefore given by the slope of the graphs.

4.8 **EXPERIMENTAL RESULTS**

The three coals and two cokes, which are the subject of study of this thesis, have been examined by the microscopic techniques described above. Results are presented in this section.

4.8.1 **Coal reflectance**

The reflectance measurements on the coals gave the following results:

<table>
<thead>
<tr>
<th>Coal</th>
<th>Reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.96%</td>
</tr>
<tr>
<td>B</td>
<td>1.11%</td>
</tr>
<tr>
<td>C</td>
<td>1.40%</td>
</tr>
</tbody>
</table>

These data clearly distinguish the English coal from the European and Australian materials, the reflectance of the latter two coals indicate that they are medium volatile coals. The English sample has undergone less metamorphism and as such has more volatile material in its composition than the other two samples. The reflectance exhibited by the coal A is that of a high volatile coking coal (van Krevelen, 1961).

4.8.2 **Spore analysis results**

It was found that whilst the British and European samples (both Carboniferous coals) displayed a similar population of
spores the Australian coal gave a negative result. On the one hand it can be argued that such an outcome would be correct since Gondwana coals are known to have a scarcity of exinite material (alginite, cutinite, resinite and sporinite). On the other hand it could be held that the photographs of the British and European material, which would be expected to contain approximately 4% exinite, were mere artifacts, despite the fact that they did have the appearance of ruptured exine coatings, having lost their intine material; this again is what should be expected since exine alone survives as a fossil (Chaloner and Muir in Murchinson and Westoll, 1968).

The coatings of spores survive because they are formed in part of an almost chemically inert protein, sporopollenin, which is resistant to most agents of decay particularly under acid or anaerobic environmental conditions, e.g. where peat bogs and lake deposits form. In oxidizing environments, however, such as most soils and exposed surfaces, sporopollenin is rapidly destroyed. This again is consistent with the conditions which could be expected for Gonwanaland coals as they were being formed.

The exinite content of the coals (BSC analysis) is as follows:

<table>
<thead>
<tr>
<th></th>
<th>British Coal</th>
<th>European Coal</th>
<th>Australian Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>up to 5%</td>
<td>up to 3%</td>
<td>0%</td>
</tr>
</tbody>
</table>
and whilst it was true that no trace of spores could be found in the Australian material, there was a scarcity of evidence from the European coals. It is considered that at least two instances arising from the examination of the two European coals could be mere artefacts and it was felt that overall the results were inconclusive.

It was decided that further information might be obtained by looking at all three maceral groups under transmitted light, incident light and fluorescence microscopy.

The sections (<10 μm) were prepared accordingly and examined under transmitted light using an Olympus photo-micrographic unit mode PM-10AD. It was anticipated that the two European coals could show more orange/red light than the Gondwana coal and this seemed to be the case, Plate 4.2, implying a high vitrinite content. Also the absence of yellow coloured material apparent in the case of the Gondwana coal does tend to confirm a lack of exinite. Polished, epoxy resin mounted material from the thin sections had been prepared and did not detract from these observations under incident light.

In an attempt to confirm the latter finding, regarding the lack of exinite, the same thin section slides were used to conduct the fluorescence microscopy work. Schoehardt (1936, 1943) had observed that all exinite material emitted fluorescence light when irradiated with ultra-violet, violet or blue light and
Plate 4.2 Coal maceral groups under transmitted light

Coal A

Coal B

Coal C

all at X250 magnification
other workers since have used this method to study coal macerals.

The three slides were exposed to blue light in this instance and observed down an Olympus BH2 microscope incorporating an OM2 camera. Only orange-brown coloured material shows up on the Gondwana coal, which is vitrinite, plate 4.3. The yellow to very dark brown material on the other two photographs is considered to be their vitrinite with different dispersal patterns in the two samples.

The petrographic analyses of the three coals (BSC data) are as shown below, and the conclusion reached after examination of the material is in accord with that assessment.

<table>
<thead>
<tr>
<th>COAL</th>
<th>VITRINITE</th>
<th>EXINITE</th>
<th>INERTINITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>British</td>
<td>80</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>European</td>
<td>81</td>
<td>3</td>
<td>16</td>
</tr>
<tr>
<td>Australian</td>
<td>76</td>
<td>-</td>
<td>24</td>
</tr>
</tbody>
</table>

4.8.3 Coke porosity

Results using the metallurgical microscope showed that the coke 2 had a pore area of 52.2%, non porous area 47.8%. Coke 1 had a pore area which was between 54.4 - 57.7%, non porous areas 45.6% and 42.3% respectively.
Plate 4.3 Coal maceral groups by fluorescent microscopy

Coal A

Coal B

Coal C

all at X500 magnification
It was observed that there could be a significant alteration in results brought about by varying the grey areas which mark the limit of the pore perimeters, but it does appear that the technique can give a reasonable result.

Plate 4.4 shows the number and extent of pores on a randomly drawn line on the enlargement to 15 x 10 cm of an electron micrograph of coke 1.

The overall length of the line A-B is 15.2 cm and the sum total of the pore length = 8.6 cm. Thus the porosity is:

\[
\frac{8.6}{15.2} \times 100 = 56.6\%
\]

The photographic enlargement was x50 hence the overall length of line A-B is \(\frac{15.2 \times 10^{-2}}{50}\) = 3040 \(\mu\)m.

Since the sum total of the pore length was made up of 9 pores the average pore diameter = \(\frac{3040}{9}\) \(\mu\)m = 191 \(\mu\)m.

Five such randomly drawn lines on a photograph gives a reasonable reliable percentage figure for porosity which is not noticeably improved by increasing the number of line counts. This particular example demonstrating the method was selected because, by chance, it was the average of five such measurements.
Plate 4.4  Coke No.1 at x50 magnification
By adopting a similar procedure for a sample of coke 2 using an enlarged micrograph of material mounted in a resin block in the same manner as for coke 1 a figure of 52% porosity was obtained, with an average pore diameter of 144 μm.

The above values compare favourably with figures of 54.2% and 56.9% respectively for the porosity of coke 2 and coke 1, obtained from sorption microbalance work (Chapter 2).

4.8.4 EDAX Results

It was found that there was broad agreement with BSC (personal communication) as regards major components for the three coal ashes but low level counts could not be distinguished from the base line trace. Figures 4.8 to 4.11 show the recorded traces for the two cokes, the coke ashes, the three coals and the coal ashes.

An energy dispersive micro-analysis carried out at the JEOL (UK) Ltd. laboratory in London, where counts were allowed to accumulate to discernible amounts did provide some additional detail. The results are based on a total of 500,000 counts where the probe sampled six locations on the "cauliflower end" and a similar number of locations on the "chemical end" of a specimen of coke 2. Percentage levels for eight environmentally potential pollution hazards were found to be as follows:
Figure 4.8 EDAX traces for two cokes

Coke No.2

Coke No.1

- 195 -
Figure 4.9 EDAX traces for two coke ashes

Coke No.2

Coke No.1

- 196 -
Figure 410 EDAX traces for three coals

Coal A

Coal B

Coal C
Figure 4.11 EDAX traces for three coal ashes

Coal A

Coal B

Coal C
The 500,000 counts exclude carbon and the other seven elements with atomic numbers from 1-8 inclusive, also atomic numbers 18, 36, 61, 84-89, 91 and 93-102.

Such information is useful in assessing what amounts of trace elements would be liberated to the atmosphere in the vicinity of a blast furnace, a matter which is of particular significance currently.

On the same basis four other elements of interest were assessed:

<table>
<thead>
<tr>
<th>Element</th>
<th>% of counts recorded</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>0.2667</td>
</tr>
<tr>
<td>Potassium</td>
<td>1.3362</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.1521</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.0135</td>
</tr>
</tbody>
</table>

When sodium and potassium accumulate they have a negative effect on the performance of the blast furnace.
Likewise quantities of sulphur or phosphorus when present have the tendency to get into the iron and this results in an unsatisfactory product.

4.8.5 Strength measurement and Young's Modulus results

Results showed that the cokes have indirect tensile strengths of 4.7 MN/m$^2$ for coke 1 and 6.3 MN/m$^2$ for coke 2. Such figures would indicate that they would perform satisfactorily in the blast furnace since the strength required for good cokes lies in the range of 3.0 to about 6.0 MN/m$^2$ (Patrick and Stacey, 1982). Of the many attempts to measure tensile strengths of the two cokes, several ended in failure for reasons such as glue failure, occurrence of fractures on setting up etc. The successful measurements with valid results are given in the table below.

<table>
<thead>
<tr>
<th>Coke 2</th>
<th>Coke 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test No.</td>
<td>MN/m$^2$</td>
</tr>
<tr>
<td>1</td>
<td>2.655</td>
</tr>
<tr>
<td>14</td>
<td>2.184</td>
</tr>
<tr>
<td>17</td>
<td>1.902</td>
</tr>
<tr>
<td>18</td>
<td>1.818</td>
</tr>
<tr>
<td>26</td>
<td>3.033</td>
</tr>
<tr>
<td>Average 2.32 MN/m$^2$</td>
<td>Average 2.28 MN/m$^2$</td>
</tr>
</tbody>
</table>

It is observed that only two coke 1 tests were considered valid and were used. It may be that tests nos. 17 and 18 of the coke 2 material are on the low side.
Based on these results it is concluded that these cokes are about twice as strong in compression than they are in tension. Young's Modulus, E, for the two cokes gave 4.4 GN/m² for coke 2 and 4.1 GN/m² for coke 1.

4.8.6 Results of electron microscopy studies

The three coals and two cokes were studied by SEM at different stages of burn-off.

Plate 4.5 shows scanning electron micrographs of coal A and of its ash obtained by carbon burn-off at 500 °C for 1 hour in air. Also shown are partially oxidised material at 300, 400 and 500 °C when the surface areas of residue from 1 g of original coal reach a maximum value. These correspond to 5.6, 125 and 83 m² per g of original material obtained after about 50% burn-off in each case (see Chapter 2).

The micrographs indicate that the product obtained at 400 and 500 °C have smaller particle sizes compared with the original coal and with the product obtained at 300 °C. This is consistent with the surface area measurements of the materials.

Plate 4.6 shows SEM results for coal B and its products. The results are similar to those obtained for the coal A. Surface area measurements also are of the same order as for coal A, though they are somewhat higher.
Plate 4.5

Coal A

Coal

Maximum surface at 300°C

Ash

Maximum surface at 400°C

Maximum surface at 500°C

Scale on all five micrographs

10 μm

- 202 -
Coal

Maximum surface at 300°C

Ash

Maximum surface at 400°C

Maximum surface at 500°C

Scale on all five micrographs

10 μm
SEM results for coal C are shown in Plate 4.7. Here the surface areas are much greater than for the European coals.

Plate 4.8 shows a scanning electron micrograph of coke produced from coal B. This is compared with the burn-off products of the coke in carbon dioxide at 1000 °C. The decrease in particle size and increase in porosity are evident in the burn-off products compared with the coke. The ash is similar in appearance to that obtained by carbon burn-off in air (cf Plate 4.6).

Plate 4.9 shows scanning electron micrographs of coke 2 and compares these with the product obtained after 50% weight loss when oxidised in carbon dioxide at 1000 °C for 5 hours. The results appear to indicate a decrease in the larger pores in burn-off but an increase in smaller pores. Coke 1 shows similar results, Plate 4.10. These observations support results for gas sorption studies (Chapter 2) which showed that the original coke samples have only macroporosity, but during the earlier stage of burn-off they develop full ranges of mesoporosity.

Plate 4.1 shows scanning electron micrograph of the fracture surface of coke 2 and coke 1 at a magnification of x100. The two materials are characterised by different textured appearances.
Plate 4.7

Coal C

Coal

Ash

Maximum surface at 300°C

Maximum surface at 400°C

Maximum surface at 500°C

Scale on all five micrographs

10 μm

- 205 -
Plate 4.8

Coal B in CO₂

Coke

25% burn off

38% burn off

60% burn off

Ash

Scale on all five micrographs

10 μm
Plate 4.9

(a) Coke No. 2 before burn-off

100 μm

(b) Coke No. 2 after 50% wt. loss

100 μm

10 μm

(c) Coke No. 2 after 50% wt. loss at greater magnification

5 μm
(a) Coke No. 1 before burn-off

(b) Coke No. 1 after 50% wt. loss

(c) Coke No. 1 after 50% wt. loss at greater magnification
When 1 g samples of the coals were heated at 500 °C for 1 hour in air, globules or beads appeared to form on the surface of the product. These globules were large enough to be removed and examined by SEM. Plates 4.11, 4.12 and 4.13 show globular formation of coal A, coal B and coal C respectively.

At low magnifications (x50) the "globules" are clearly seen as approximately spherical beads of diameters of the order of a fraction of a millimetre.

At a higher magnification (x500) the "fine structure" is more clearly visible and coal C shows differences compared with the two European coals. The Australian coal "globules" show cracks in the form of long parallel pores in a compact particle; in contrast the European coal "globules" show large fissures corresponding to separations between discrete particles.

At still higher magnification (x2500) the three coals develop characteristic surface texture at the micrometre or sub-micrometre level. The European coal shows micrometre size cylindrical pores on a relatively flat surface. The English coal has a very uneven surface, and the Australian coal shows the parallel pores more clearly. All three materials have debris scattered on the surface.
Coal A at 500 °C
globular formations
Coal B at 500 °C
globular formations
Plate 4.13

Coal C at 500 °C
globular formations
REFERENCES

CHAPTER 4


Ramdohr, P. Arch. Eisenhuettenwes 1, pp. 669-672.


Willmers R R. Private communication.
Besides gas sorption analysis, thermal analysis and microscopy, a number of other techniques have been used in the study of the cokes and coals and their products. The results of these are described in this chapter.

Of the techniques described, some provide not much more than characterisation methods in this research. These include ir/uv spectroscopy, NMR spectroscopy and GC-MS. These techniques provide a finger-print for the characterisation of the materials. Others, such as X-ray diffraction, provide a means of identification of components in the substances. Other techniques, e.g. flame photometry and atomic absorption spectroscopy, yield quantitative analytical data on the materials.

5.1 VICKERS HARDNESS TESTS

Three coals and two cokes used in the steel industry were subjected to a series of Vickers hardness tests.

5.1.1 Apparatus

The apparatus used consists of a diamond indenter, in the form of a right pyramid with a square base and an angle of 136°.
between opposite faces, which is forced into the sample under a load. The two diagonals, \( d_1 \) and \( d_2 \), of the indentation left in the surface of the material after removal of the load are measured and their arithmetic mean, \( d \), calculated. The area of the sloping surface of the indentation is calculated, the indentation being considered as a right pyramid with a square base of diagonal \( d \) and a vertex angle of \( 136^\circ \pm 0.3^\circ \); the faces of the diamond pyramid are inclined to the axis of the indentor at an angle of \( 68^\circ \pm 0.3^\circ \). (Fig. 5.1).

In the test the diagonal length of the square impression is measured by means of a microscope which has a variable slit built into the eyepiece (Fig. 5.2). The width of the slit is adjusted so that its edges coincide with the corners of the impression and the diagonal length of the impression is then obtained from a small instrument attached to the slit which works on the principle of a revolution counter.

The Vickers hardness is the quotient obtained by dividing the load \( F \), expressed in kilogrammes-force, by the sloping area of the indentation expressed in square millimetres (BS427: Pt.1: 1961).

\[
F = \text{load in kilogrammes-force (kgf)} \\
\]

\[
d = \text{arithmetic mean of two diagonals } d_1 \text{ and } d_2 \text{ in millimetres (mm)} \\
HV = \text{Vickers hardness}
\]

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Figure 5.1  Basic principles of the force application system in the Vickers Hardness Testing Machine.

Figure 5.2  The Diamond Pyramid Indentor and its resulting impression.
\[ HV = \frac{2F \sin \frac{\theta}{2}}{d^2} = \frac{1.854F}{d^2} \]

5.1.2 Procedure

Samples of the three coals and the two cokes were mounted in "Metaserv" resin and assessed on a Vickers pyramid hardness testing machine. The load time was 10-15 seconds and the load applied was 2.5 kg.

5.1.3 Results

The data reveals that the tests all returned figures of the order of Vickers Hardness Number (VHN) 21-22, apart from two erratic results outside this range. It is apparent that such close values render assignment of a definite VHN to each coal sample somewhat theoretical, but the values obtained are consistent with the work carried out by Honda and Sanada (1956). It is considered that it is not possible to use such information for determining the rank of a coal because there are such small changes in hardness readings over all the samples and there was also an over-lapping factor involved. This observation is in accord with those which Nandi (1977) found when he examined a range of Canadian coals.

The readings for the two cokes also are too close to arrive at a balanced judgment as to hardness by this method of
assessment. Vickers Hardness Numbers were found to be:

<table>
<thead>
<tr>
<th>Coke</th>
<th>Vickers Hardness Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke 2</td>
<td>20.5</td>
</tr>
<tr>
<td>Coke 1</td>
<td>19.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coal Sample</th>
<th>Vickers hardness Number (VHN) (average of three tests)</th>
<th>Carbon % (dry mineral matter free (dmmf))</th>
<th>Apparent density Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal A</td>
<td>21.05</td>
<td>86.66</td>
<td>1.27</td>
</tr>
<tr>
<td>Coal B</td>
<td>21.91</td>
<td>87.92</td>
<td>1.28</td>
</tr>
<tr>
<td>Coal C</td>
<td>22.03</td>
<td>88.50</td>
<td>1.30</td>
</tr>
</tbody>
</table>

The outcome for the three coals have been plotted on two graphs Figs 5.3 and 5.4. The graphs were taken from reviews by van Krevelen (1961) and Williamson (1967) where VHN were set against apparent densities and carbon percentages. The carbon percentage figures for the three coals currently being examined were taken from a BSC assessment whilst the apparent densities were determined by immersing a weighed sample of each coal in water followed by accurate measurement of the liquid that was displaced. Speight (1983) commented that for this procedure the liquid used should:
Figure 5.3 Variation in Vickers microhardness with coal rank.

Figure 5.4 Relationship between apparent density and the rank of coal (as indicated by the carbon content).
a. wet the surface of the coal
b. not absorb strongly to the coal surface
c. not cause swelling
d. penetrate the pores of the coal.

Speight added that it is probably not possible to satisfy all these conditions as evidenced by the differing experimental data obtained with solvents such as water, methanol, carbon tetrachloride, benzene and other fluids. Care was taken to allow 24 hours immersion before any measurements were taken to allow the water to penetrate the pore system of the coals to the maximum extent.

The two erratic results mentioned were for Coal A where values VHN of 27.8 and 23.2 were recorded.

5.2 EXTRACTION OF COAL TARS BY PYROLYSIS FOR SUBSEQUENT EXAMINATIONS

Speight (1983) made the comment that as the major part of coal is notoriously insoluble in a variety of solvents, it has been the custom of investigators to examine thermally treated materials and products; and Pitt and Millward (1979) mention that some workers have used extracts of coal.
During the course of the current work tars extracted by pyrolysis from three coals, currently used in the steel industry, were prepared for subsequent examinations using GLC, mass spectrometry, NMR, infra-red and ultra-violet spectroscopy. In some preliminary work it had been found that finely ground samples of coal to which solvents had been applied failed to yield any positive data for characterisation subsequently.

However, tar extracts from the three coals provided material which did give acceptable results for the five methods of analysis mentioned.

5.2.1 Apparatus

The apparatus consisted of a side-arm still head, a small Liebig condenser and a multi-necked receiver adaptor.

5.2.2 Procedure

Ground quantities of each coal were heated using a bunsen flame and the tar which came off was collected. The apparatus was cleaned out between each sample using analar grade chloroform.

5.3 GAS-LIQUID CHROMATOGRAPHY

Chromatography embraces any one of several semicontinuous techniques for separating and purifying species from solution by causing the extracting and solution phases to flow past each
other. Gas-liquid chromatography is a particular form of the general chromatographic technique in which the moving phase is a gas and the stationary phase is a liquid. The technique is suitable for separation of materials which are volatile without decomposition and it has been used at temperatures ranging from below or around room temperature, for the analysis of gases up to 300 °C or above, for example, for long-chain fatty acids. Further increase in temperature results in considerable experimental difficulties.

Two forms of gas chromatographs are in use. For fine resolution in the microgramme range, a capillary tube up to 30 m long with an internal diameter of 0.2 mm is coated on the inside with a nonvolatile liquid such as a diester of phthalic acid. For routine analysis or even actual separation of macroscopic amounts of material a 5 - 50 mm column packed with liquid-coated particles of fine-brick 0.2 mm in diameter is used. An inert, unabsorbed carrier gas like H₂, He, Ar, N₂ or CO₂ is used to flush the sample through the column after it is injected all at once into the flowing carrier gas. Eventually the whole sample is eluted from the column, slightly absorbed species of high volatility coming through first, highly absorbed species of low volatility coming out last.

The two usual means of detecting the species eluted in the carrier gas are (i) to note the sudden decreases in thermal conductivity of the effluent gas, and (ii) to observe the
sudden increases in electrical conductivity of a $\text{H}_2 - \text{O}_2$ flame. Such changes are automatically plotted by a recording potentiometer as functions of time. A species is characterised by the time a peak appears after sample injection and the area of the peak indicates its amount.

5.3.1 Apparatus

The apparatus used was a Fractovap 4160, which is a high resolution capillary column gas chromatograph supplied by Carlo Erba Strumentazione.

The equipment consists of dual capillary columns contained in an oven. Gas lines to the apparatus are fitted with metal bellows and diaphragm pressure controllers. Pressure gauges and metal on-off valves are also fitted so that flow rate measurements and leak checks can be made. Flow control is provided for use during temperature programming cycles to ensure a constant delivery. There is forced air circulation in the column oven and an electronic temperature programme. Multicoloured coded lights indicate the status of the various controls.
5.3.2 Procedure

A known weight of each of the three tar extracts from the coals was placed in a 50 cm$^3$ centrifuge tube to which was added 20 cm$^3$ of nanograde hexane. The samples were placed then in an ultra-sonic bath for 20 minutes and after withdrawal the hexane extract was passed through an anhydrous sodium sulphate column to remove any water in the sample and also to filter out any coal particles. The columns were then washed through twice with 10 cm$^3$ of nanograde hexane and the resulting solutions combined.

The hexane was removed from the extracts under reduced pressure using a rotary evaporator and the extracts washed into pre-weighed vials.

Each extract was diluted with 50 microlitres of nanograde hexane and 1 microlitre aliquot injected into the GLC. At the same time a hexane blank was run to detect any contamination from the hexane used during sample preparation.

5.3.3 Results

The chromatographs of the extracts of the three coals are shown in Figure 5.5.

More comprehensive results are obtained by the combined GC-MS techniques and are discussed in Section 5.8.
Figure 5.5 Gas - liquid chromatograms for three coals.

No peaks or groupings present to give a distinctive pattern.

Coal A

Two apparent maxima situated at nC16 and nC21.

Coal B

Carbon No. range nC12 - nC24, no odd/even predominance presence of pristane and phytane. Pr iC19; Ph iC19.

Coal C
5.4 **FLAME PHOTOMETRY**

Flame photometry is a form of analysis based on the phenomenon that atoms of all elements absorb energy at a sufficiently high temperature and pass into an excited state. In returning to the ground state they release the absorbed energy as light, the wavelength of which is characteristic of the atom in question. The alkali metals of Group 1 of the periodic table, have low excitation energies and thus are particularly well suited for analysis by flame emission. Sodium and potassium can both be analysed by flame photometry in less time, at lower concentration and with greater precision and accuracy than by any other technique.

The necessary high temperature can be produced by an electric discharge (emission spectrometry), or by the combustion of gases (flame photometry). In the first case the sample is usually examined as a solid, in the second almost invariably as a solution. When employing the technique of flame photometry the solution is atomized into a fine mist and introduced into a flame. In the flame the solution evaporates, and the solid dissociates wholly or partially into its component atoms. The atoms become excited and will then emit light. If the conditions, flame temperature and amount of liquid atomised, remain steady the intensity of light will be proportional to the concentration in the solution of the element concerned.
The flame temperature varies, dependent upon the gases used for combustion - anywhere between 1800 °C and 3000 °C, which is considerably lower than the temperatures used in emission spectrometry (in the region of 5000 °C). The results are first, that the sensitivity for most elements is lower, and secondly, that the spectra emitted contain fewer lines. This latter fact can be considered to be a real advantage in that the required spectral line can be filtered out easily.

The advantages in using flame photometry are that the method is rapid, the sample required is small and that good results are obtained with relatively inexpensive apparatus. The disadvantages are that the substance to be analysed must be in solution, interference between two substances may occur and regular calibration by means of standard samples is necessary.

5.4.1 Apparatus

A IL343 Digital Flame Photometer 343 supplied by Instrumentation Laboratory was used. It is a selective wavelength photometer. Whilst aspirating the sample it runs an internal Li standard so that any variation in flame quality is compensated for in the final result. The machine automatically carries out a 200:1 dilution of a sample before aspirating into the flame and the readout is automatically adjusted accordingly.
5.4.2 Procedure

Ashes were prepared by combustion in air at 500 °C. The machine was standardized by using proprietary standards of 100 Na/100 K Standard mmol/l.

Samples of 0.08 g of each coal ash were weighed out in separate dishes and 1 ml of HCl (1 M) was added and left for 40 minutes. The 10 ml of distilled water was added to each sample and materials were filtered. The coal C sample filtrate was colourless, the remaining two were coloured light yellow (attributed to iron).

Samples were aspirated in turn through the IL 343 digital flame photometer, rechecking the calibration between each sample. The injection procedure for all three coals was then repeated as a check on consistency.

5.4.3 Results and discussion

From the data obtained it was calculated that the following amounts of K and Na were present in the coals:
It is of importance to be aware of the levels of K and Na in a blast furnace operation.

K₂O and Na₂O enter the furnace in both coke and ore. They are partially reduced to K and Na vapour near the bottom of the furnace (Lowing, 1977) and the vapour subsequently rises to the cooler parts of the furnace where a portion reoxidizes to become entrapped in solid form in the descending burden. The process becomes cyclic and it leads to an accumulation of potassium and sodium compounds in the furnace. The physical signs of this build up are a restriction of gas flow through the burden and an erratic descent of the charge, a situation which can be met by choosing the composition of the slag.
5.5 Mössbauer Spectroscopy

The Mössbauer effect is the recoil-less emission or resonant absorption of γ-rays in some elements whose isotopes must be radioactive and must emit γ-rays with an energy less than 150 keV. It occurs when the nuclear energy levels of a source and the absorber match and give a very sharp absorption peak. Normally there is a recoil when a nucleus emits a high energy photon and due to the Doppler effect frequency is shifted and broadened sufficiently to wipe out the natural line-width of the absorption peak. However, if the nucleus is located rigidly in a crystal lattice, in a fraction of cases the momentum of recoil is assimilated by the whole of the material, which reduces recoil velocity and the line broadening. Because the number of recoil-less nuclei increase with lower temperatures, liquid nitrogen is employed. The use of measurement at liquid nitrogen temperatures is also more likely to produce magnetic spectra in most iron oxides.

The γ-ray frequency is modulated using the Doppler effect by mounting the source on an adjustable support. A range of vibration of a few mm s\(^{-1}\) is adequate to match the γ-ray frequency to the absorber energy levels. Resonant absorption takes place when the source is operated at a certain velocity but not infrequently absorption can be recorded for several velocities due to a number of energy levels. Data obtained are presented as a plot of the number of γ-ray counts versus the velocity of the source.
The use of $\gamma$-emitting isotopes limits the technique to the selected low energy and long $\gamma$-ray half life elements, the lightest isotope for which the effect can be observed is $^{40}$K and the next $^{57}$Fe. The natural abundance of $^{57}$Fe is 2.2% which provides an adequate basis for most measurements.

The technique was used in the current research to examine three coals and their 1000 °C and 500 °C ashes together with two high temperature metallurgical cokes currently used in British industry in the process of steel making with the object of identifying their iron content.

5.5.1 Apparatus

The equipment used comprised of a velocity transducer and drive similar to that described by P.E. Clark et al (1967). The source was 25 mCi $^{57}$Co in a rhodium matrix, the manufacturer being Amersham International.

The detection system was made up of an AERE Harwell proportional counter, model MPC 200 and an AERE cryostat for liquid nitrogen, model MNC 200. The proportional counter was supplied with EHT by an ORTEC high voltage supply, model 456, and the signal amplified by an ORTEC preamplifier 109PC and main amplifier 485. The pulses were analysed and stored in an Inotech 5200 multichannel analyser. The velocity drive signals were also initiated by the multichannel analyser. The data was transferred to an Apple II* computer for processing and plotted using an Epson printer/plotter, model LX80 or MX85 F/T.
The velocity scale was calibrated with reference to an iron foil absorber at room temperature. All isomer shifts are with respect to iron at 293 K. The system had been checked and assessed to be linear to better than one part in three hundred. This would give errors which are smaller than those usually quoted for the isomer shift, quadrupole splitting and magnetic field for which the probable error is quoted as $\pm 0.05 \text{ mm s}^{-1}$, $0.10 \text{ mm s}^{-1}$ and $0.5 \text{ T}$ respectively. This allows for possible drift with time and for other sources of error and is certainly large enough to contain all similar measurements, i.e. reproducibility.

5.5.2 Procedure

Standards were prepared from laboratory held samples of illite (a clay mineral, basic potassium aluminium aluminosilicate; illite group formula $K_{1-1.5}Al_4(Si,Al)_8O_{20}(OH)_4$), siderite ($\text{FeCO}_3$), hematite ($\text{Fe}_2\text{O}_3$), magnetite ($\text{Fe}_3\text{O}_4$) and pyrite ($\text{FeS}_2$).

Appropriate indicator scales were inserted on the spectra printouts with points marked where peaks occur on the standards. Comparison was then carried out with the coal, ash and coke samples under examination.

A summary of the findings Table 5.1 is as follows:
Table 5.1 A summary of minerals in three coals and two cokes identified by Mössbauer spectroscopy

<table>
<thead>
<tr>
<th>Material</th>
<th>Coals</th>
<th>500 °C Coal ash</th>
<th>1000 °C Coal ash</th>
<th>Cokes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>A</td>
</tr>
<tr>
<td>Illite Group formula</td>
<td>K1-1.5Al4(Si, Al)gO20(OH)4</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Pyrite (FeS2)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Siderite (FeCO3)</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hematite (Fe2O3)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Magnetite (Fe3O4)</td>
<td>X</td>
<td>X</td>
<td>small amount</td>
<td>small amount</td>
</tr>
<tr>
<td>Fe3+ unidentified</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe metal</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.5.3 Results and discussion

Figures 5.6 - 5.9 show the Mössbauer spectra of the cokes and the three coals and that of their ashes at 500 °C and 1000 °C. From examination of the spectra printouts it seems that there is a higher level of iron compounds in the European coal B than there is in the British coal A material; the Australian coal C has very much less iron and this fact is borne out by the appearance of the coal C ash which is grey rather than the red/brown colour of the other two coal ash samples.

All three coal ashes contain what seems to be substantial quantities of some form of degraded illite.

It appears that the sulphur level in the coal B is higher than in the coal A, whereas coal C has quite a minor component. Such differences in level of sulphur content is a sure pointer to the conditions under which the coals were laid down. It is consistent with the fact that the two coals of Europe were laid down in tidal areas whereas the Australian coal experienced a freshwater environment and as such this information provides a useful diagnostic indicator in the characterisation of the three coals.

From the results section summary it is clear that the cokes contain all the components found in the coals and it is observed that the highly undesirable component sulphur enters
Figure 5.6 Coal A Mössbauer spectra

- 237 -
Figure 5.7. Coal B Mössbauer spectra

**Coal**

**500 °C ash**

**1000 °C ash**
Figure 5.8. Coal C Mossbauer spectra

- 239 -
Figure 5.9. Cokes Nos. 1 and 2 Mössbauer spectra.
the blast furnace by way of the coke in addition to whatever sulphur is in the iron ore charge.

5.6 ULTRA-VIOLET AND INFRA-RED SPECTROSCOPY

Of the physical techniques available, infra-red spectroscopy probably provides the most valuable information about the constitution of organic materials. Infra-red spectra arise from the absorption of infra-red radiation when its frequency equals the frequency of vibration within the molecules. Absorption of radiation in the infra-red region, with an energy content of 2.1 kJ/mol is capable of stimulating the complete molecule under investigation to undergo vibrational and rotational changes which reflect the whole structural entity.

In contrast the visible and ultra-violet spectra of molecules and ions are related only to transitions between electronic energy levels of some particular groups or types of atoms within the molecule and thus do not characterize the molecule as a whole. There are much larger energies involved in the absorption of radiation in the ultraviolet region, with an energy content of 42 kJ/mol causing electronic as well as the associated vibrational and rotational changes. Complete elucidation of the electronic and closely spaced vibrational and rotational bands is not possible, the overall shape of the absorption band is broad.
Two clearly defined regions exist in the ultra-violet spectral range, viz, (i) the near-ultra-violet, 400-190 nm, and (ii) the far-ultra-violet 190-100 nm. Normal working deals in the near-ultra-violet because the absorption by silica used for cells and optics and by atmospheric oxygen below 190 nm interfere with measurements in the far-ultra-violet. A group of atoms that absorb in the near-ultra-violet is known as a chromophore. Most unsaturated groups and heteroatoms carrying lone pair electrons are potential chromophores and are the main subject of structural resolution in the near-ultra-violet.

In the current work infra-red spectroscopy supported by ultra-violet spectroscopy has been undertaken. Finely ground coal samples in two different solvents (Nujol and subsequently Fluorolube) were used without acceptable outcomes being achieved. Success was subsequently attained by using distillates of the three coals dissolved in hexane. It is considered that this method is valid since Pitt and Millward (1979) have commented that lack of detail in coal spectra can be overcome by the use of extracts in solution.

Speight (1983) detailed the carbon skeleton obtained by the infra-red analysis of coal.

5.6.1 Apparatus for ultra-violet spectroscopy
A Perkin-Elmer Model 552 double beam - visible spectrometer was used. The recorder print-out was made on a Perkin-Elmer PE 561 chart recorder.
5.6.2 Procedure for ultra-violet spectroscopy
Each of the three coal tar distillates was dissolved in hexane and the solutions in turn were placed in a 1 cm quartz cell. The spectrum was then recorded on low sensitivity, 3 AUFS 900-190, scanning speed 20 nm/cm and chart speed 120 mm/min.

The quartz cell was cleaned with hexane between sample examinations.

5.6.3 Apparatus for infra-red spectroscopy
The equipment used was a Perkin-Elmer 298 infra-red spectrometer.

5.6.4 Procedure for infra-red spectroscopy
Distillates of the three coals were dissolved in hexane and allowed to evaporate on 25 mm diameter sodium chloride discs. Each preparation was scanned in turn for 3 minutes and for 12 minutes.

5.6.5 Results
The present research found all twelve entries detailed on page 287 of Speight (1983) to be present in the three coal samples and this was checked by preparing additional coal tar distillates using carbon tetrachloride as the solvent. The infra-red traces (Fig 5.10) gave the same absorption patterns as they had using hexane.
Figure 5.10 IR scans of coal tar distillates

Coal A

Coal C

Coal B

Vertical lines as Spight (1983) indicate carbon skeleton
Coal A (British) and coal B (European) which are both Carboniferous coals give very similar traces but coal C (Australian) which is a Gondwanaland coal presents a difference at 1640 cm\(^{-1}\) to the other two traces. This may be a CHR = CH\(_2\) bond. The somewhat different pattern above 3030 cm\(^{-1}\) is due apparently to some water being present in coal A and coal B material.

The ultra-violet traces (Figs 5.11 - 5.14) of all three coals were found to give a very similar pattern which indicated that there were just alkanes present.

5.7 X-RAY DIFFRACTION

Surveys of the theory and practice of X-ray diffraction as applied to single crystals and powder samples have been given by Stout and Jensen (1968) and Lipson and Steeple (1970).

Solids are mostly crystalline and thus consist of regular three-dimensional arrays of atoms. The size of the individual crystallites may be very small. Points which have identical surroundings in a structure are known as lattice points. The lattice of a crystal may be defined with reference to three co-ordinate axes along which the lattice points have spacings a, b and c. The angles between the axes are denoted by \(\alpha\), \(\beta\) and \(\gamma\). The volume defined by the parallelepiped of sides a, b and c is termed the primitive unit cell when a, b and c are the smallest distances that can be chosen. The lattice points are then only
Figure 5.11  UV scan of coal A tar distillate
Figure 5.12  UV scan of coal B tar distillate
Figure 5.13 UV scan of coal C tar distillate
Figure 5.14 UV scan of Hexane only
at the corners. More complex unit cells may in addition have lattice points at the centre of the cell (body-centred) or cell face (face-centred).

Crystal lattices can be classified into seven different systems (Kelley and Groves, 1973). Symmetry operations of reflection, rotation and inversion yield the 32 point groups. When all symmetry elements (including, for example screw axes and glide planes) and non-primitive cells are considered, one obtains 230 space groups.

Sets of parallel planes may be drawn through lattice points. Each set of planes can be described by three intergers \((h, k, l)\), the Miller indices, corresponding to the three axes \((a, b, c\) respectively). Index \(h\) is the reciprocal of the fractional value of the intercept made by the set of planes on the \(a\) axis etc. From the observation of sets of \(h, k, l\) reflections that are systematically absent the lattice type can be deduced.

As the dimensions of a crystal lattice are of the same order of magnitude as X-ray wavelengths, the lattice behaves as a three-dimensional diffraction grating. Diffraction is governed by Bragg's Law:
\[ 2d \sin \theta = n \lambda \]

where \( \lambda \) = X-ray wavelength
\( n \) = order of reflection
\( d \) = interplanar spacing of lattice plane
and \( \theta \) = angle of incidence of the X-ray beam to the set of lattice planes - "the Bragg angle".

d is related to the unit cell dimensions by the Miller indices.

With the powder diffraction method small crystalline particles are in random orientation and produce reflections from those planes that happen to be at the correct angle \( \theta \) to the incident X-ray beam. The intensity and distribution of the diffracted beams with respect to the Bragg angle is characteristic of a particular structure and may be used to identify the phases present. Diffraction patterns for most crystalline compounds are listed in the Joint Committee for Powder Diffraction Standards file (JCPDS, 1967 et seq).

5.7.1 Apparatus

A Philips PW 1729 generator was used fitted with a Philips X-ray tube and copper target.
5.7.2 Procedure

Voltage and current were set at 50 kV and 20 mA respectively. The X-rays generated were filtered with a nickel foil to reduce the Kβ component and passed through a collimator and slits before impinging on the sample of lightly powdered ash or coarsely ground coke which were placed on a single horizontal slab of silicon at the centre of a Philips 1710 micro-processor control diffractometer, the diffractometer having been aligned and calibrated with a single graphite crystal.

5.7.3 Results

The results were printed out on a digital DecWriter IV and on a Philips PM 8203A on-line recorder and are shown in Figs 5.15 to 5.20 and tabulated in tables 5.2 to 5.6.

5.8 MASS SPECTROMETRY

A mass spectrum can be obtained by converting the compounds of a sample into rapidly moving ions, which are usually positively charged, and resolving them on the basis of their mass-to-charge ratio. The utility of mass spectrometry comes from the fact that the ionization process normally produces a collection of positive particles whose mass distribution is characteristic of the parent species. Thus, a mass spectrum provides information that is useful for elucidating chemical structures. Mass spectral data are easier to interpret than infrared and NMR spectra in some respects, because they supply information
Figure 5.15 X-ray diffraction patterns of three 500 °C coal ashes

Coal A

Coal B

Coal C

θ, degrees

- 253 -
Figure 5.16 X-ray diffraction pattern of coal A 500 °C ash
### TABLE 5.2:
X-ray diffraction data of Coal A 500 °C Ash (Figure 5.16)

<table>
<thead>
<tr>
<th>I</th>
<th>$0^\circ$</th>
<th>dA</th>
<th>hkl</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>9.75</td>
<td>4.49-4.51</td>
<td>100</td>
<td>$\sim$SiO$_2$</td>
</tr>
<tr>
<td>M</td>
<td>10.40</td>
<td>4.25</td>
<td>100</td>
<td>$\sim$SiO$_2$</td>
</tr>
<tr>
<td>M</td>
<td>11.05</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>11.85</td>
<td>3.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>12.75</td>
<td>3.48</td>
<td>220</td>
<td>CaSO$_4$</td>
</tr>
<tr>
<td>VS</td>
<td>13.30</td>
<td>3.33</td>
<td>101</td>
<td>$\sim$SiO$_2$</td>
</tr>
<tr>
<td>S</td>
<td>15.40</td>
<td>2.89</td>
<td>220</td>
<td>Fe$_3$O$_4$</td>
</tr>
<tr>
<td>M</td>
<td>16.50</td>
<td>2.70</td>
<td>104</td>
<td>$\sim$Fe$_2$O$_3$</td>
</tr>
<tr>
<td>M</td>
<td>17.75-17.4</td>
<td>2.52-2.57</td>
<td>104, 311 and 110</td>
<td>Al$_2$O$_3$, Fe$_3$O$_4$ and $\sim$Fe$_2$O$_3$</td>
</tr>
<tr>
<td>M</td>
<td>19.25</td>
<td>2.33</td>
<td>212</td>
<td>CaSO$_4$</td>
</tr>
<tr>
<td>M</td>
<td>20.35</td>
<td>2.21</td>
<td>113 and 102</td>
<td>$\sim$Fe$_2$O$_3$ and SiO$_2$</td>
</tr>
<tr>
<td>S</td>
<td>25.10</td>
<td>1.815</td>
<td>112 and 024</td>
<td>$\sim$SiO$_2$ and $\sim$Fe$_2$O$_3$</td>
</tr>
<tr>
<td>M</td>
<td>26.90</td>
<td>1.70</td>
<td>116</td>
<td>$\sim$Fe$_2$O$_3$</td>
</tr>
<tr>
<td>M</td>
<td>27.80</td>
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<tr>
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<td>214</td>
<td>$\sim$Fe$_2$O$_3$</td>
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VS = Very strong  
S = Strong  
M = Medium  
W = Weak
Figure 5.17 X-ray diffraction pattern of coal B 500 °C ash

θ, degrees
### TABLE 5.3:
X-ray diffraction data of Coal B 500 °C Ash (Figure 5.17)

<table>
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<td>Fe₃O₄ and α-Fe₂O₃</td>
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<td>104, 110 and 311</td>
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VS = Very strong
S = Strong
M = Medium
W = Weak

- 257 -
Figure 5.18 X-ray diffraction pattern of coal C 500 °C ash
TABLE 5.4:
X-ray diffraction data of Coal C 500 °C Ash (Figure 5.18)

<table>
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<td>110</td>
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Figure 5.19 X-ray diffraction patterns of three 1000 °C coal ashes
Figure 5.20 X ray diffraction patterns of two cokes 1000 °C ash

Coke No.1

Coke No.2
### TABLE 5.5:
X-ray diffraction data for coke No. 2 1000 °C Ash (Figure 5.20)

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VS = Very strong
S = Strong
M = Medium
W = Weak
### TABLE 5.6:
X-ray diffraction data for Coke No. 1 1000 °C Ash (Figure 5.20)

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<td>Fe₂O₃ Al₂O₃</td>
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</table>

VS = Very strong
S  = Strong
M  = Medium
W  = Weak
in terms of molecular mass of the structural components of a sample and in addition an accurate measure of the molecular weight of the analyte can usually be ascertained from the data.

The current work was conducted on a combined gas chromatograph/mass spectrometer. Operation of the gas chromatograph for the apparatus is the same as any gas chromatograph with one exception, i.e. the end of the column is under vacuum which prevents the solvent from entering the mass spectrometer. This method results in flow rates and ranges of gas velocities experienced by the column to be higher than those which are normally found in conventional gas chromatograph conditions. The use of jet separators operating at 20-60 ml min⁻¹ helium makes it ideal for interfacing the packed columns to a mass spectrometer.

5.8.1 Apparatus
A Kratos Mass Spectrometer 25 with Carlo Erba Mega high resolution gas chromatograph was used.

5.8.2 Procedure
Sample preparation was exactly the same as for GLC; 0.5 l of each sample was injected onto the column in turn and heated from 40 to 300 °C at 4 °C per minute. Temperature was then held at 300 °C for 10 minutes. The recording programme was initiated 2.5 minutes after injection and data collected from 4 minutes onwards. The electron energy was 40 eV, carrier gas
was helium and stationary phase of the gas chromatograph column was CP Sil 5. Gas column length 30 m with internal diameter 0.32 mm was used. The emission current was 0.35 mA.

5.8.3 GC/MS Results and discussion

Total ion chromatograms for the coal extracts are shown in Figure 5.21. Coal A chromatogram indicates considerable low molecular weight material which is not present in the other two coals to the same extent. This is consistent with the fact that it is classed as NCB 501 which is a high volatile coal volatile material rating 32.1 - 36.0% dmmf. The C17/Pristane (i19) ratio is 0.5. (With coal 17/19 ratio is low because Pristane level is high, in marine derived oil 17/19 ratio is usually high because Pristane level is low).

Coal B coal displays a somewhat less amount of low molecular weight material than coal A. The C17/Pristane (i19) ratio is 2 which distinguishes this coal from coal A sample. The reasons for the higher ratio are contentious. One possible explanation is that the coal may have experienced more anaerobic conditions in the settlement area than is usual (Brooks et al, 1969). This European coal is a NCB 301b prime coking coal with a volatile material rating of 27.6 - 32.0% dmmf.

Coal C is a coal of Gondwanalnd as opposed to the other two samples which are Carboniferous coals. The chromatogram indicates a low volatile hydrocarbon content compared with coal
Figure 5.21. GC/MS total ion chromatograms for three coals

Coal A

Coal B

Coal C
A. The C17/Pristane (i19) ratio is 2. This is an NCB 301a, a prime coking coal with a volatile material rating of 19.6 - 27.5% dmef.

The annotated chromatograms for the three coals Figure 5.22 support these findings and the GLC results (Section 5.3) for all three coal samples give the same results.

5.9 ATOMIC SPECTROSCOPY

In this section of the current work the examination of three coals and two cokes by atomic spectroscopy is reported. Atomic spectroscopy employs the phenomena of emission, absorption or fluorescence of radiation by atoms as a basis for analyses. These three types of spectroscopy are summarized diagrammatically in Fig 5.23.

The horizontal lines represent different energy levels in an atom. $E_0$ is the ground state $E_i$ and $E_j$ refer to other energy levels. All practical absorption measurements originate from atoms in the ground state as do virtually all fluorescence measurements. Solid vertical lines refer to a transition involving absorption or emission of energy as radiation.

The wavy line symbolizes a non-radiative transition. Energy of the radiation absorbed or emitted is quantized according to Planck's equation, $E = h\nu$, where $h$ is Planck's constant, $\nu$ is the frequency of the radiation and $E$ is the energy difference.
Figure 5.22. GC/MS total ion chromatograms for three coals

GC/MS delimited ion chromatogram and fragmentograms for masses 85 and 83 for coal A.

GC/MS delimited ion chromatogram and fragmentograms for masses 85, 83 and 57 for coal B.

GC/MS delimited ion chromatogram and fragmentograms for masses 85 and 57 for coal C.
Fig 5.23 Summary of AES, AAS and AFS.
between the two energy levels in the atom. Figure 5.24 shows a
diagrammatic form of the instrumentation required for each
technique.

5.9.1 Apparatus

Initially a Pye Unicam SP9 atomic absorption
spectrophotometer was employed for the coal and coke
examinations and this was followed by ICPOES – inductively
coupled plasma optical emission spectroscopy on a Plasmakon S35
instrument to ascertain the aluminium content of the three
coals which raises problems (discussed later).

The Pye Unicam SP9 was the standard chemical laboratory
apparatus and a schematic diagram of the sequential system used
in the Plasmakon S35 is shown in Figure 5.25.

A diagram of the plasma torch where exitation, and therefore
emission, occurs is shown in Figure 5.26.

The torch consists of three concentric tubes, the outer two
usually being made of quartz. This is placed in the working
coil of a radio frequency generator. The radio frequency
generator may produce between 2 and 30 kW forward power at
between 5 and 50 MHz, the usual combination being a few
kilowatts at 27.12 MHz. When the power is switched on to the
2- or 3- turn induction coil, an AC magnetic field is generated
axially through the coil. When the argon gas flowing through
Fig. 24 Basic instrumental systems used in analytical atomic spectroscopy.
Figure 5.25 Schematic diagram of a sequential ICP system
Figure 5.26 Schematic diagram of an inductively coupled plasma torch.

1 Tail flame
2 Viewing zone
3 Annular plasma fire-ball
4 Direction of current in coil
5 Lines of force of magnetic field
6 Quartz torch (concentric tubes)
7 Injector tube
8 Tangential coolant flow (argon or nitrogen)
9 Argon plasma gas - tangential flow
   (Optional in all argon plasma)
10 Aerosol of argon+sample
    (injector flow)
11 Induction coil
   (2 or 3 turns of water-cooled copper tubing)
the outer tubes of the torch is seeded with electrons using a
tesla spark, these electrons accelerate in the field. The
electrons quickly reach ionizing energies and collisions with
the gas in the field produce further breakdown and an avalanche
effect. This condition occurs practically instantaneously and
the magnetic field causes the ions and electrons to flow in
closed circular horizontal paths. These eddy currents heat the
neutral argon by collisional energy exchange and a white hot
fireball is produced. The sample is introduced by the injector
gas, argon, which forces a hole in the fireball, producing an
annulus. The plasma formed is stable with a temperature
exceeding 6000 K.

5.9.2 Procedure

Determination of some of the elements in the three coal
ashes, sufficient to characterize each coal, were undertaken as
follows.

Coal samples were ashed at 1000 °C individually and the samples
of ash were then heated in aqua regia at 90 °C. The resulting
solutions were then evaporated to dryness, dissolved in water
and made up to 100 cm³. The samples were then aspirated
into the flame of the AA spectrophotometer. The weight of each
ash sample used was 0.1 g.
5.9.3 Results and discussion

BSC (personal communication) had given the ash chemical analyses in the usual form as percentage oxides for the three coals as set out in Table 5.7.

<table>
<thead>
<tr>
<th>Coal</th>
<th>European</th>
<th>Australian</th>
<th>British</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>13.74</td>
<td>4.30</td>
<td>9.59</td>
</tr>
<tr>
<td>CaO</td>
<td>9.92</td>
<td>0.72</td>
<td>2.78</td>
</tr>
<tr>
<td>MgO</td>
<td>5.06</td>
<td>0.62</td>
<td>1.32</td>
</tr>
<tr>
<td>SiO₂</td>
<td>33.95</td>
<td>59.15</td>
<td>48.43</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>23.52</td>
<td>30.21</td>
<td>28.87</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.44</td>
<td>0.45</td>
<td>0.14</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.19</td>
<td>0.51</td>
<td>0.86</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.65</td>
<td>1.13</td>
<td>2.46</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.78</td>
<td>1.71</td>
<td>1.22</td>
</tr>
<tr>
<td>BaO</td>
<td>-</td>
<td>0.08</td>
<td>0.10</td>
</tr>
<tr>
<td>PbO</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td>MnO</td>
<td>0.23</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.07</td>
<td>0.08</td>
<td>0.17</td>
</tr>
<tr>
<td>SO₂</td>
<td>6.93</td>
<td>0.14</td>
<td>3.18</td>
</tr>
</tbody>
</table>

Table 5.7. Ash chemical analyses of three coals
Table 5.8 shows the metal contents of the coal ashes. It was confirmed that coal C (Australian) contained a low level of Fe. Very low readings were found for Cu and Ni. About 30-40 other elements have been identified in coal either as minor components or in trace quantities, (Ward, 1984). The list could be expected to be even more extensive than it is, considering that coal is a porous material embedded in the earth's crust for some 300 million years and would act like a sponge and trap such trace material readily (Williamson, 1967).

<table>
<thead>
<tr>
<th></th>
<th>Coal A</th>
<th>Coal B</th>
<th>Coal C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$ %</td>
<td>10.04</td>
<td>14.72</td>
<td>4.52</td>
</tr>
<tr>
<td>Cu ppm</td>
<td>43</td>
<td>19</td>
<td>12</td>
</tr>
<tr>
<td>Ni ppm</td>
<td>24</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>Zn %</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO %</td>
<td>1.51</td>
<td>5.23</td>
<td>0.73</td>
</tr>
<tr>
<td>CaO %</td>
<td>3.61</td>
<td>10.31</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 5.8 Metal content of coal ashes

The outcome of the current work was less definite as regards the alumina component which is a well known difficulty that can be encountered due to the fact that it is not easy to get aluminium into its atomic state and a nitrous oxide flame has to be used which is hotter and thus more able to reduce the material, but it is not very sensitive.
Work was also undertaken using the same apparatus on samples of coke 1 and coke 2 blended from that of the three coals (amongst other material). The main constituents of coke ash or residue from coke after combustion were magnesia, iron, sulphur, phosphorus, lime, silica and alumina with the last two materials making the largest contribution.

At this juncture it was considered appropriate to extend the assessment to embrace the actual coals and attempt to ascertain the aluminium content in them using inductively coupled plasma emission spectrometry rather than merely repeat the work done on the ashes with the Pye Unicam SP9.

It was reasoned that a check could be made on the iron component of the coals and if the outcome compared favourably with the results obtained with those of the previously used technique, then the determination of the aluminium content would be of the right order.

Accordingly, the unused portions of the coal samples that had not been ashed for the previous assessment were prepared for injection into the Plasmakon S35. The material had already been ground by mortar and pestle to pass through a 180 μm sieve, but as sample particle size is of considerable importance with this apparatus the samples were subjected to further grinding by zirconia beads. The samples and beads were mixed together in polypropylene screw cap bottles and shaken
with 4 cm$^3$ of surfactant (0.1% AEROSOL OT) on a flask shaker for 3 hours to reduce particle size to below 10 μm. Slurries were then made up and were aspirated into the plasma. Slurry atomization was decided upon since coals and their ashes are notoriously difficult to get into solution and therefore hazardous acids have to be employed. The method, when compared with a solution based technique, offers the following advantages:

i) elimination of the requirement for acid digestion,

ii) minimum risk of contamination, and

iii) decrease in sample preparation time.

Element levels converted into oxides as percentages, were as follows:

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>COAL A %</th>
<th>COAL B %</th>
<th>COAL C %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>9.14</td>
<td>15.79</td>
<td>3.64</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>25.76</td>
<td>23.33</td>
<td>28.90</td>
</tr>
</tbody>
</table>

The determinations were undertaken using National Bureau of Standards certified reference coals 1635 and 1632(a), the relevant authentication details were as follows:
<table>
<thead>
<tr>
<th></th>
<th>Coal 1635</th>
<th></th>
<th>Coal 1632a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slurry</td>
<td>Certified</td>
<td>Slurry</td>
</tr>
<tr>
<td>Fe</td>
<td>0.217</td>
<td>0.239</td>
<td>1.08</td>
</tr>
<tr>
<td>Al</td>
<td>0.290</td>
<td>0.320</td>
<td>2.88</td>
</tr>
</tbody>
</table>

Results obtained in both sections using atomic spectroscopy techniques support the analyses conducted by BSC.

The coal ashes examined are in a chemically inert form, consisting of stable oxides particularly those of silicon, aluminium and iron; calcium, sodium, potassium and magnesium can be other common constituents. Other elements are generally considered as trace elements. The major constituents are non-toxic and thus do not present any hazard.

Where Cu and Ni were recorded, the elements were present in concentrations similar to their abundances in the earth's crust. Considerable variability coupled with generally low levels is the normal pattern found with trace elements in coal (Grainger and Gibson, 1981).
5.10 **CALORIFIC VALUES**

The calorific value of coal is a direct indication of the energy content of the material and is one of the means by which a coal can be evaluated. It is defined as the quantity of heat produced by a given mass of the fuel on complete combustion.

The calorific value of coal is a complex function of the elemental composition and is usually reported as the gross calorific value with a correction applied if the net calorific value is required. For the analysis of coals, the calorific value is determined in a bomb calorimeter either by a static (isothermal) or an adiabatic method in accordance with BS 1016: 1977: Part 5.

In the isothermal method the value is ascertained by burning a weighed sample of coal in oxygen under controlled conditions and the calorific value is computed from temperature observations made before, during and after combustion with appropriate allowances made for the heat contributed by other processes.

The adiabatic method consists of burning the coal sample in an adiabatic bomb calorimeter under controlled conditions. The calorific value is calculated from observations made before and after combustion. This latter method was used in the current study.
The computed value for the calorific value of coal is usually expressed in calories per gramme, British thermal units per pound or on occasions, as absolute joules. Whatever form of measurement is used the recorded calorific value is the gross value whereas the net value is calculated from the gross value (at 20°C; 68°F) by making a suitable correction (= 1030 Btu/lb = 572 cal/g = 2.395 kJ/g) to allow for the water originally present as moisture as well as that moisture formed from the coal during the combustion. The deduction is not equal to the latent heat of vapourization of water (1055 Btu/lb at 20°C) because the calculation is made to reduce from the gross value at constant volume to a net value at constant pressure for which the appropriate factor under these conditions is 1030 Btu/lb.

If a particular coal does not have a measured calorific value, it is possible to make estimations by means of various formulae, of which the most commonly used are:

i) the Seyler's formula
   \[
   \text{Calorific value} = 1.62(\%H)+0.52(\%C)-17.88 \text{ MJ kg}^{-1}
   \]

ii) the Dulong-Berthelot formula
   \[
   \text{Calorific value} = 81,370+345\left[\%H-(\%O+\%N-1)/8\right]+22.2(\%S)\text{MJ kg}^{-1}
   \]
where %C, %N, %O and %S are the respective carbon, hydrogen, nitrogen, oxygen and organic sulphur contents of the coal, all of which are calculated on a dry, ash-free basis.

Francis and Peters (1980) report the calorific values of carbonaceous materials:-

\[
\begin{align*}
\text{High temperature cokes} & = 28.0 - 31.5 \text{ MJ kg}^{-1} \\
\text{Bituminous coal} & = 32.0 - 33.5 \text{ MJ kg}^{-1} \\
\text{Anthracite} & = 32.9 - 37.4 \text{ MJ kg}^{-1} \\
\text{Lignites} & = 25.0 - 30.5 \text{ MJ kg}^{-1}
\end{align*}
\]

Coal utilization is vitally dependent upon calorific assessments since a whole range of varied requirements exist (Chapter 1).

A series of calorific value determinations were carried out on the two cokes currently in use in the Steel Industry and on three coals which are used in the manufacture of the two cokes.

5.10.1 Apparatus

An adiabatic bomb calorimeter, Figure 5.27, was used for these determinations. The instrument is different from the normal bomb calorimeter in that the calorimeter itself is immersed in a water jacket containing a heating coil. The heater is controlled by two thermistors which compare the temperature inside the calorimeter with that in the water.
The adiabatic bomb calorimeter

<table>
<thead>
<tr>
<th>No.</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Precision thermometer</td>
</tr>
<tr>
<td>2</td>
<td>Firing lead</td>
</tr>
<tr>
<td>3</td>
<td>Bridge circuit</td>
</tr>
<tr>
<td>4</td>
<td>Controller</td>
</tr>
<tr>
<td>5</td>
<td>Screw collar</td>
</tr>
<tr>
<td>6</td>
<td>Lid</td>
</tr>
<tr>
<td>7</td>
<td>'O'-ring</td>
</tr>
<tr>
<td>8</td>
<td>Oxygen inlet and earth lead</td>
</tr>
<tr>
<td>9</td>
<td>Bomb lid</td>
</tr>
<tr>
<td>10</td>
<td>Metal fuse wire</td>
</tr>
<tr>
<td>11</td>
<td>Thermistors</td>
</tr>
<tr>
<td>12</td>
<td>Heater</td>
</tr>
<tr>
<td>13</td>
<td>Stirrer</td>
</tr>
<tr>
<td>14</td>
<td>Sample</td>
</tr>
<tr>
<td>15</td>
<td>Cotton fuse</td>
</tr>
<tr>
<td>16</td>
<td>Sample bucket</td>
</tr>
<tr>
<td>17</td>
<td>Bomb body</td>
</tr>
<tr>
<td>18</td>
<td>Water</td>
</tr>
<tr>
<td>19</td>
<td>Water</td>
</tr>
<tr>
<td>20</td>
<td>Air gap</td>
</tr>
<tr>
<td>21</td>
<td>Stirrer pump</td>
</tr>
<tr>
<td>22</td>
<td>Cooling coil</td>
</tr>
</tbody>
</table>
Fig 5.27 An adiabatic bomb calorimeter
jacket. If the calorimeter is warmer than the water bath then the heater is switched on by the thermistors and the heater warms the water in the water bath until the temperatures are equal. In fact, the temperature of the outer water jacket is slightly lower than that of the calorimeter so that a heating effect by the water bath on the calorimeter is avoided. This slightly lower temperature of the jacket is maintained by cooling the jacket continually by mains water flowing around the jacket. After a firing of the instrument the heat increase arising from the combusted sample will be registered on the thermometer. No heat is lost to the environment and this makes determinations extremely accurate. There is also the important point that the water jacket maintains the maximum temperature for some time so that the experimenter has sufficient time to record the maximum heat rise.

On each occasion the instrument is used, the internal conditions vary which necessitates calibration before carrying out a series of determinations. This is achieved by firing a pellet of a material whose calorific value is known; benzoic acid was used in this series of tests.

5.10.2 Procedure

The flow of water through the cooling loop was set at 300 cm$^3$/min, which ensures that the heater in the water bath does not directly heat the calorimeter. The calorimeter was filled with distilled water so that the calorimeter and water weighed 3 kg.
The heating coil current was set to be between 6-8 A; if it had been found to be less, a small amount of $\text{Na}_2\text{CO}_3$ would have been added - if higher, some of the water in the jacket would have been replaced with fresh distilled water.

The instrument was operated by placing a single strand of gun cotton 5 cm in length in the groove of the conical half of the pellet mould and allowing 2 cm to protrude. The mould was then assembled and approximately 1 g of the dried ground sample was added. Finally the cylindrical half of the mould was placed in position and the pellet was formed by compressing the sample in the mould by the use of a hand operated screw press. The pellet was removed from the mould by placing a raised platform beneath the mould and tightening the press which forced the pellet and the two halves of the mould out of the pellet. The pellet was then weighed accurately.

Next a piece of platinum wire, 4-5 cm long was secured between the electrodes of the bomb and clamped in place by ferrules sliding down over each end of the wire. A clean crucible was placed in the receptacle and the pellet added. The protruding thread of gun cotton was tied to the platinum wire using two pairs of forceps and it was then checked that the O-ring inside the rim of the bomb assembly was in place. 1 cm$^3$ of distilled water was pipetted into the bomb casing, which was to absorb the combustion gases. The bomb was closed by securing the electrode assembly into the bomb casing by a knurled
retaining ring just hand tight.

The bomb was then connected to an oxygen supply by means of the Schrader valve on the cap. By controlling the gas flow using the regulator the bomb was filled with oxygen to a pressure of 30 bar which ensured complete combustion. The gas supply was then disconnected.

Testing the bomb electrics was carried out by placing the bomb on top of the instrument and connecting it to the firing circuit using the test plug. By depressing the test switch a bulb lights up indicating a complete circuit. Failure of the bulb to light up would entail dismantling the bomb to rectify the fault.

The temperature of the water jacket was then taken. When the calorimeter was found to be cooler than the jacket it was necessary to increase the flow rate in the cooling loop until the two temperatures were equal. If the calorimeter was found to be warmer, the water jacket was heated. If the temperatures had failed to equalise thereafter the initial balance would have been adjusted.

The bomb was then placed in the calorimeter so that the electrical connections were aligned and the lid lowered with care so that the thermistors were not damaged. The bomb was connected up by pressing the bomb firing plug located in the
centre of the lid which completed the firing circuit. The ready-to-fire lamp should light up and, if this did not occur, the bomb had to be removed and retested. In such circumstances it was essential that before replacing the bomb, it was thoroughly dried and the calorimeter refilled to weigh precisely 3 kg.

The initial temperature was recorded as accurately as possible; the graduation of the thermometer with its magnifier reading permitted this to be done to the nearest 0.001 of a degree Celsius. The firing switch was then pressed until the lamps went out. A 10-15 second delay followed before a temperature rise could be observed. The rise was rapid at first but did not reach a maximum until 3-4 minutes later; this was normal and the maximum temperature has to be recorded accurately. During the rise in temperature the heating coil was triggered again and again so that the water jacket maintained the temperature of the calorimeter in a stepwise fashion.

Calculation of the calorific value was undertaken using the calibration and test firing results:

\[
\text{Calorific value of sample in cal/g (dry weight)} = \frac{\Delta t\text{ of sample}}{\Delta t/g\text{ of Benzoic acid}} \times 6319\text{ cal}
\]

Weight of sample
\[ \text{cal/g} \times 4.1855 \times 10^3 = \text{J/kg} \]

where \( \Delta t \) of sample = rise in temperature of sample
and \( \Delta t/g \) of benzoic acid = rise in temperature per gramme of benzoic acid.

The bomb had to be disassembled after each firing, washed and dried. The crucibles were cleaned and the calorimeter topped up to 3 kg with distilled water. It was important that the internal pressure of the bomb was relieved before opening up.

5.10.3 Results

Calorific values for coals:

- Coal A = 34.1 MJ kg\(^{-1}\)
- Coal B = 33.7 MJ kg\(^{-1}\)
- Coal C = 32.7 MJ kg\(^{-1}\)

Calorific values for cokes:

- Coke No. 2 = 29.8 MJ kg\(^{-1}\)
- Coke No. 1 = 28.7 MJ kg\(^{-1}\)
5.11 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

It is an established experimental fact that any nucleus with either an odd number of protons or an odd number of neutrons, or both, has the property of nuclear spin.

A spinning proton will create a circulating electric current which in turn produces a magnetic field and it is thus possible to conceive the spinning proton behaving in the fashion of a small magnet. When a spinning proton is placed in a magnetic field it will position itself in one of two orientations, the low energy alignment of the nucleus, in which the magnetic field of the nucleus is in the same direction as the applied magnetic field or the high-energy position in which the two magnetic fields are opposed. A switch from the low-energy state of the nucleus to the high-energy state can be accomplished by supplying an amount of energy equal to the difference in energy between the two states, E. This energy may be supplied by electromagnetic radiation and since the energies themselves are dependent on the extent of the applied field, it is possible to select an external field to give absorption of electromagnetic radiation in a suitable part of the spectrum. In practice for the single hydrogen proton a field of approximately 2.3 Tesla (23000 Gauss) results in absorption at radio frequencies of 100 MHz and this is the region in which NMR is normally observed.
In part, the difficulty in constructing the arrangement for the observation of radiation by a proton is that of obtaining a magnet of high field strength and uniformity of field, 1 part in $10^8$ is necessary. As opposed to most other absorption methods the frequency of the radiation is kept constant and the magnitude of the applied magnetic field is varied until absorption of radiation by the proton occurs. This small variation in the magnetic field is obtained by passing current through wire coils wrapped round the pole-pieces of the magnet. Absorption of radiation is detected on a radio frequency bridge which goes out of balance when absorption occurs and the resulting signal is then amplified and recorded.

In chemical compounds protons appear in different chemical environments and such protons absorb radiation at slightly different field strengths. This is because such protons are encompassed by electron clouds and in a magnetic field electrons circulate around the lines of force and produce a local field, $B_{\text{local}}$, in opposition to the applied field $B_0$. A proton surrounded by electron clouds thus experiences a field somewhat less than that applied and this field has to be increased for absorption of energy to occur. The extent to which a proton is shielded by electron clouds is determined by the electron-attracting properties of nearby atoms and groups. As an example, the proton of hydrogen in $\text{O-H}$ is not so well shielded as in $\text{C-H}$, since oxygen is more electronegative than carbon and consequently resonance occurs for the $\text{O-H}$ proton at
a lower field strength than for the C-H proton. In reality these differences are very small, in the order of parts per million, but the whole technique of NMR is based upon measuring these slight variations in applied field with precision.

Field differences are not measured in actual magnetic field units but by reference to the resonance condition for an arbitrary standard. The standard is the compound tetramethyldisilane, Si(CH₃)₄, known as TMS. The compound under investigation, either the pure liquid or a solution in a non-protonic solvent, is mixed with a small amount of TMS and the spectrum recorded. It will show an absorption for TMS at a magnetic flux density B_standard and for a particular proton in the compound at say B_sample. Then the chemical shift for this type of proton is given by

$$\delta = \frac{\Delta B}{B_0} \times 10^6$$

where \( \Delta B = B_{\text{standard}} - B_{\text{sample}} \) and \( B_0 \) is the magnetic flux density of the magnet used. The factor \( 10^6 \) makes the numerical values convenient to handle and they can be quoted as parts per million. Chemical shifts can be quoted as units in which TMS is given an arbitrary value of 10 and other values related to it by the expression:

$$\tilde{\gamma} = 10 - \delta$$
In any NMR spectrum printout the area under each absorption peak is proportional to the number of protons giving rise to that peak and thus would be shown by the integrator trace which is incorporated into the instrument. From the step heights it can also be ascertained what ratio the protons are in.

5.11.1 Apparatus
The equipment used in the present work was a standard Perkin-Elmer Nuclear Magnetic Resonance Spectrometer R12B and the associated double resonance accessory R12. The apparatus operates at 60 MHz.

5.11.2 Procedure
Tar distillates were dissolved in DMS-D6 and TMS internal standard added. Coal tar was at 10% by volume of the solvent. Each sample was then injected into a 5 mm diameter NMR tube and in turn was placed in the spectrometer. The machine was operated with a 10 minute sweep time and a 10 ppm spectrum was recorded.

5.11.3 Results and discussion
The three traces Figures 5.28 - 5.30 show some clear differences. They all indicate a peak at 6.7 - 8.0 which is due to the aromatics. The sharp peak at 5.9 on the trace could be attributed to protons within a hetero-aromatic system. No such peak occurs on the other two traces. This may co-relate to the high nitrogen, sulphur, oxygen of coal A.
Figure 5.29 NMR spectra of coal A tar distillate
Figure 5.29 NMR spectra of coal B tar distillate
Figure 5.30 NMR spectra of coal C tar distillate
Between 0.8 - 2.7 the traces show the aliphatic component when again there are differences. In coal, the exinite macerals (leaf cuticles and material from algae and resin bodies) represent a diverse assemblage of small organic particles, characterised by a high hydrogen content and a high proportion of volatile matter. Such material contains mostly aliphatic organic components where the inertinite (seat earth on which the coal plants grew, miscellaneous oxidised matter and other detritus) and vitrinite (wood, stems, roots and leaves of plants) have a higher carbon and a lower hydrogen content and contain the most aromatics.
REFERENCES

CHAPTER 5


Willmers, R R. Private communication.
Chapter 6

CONCLUSIONS

The fore-going chapters have described the results of a variety of techniques used to study two metallurgical cokes and three coals used in the manufacture of one of the cokes. Whilst each technique, in its own right, can provide valuable information on the materials and their reactions with oxidising species, together they produce more complete evidence for the interpretations offered and the conclusions made.

6.1 COALS

The techniques reported in Chapter 5 mainly provide information characterising the coals and cokes. These properties, inter alia, govern the changes occurring during oxidation in terms of surface, thermal and optical properties which are described in Chapters 2, 3 and 4 respectively.

Of the three coals studied in this work, the Australian coal is different geologically from the two European coals (Williamson, 1967). Its lower volatile matter content compared with the European coals is indicated by its slower burn-off rates and surface area development (Section 2.5.2), by thermal analysis results (Section 3.3 and 3.4) and by its higher optical reflectance (Section 4.8.1). These data are consistent with the rank (Section 2.3).
The nature of the volatile matter is also a characteristic property of each coal. This has been established by IR/UV spectroscopic, NMR spectroscopic and GC-MS "finger-prints" (Sections 5.6, 5.11 and 5.8 respectively) of the coal distillates. The presence of low molecular weight components in coal A is consistent with its high volatile matter content. Likewise coal C shows little volatile hydrocarbons in its distillate. NMR spectra of the tar distillate of coal A show protons in hetero-aromatic systems; this is in accordance with the high nitrogen, sulphur and oxygen content shown by ultimate analysis. The European and Australian coals do not show this feature in their NMR data.

The "fixed" carbon contents of the coals, as shown by proximate analysis by TG (Section 3.3.5) is in accord with their calorific values (Section 5.10). This is also in agreement with DTA data (Section 3.4), although no attempt was made in this research to estimate heats of reactions by DTA peak area measurements.

Elemental analyses of the coals and their ashes for potassium and sodium by flame photometry (Section 5.4) and for iron by Mössbauer spectroscopy (Section 5.5) show that the coal C has the least quantities of these metals. Coal C has the highest ash content as shown by proximate analysis by TG (Section 3.3.5). Coal A is highest in K and Na, but coal B is richest in Fe₂O₃. The S contents of the coals vary as the Fe content,
highest for coal B and lowest for coal C. This is consistent
with the two elements occurring largely in the form of iron
pyrites, FeS₂.

The apparent densities of the coals (largest for coal C and
least for coal A) give an indication of their porosities. This
property, in turn, is related to their mechanical strength,
e.g. coal C has the largest Vickers hardness number and coal A
the least (Section 5.1). However, the variations of these
parameters with burn-off are probably more significant in the
use of the coals in coke manufacture. Changes in surface area
and porosity of the three coals during burn-off have been
extensively investigated by gas sorption analysis (Chapter 2).
The results correlate with microscopic studies of these
properties (Chapter 4) and the rates of burn off are consistent
with thermal analysis data (Chapter 3).

6.2 COALS FOR COKE MAKING
The quality of metallurgical coke depends on two main
variables, namely (i) the coal blend composition, and (ii) the
process conditions. Only coals with a specific range of rank
and type are capable of forming high quality metallurgical
coke.

The ability of a coal to soften on heating and to form a
coherent residue is termed "caking". It is a necessary
requirement of a coking coal that it should "cake" or fuse when
heated. Successful coke manufacture involves achieving the correct balance between behaviour of the oven charge in the plastic zone and its post-plastic contraction characteristics.

In a prime coking coal with good caking properties, an optimum ratio of reactive to inert components is present. However, caking capacity is not solely determined by the nature of the carbonised coal, because it can be altered by increasing the rate of heating in the oven and by increasing the pressure to prevent the escape of volatile material.

Coke has three main roles to fulfil in the blast furnace, namely, as a chemical reductant, as as fuel and as a support refractory, providing good permeability to furnace gases. For maximum permeability, the coke should have a large size and narrow size range. In addition a good coke should have an optimum level of resistance to the chemical and physical degrading forces encountered in the blast furnace.

Thus, in summary, the qualitative properties a good coke should fulfill are a narrow size range, optimum size and shape, high strength throughout the furnace temperature regime, low levels of ash, sulphur and moisture, resistance to chemical attack and thermal degradation, and perhaps most of all, consistency. It is in this context that the results for the two metallurgical cokes will be reviewed.
6.3 RELATIONSHIP BETWEEN COKE PROPERTIES, STRUCTURE AND CHEMISTRY

Microscopic studies have shown that coke 1 has a greater porosity than the coke 2 and that the average pore diameter of the former coke is also higher (Section 4.8.3). Porosity data are in good agreement with those obtained by apparent density determination (Section 2.4). Variations of porosity and surface area with carbon burn-off have been extensively studied for the two cokes by gas sorption analysis (Chapter 2) and verified by microscopy (Chapter 4). As in the case of the coals, the surface areas initially increase with carbon burn-off and reach a limiting maximum before decreasing. The more heterogeneous nature of the coke 2 is shown by its second maximum in the burn-off curve.

Thermal analysis reveals the greater reactivity of coke 1 compared with coke 2 (Chapter 3). This is consistent with porosity data of the cokes. However, coke 2 retains its reactivity at high carbon burn-offs, a property ascribed to the presence of the European component of the coke. Coke 2 also has a higher calorific value (Section 5.10).

The higher porosity of coke 1 is consistent with its lower mechanical strength. Thus the tensile strength (Section 4.8.5), Vickers hardness number (Section 5.1) and Young's modulus (Section 4.7.4.3) of coke 1 are inferior to those of the coke 2.
The aims of this research as set out on page 23 have all been pursued, giving additional information as to the mechanism of coal and coke combustion and its kinetics.

This information assists in the blending of the coals to produce coke which gives a more uniform rate of combustion. Thus, in the combustion of the cokes in carbon dioxide at 1000°C the maxima in surface areas occur within 25% burn-off. However, one the cokes shows a second maximum at later stages of burn-off, ascribed to the European component in the parent coal blend. This gives a more uniform rate of burn-off which is advantageous industrially.

In the course of research additional work was undertaken to ascertain the mechanical strength of the coals and cokes and the suitability of the latter for blast furnace practice.

This work could be usefully extended by examining a wider range of cokes derived from different component coals, especially in relation to surface area changes and thermal analysis studies, which could provide new information on carbon solution and combustion processes.

REFERENCES

CHAPTER 6

Computer programme for ascertaining porosity of coke

LIST

100 DI = CHR$(4)
200 DIM Z(44)
300 FOR I = 1 TO 64
400 IF Z(I) = 0
500 NEXT I
600 PRINT "MICROWORKS 65 DIGIS"
700 PRINT "**********PROGRAM****
****".
800 PRINT DI="PRINT"
900 PRINT "I"
1000 PRINT DI="PRINT"
1100 PRINT "ORIGINAL IMAGE SHOWN"
1200 PRINT "TYPE 'S' FOR TEST AREA"
1300 GET AS
1350 IF AS = "S" THEN GOSUB 900
1400 INPUT "LEFT MARGIN 11":J1
1500 INPUT "RIGHT MARGIN 12":J2
1600 INPUT "TOP LINE 11":J1
1700 INPUT "BOTTOM LINE 12":J2
1800 INPUT "BRIGHT FRACTION 0";

1900 PRINT ; PRINTER 2
2000 FOR I = 11 TO 12
2100 FOR J = J1 TO J2
2200 PEEK 64,1
2300 PEEK AS, J
2400 PRINT "\n"
2500 B = PEEK (66) + 1
2600 Z(B) = Z(B) + 1
2700 POKE 0: PRINTER = 2
2800 POKE 267: PEEK 1
2900 POKE AS, J+1
3000 NEXT J
3100 NEXT I
3200 POKE 256,0
3300 POKE 256,0
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3500 IF VS$ = "Y" THEN GOSUB 7300
3600 PRINT TEXT
3700 IF VS$ = "Y" THEN GOSUB 7300
3800 PRINT TEXT
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4100 PRINT TEXT
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4500 PRINT "GREY LEVEL DC CURVE";
4600 FOR I = 1 TO 64
4700 PRINT I,Z(I)
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5000 PRINT "****VOLUME FRACTION CALCULATION****"
Appendix 1(b)

Print run for coke No.1 porosity

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Appendix 1(b)

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DARK OR BRIGHT FRACTION (D/B) 1
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DO YOU WISH TO TRY ANOTHER INPUT (Y/N)?
SAVE PICTURE TO DISC?
ENTER FILENAME

coke No.1

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00 COPY-OBJO
00 PLOTPRINT
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02 SID440
01 BOO
04 TEMP
01 UFI
05 VOL
05 PETRVM
02 NOISE
03 TEMP1
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01 DATA
00 PID
00 FBASIC
00 INTRASIC
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03 SCRUN
03 coke No.1

RUN PLOTPRINT

PLOT AND PRINT PROGRAM
JS 270061

THIS PROGRAM WILL EITHER
STORE OR RETRIEVE A HI-RES PICTURE

ENTER 1 TO STORE HGR PICTURE
ENTER 2 TO STORE HGR2 PICTURE
ENTER 3 TO RETRIEVE PICTURE
ENTER 4 FOR CATALOG
ENTER 5 TO PRINT PICTURE
ENTER 6 TO QUIT

INPUT NUMBER NOW:5
need a CATALOG
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EXPAND SCREEN

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Appendix 1(b)

Coke No.1
## Appendix 1(c)

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IA 005 COPY.OBJ
IA 003 PLOTPRINT
A 013 VF
IA 003 IDS140
IA 010 BGUL13
A 004 TERR
A 012 VFI
A 005 FAUL
A 005 PETETVAL
A 002 NOISE
A 003 TEMP1
A 004 DESIGN
T 001 DATA
IA 020 FTD
IA 050 FPBR\.
IA 050 INTR\.
A 007 KEN\.
T 003 HEUL
T 003 coke No.2
IA 027 HUFFIN
B 034 PAREZ2
T 003 coke No.2
B 034 PAREZ2\.

RUN PLOTPRINT

PLOT AND PRINT PROGRAM
JS 290581

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ENTER 2 TO STORE HGR2 PICTURE
ENTER 3 TO RETRIEVE PICTURE
ENTER 4 FOR CATALOG
ENTER 5 TO PRINT PICTURE
ENTER 6 TO QUIT

INPUT NUMBER 1-4466

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DIFFERENT PICTURE  (Y/N) ?
INVERT SCREEN  (Y/N) ?
EXPAND SCREEN  (Y/N) ?

vi
Appendix 2

Thermochimica Acta. 82 (1984) 121-130
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

VACUUM BALANCE AND RELATED STUDIES OF COKES USED IN STEEL PRODUCTION

K. ADAHS, D.R. GLASSON and S.A.A. JAYAWEERA
John Graymore Chemistry Laboratories, Department of Environmental Sciences,
Plymouth Polytechnic, Plymouth PL4 8AA, Devon, England

ABSTRACT

The reactivities of coals derived from coal blends used in the steel industry have been compared. Kinetics and rates of oxidation have been correlated with changes in surface area and porosity determined by gravimetric gas sorption using vacuum microbalances.

During the earlier stages of oxidation of the coals in carbon dioxide at 1000 °C, the surface area increases considerably, reaching a maximum at about 20 % burn-off. This change in surface area is ascribed to formation of pores at the surface, including opening of initially-closed pores as the burning proceeds.

At higher percentage burn-offs, the surface area decreases to a very low value as the ash sinters with loss of porosity.

INTRODUCTION

Steel production requires metallurgical coals of suitable physical and chemical properties. Coals are preferred having high mechanical strength and moderate reactivity (measured by weight loss in carbon dioxide at 1000-1100 °C). Optimum properties are achieved generally by blending coals. The blends may consist entirely of coals indigenous to the United Kingdom or blends of foreign and U.K. coals.

At 1000-1100 °C, the oxidation occurs by the Boudouard reaction, viz.,

C + CO₂ → 2CO

Kinetics and rates of oxidation will depend on the area of the coke surface and its accessibility to carbon dioxide. Thus in the present research, changes in surface area and porosity during oxidation have been studied in detail for two coals - one derived from U.K. coals and the other from mixed foreign and indigenous coals. The constituents of the coke ash sinter appreciably at 1200 °C and tend to impede oxidation, particularly in the second half of the coke burn-off.

EXPERIMENTAL

Thermogravimetric studies of the oxidation of Scunthorpe and Redcar coals in air or carbon dioxide were made, using a Stanton-Redcroft mass-flow balance MF-HS (1). Larger samples of coke at various degrees of burn-off were prepared in a furnace at 1000 °C, using coke lumos of an outer 5 mm diameter. Surface
areas were determined by a gravimetric B.E.T. method (2), using nitrogen gas
sorption at -196 °C recorded on a C.I. Electronics Mark 2B microforce
balance (3). Samples of up to about 200 mg weight could be examined, using
balance ranges of 0-2.5 mg, 10 mg and 100 mg for measuring the gaseous adsorption.
The adsorption isotherms also provided data on the micro- and meso-porosity
of the materials. Information on the macroporosity was obtained from density
measurements by gas or liquid displacement. Further information was obtained
from electron-micrographs.

RESULTS AND DISCUSSION
Surface activity and kinetics during coke oxidation

Variations in surface area during oxidation of Scunthorpe and Redcar cokes
in carbon dioxide at 1000 °C are presented in Fig. 1 and 2.

![Graph showing variations in surface area during oxidation of Scunthorpe and Redcar cokes in carbon dioxide at 1000 °C.](image_url)

Fig. 1. Oxidation of British Steel Scunthorpe coke in carbon dioxide at 1000°C
Indigenous: - 60% Yorkshire,
25% Northants,
15% S. Wales (or Kent)
At lower percentage burn-offs, the surface areas increase considerably, reaching maxima during the first 25% burn-off. There is evidently formation of pores at the coke surface, including opening of initially-closed pores as the oxidation proceeds. Thus although the original coke samples have only macroporosity, yet they develop full ranges of mesoporosity (pore sizes of 2-50 nm diameter) in the earlier stages of burn-off in carbon dioxide or in air, cf. Fig. 3 and 4, where there is adsorption hysteresis in the relative pressure range 0.17-0.96. Similar maxima are shown for the actual changes in surface, \( S' \), (rather than the specific surfaces, \( S \)) of 1 g-samples of initial coke blend at various degrees and times of burn-off. The Redcar coke shows a second maximum at about 40-50% burn-off, which is ascribed to the behaviour of the Polish component. Experiments on cokes prepared from indigenous coals, e.g., Scunthorpe coke and separately on South Wales cokes (Nantgarw and Cwm) show development of maximum surface at 10-25% burn-off, whereas the Polish coke produces maximum surface at as much as 40-50% burn-off. (4). The Polish component helps the Redcar coke to retain its reactivity in the later stages of burn-off, where the
The adsorption of $N_2$ on Scunthorpe coke oxidised 22.6% in $CO_2$ at 1000°C is shown in Fig. 3. Activity gets reduced by sintering of the increasing proportion of adsorbed gas, cf. Fig. 5, 6 and 7. Hence the kinetics of the later stages of burn-off of the Scunthorpe coke resemble a two-thirds order reaction impeded by solid products (Fig. 8), where the two-thirds order plot deviates from linearity, becoming concave upwards.

**Development of porosity during coke oxidation**

Electron-micrographs of sections of initial coke particles in Fig. 9 indicate mainly macroporosity internally and externally. Apparent density measurements from gas or liquid displacement enable the closed pore volumes to be estimated. In Table 1, the apparent densities have been determined by nitrogen gas displacement on the vacuum microbalance. The pore volumes have been estimated...
Fig. 4. Redcar coke burnt at 1000°C in air (10 h) 16.8% burn-off. Adsorption of $N_2$ at -196°C.

<table>
<thead>
<tr>
<th>Coke</th>
<th>Apparent density</th>
<th>Pore volume, cm$^3$g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Scunthorpe</td>
<td>1.27</td>
<td>0.146</td>
</tr>
<tr>
<td>Redcar</td>
<td>1.34</td>
<td>0.305</td>
</tr>
<tr>
<td>Polian, Cwm</td>
<td>1.40</td>
<td>0.273</td>
</tr>
<tr>
<td>Nantzarv</td>
<td>1.48</td>
<td>0.232</td>
</tr>
</tbody>
</table>

TABLE 1
Apparent densities and pore volumes of cokes
Fig. 5 and 6. Scunthorpe and Redcar cokes oxidised in CO₂ at 1000 °C.
using true densities and volumes of (A) 2.27 and 0.441 cm$^3$ g$^{-1}$ and (B) 1.90 and 0.526 cm$^3$ g$^{-1}$ corresponding to values adopted for the X-ray density of graphite and the true density of coals carbonised at 1000–1100°C.

When 1 g of Redcar coke burns off 16.8% carbon in air at 1000°C (wt. loss 15.1%), its surface area increases from 0.8 to 6.9 m$^2$. If it had burnt as particles which were non-porous contracting spheres without forming new pores, its surface would have decreased from 0.8 m$^2$ to 0.72 m$^2$, i.e., 0.8 x (fractional wt. loss)$^{1/3}$. Thus 6.2 m$^2$ of surface was developed in burning off 0.151/1.90 cm$^3$ of carbon = 0.0795 cm$^3$, compared with pores volume opened of 0.151 x 0.220 = 0.0332 cm$^3$. Since the pores opened are mainly macropores > about 0.1 μm diameter, the surface of the opened pores is estimated from the formula radius of cross-section, $r/2 = \text{Volume/Surface}$, whence $r/2 > 25$ μm = 0.12 x 10$^{24}$/s x 10$^{30}$ making $s < 8.8$ m$^2$ per g coke, i.e., < 1.8 m$^2$ for 0.151 g coke. Thus most of the increase in surface is due to formation of new pores.
These should have an average size of about 65 nm or less, depending on how much of the oxidation forms new pores. There will be direct burn-off from the external surface, but some oxidation can form new pores or open and enlarge macro pores. Accordingly, the hysteresis loop of the nitrogen adsorption isotherm (Fig. 4) indicates pore sizes across the whole of the mesopore range of 2-50 nm, the commonest size (at the widest part of the loop) being about 7 nm.

Similar calculations for the Scunthorpe coke give a development of surface of 16.8 m$^2$ for 22.6 % burn-off of a 1 g-sample, compared with < 2.2 m$^2$ for opened macro pores. This leads to an estimate of 31 nm or less for the size average of the newly-formed pores. Again the nitrogen adsorption hysteresis loop indicates pore sizes over the whole of the mesopore range of 2-50 nm, the commonest size being about 5 nm.

An estimate of how much of the oxidation forms new pores can be made by measuring the uptake of nitrogen during the filling and emptying of the
Fig. 9 Scanning electron micrographs of Scunthorpe and Redcar coals.
mesopores from the adsorption isotherms (Fig. 3 and 4). This is approximately the difference between the highest and lowest weight readings of the hysteresis loop, using a value of 14.67 cm$^3$ for the volume of a mole of liquid nitrogen at -196 °C. These calculations indicate that only about 2.6 % of the oxidation of the Redcar coke in air and 2.5 % of the Scunthorpe coke in carbon dioxide forms mesopores, so that the appreciable increases in surface are associated with only a small proportion of the oxidation and the new surface is located in mesopores, giving it poor access to air or carbon dioxide. Hence, any increase in oxidation rate due to new surface being formed will be comparatively small, but could tend to make a two-thirds order rate become approximately linear during the earlier stages of oxidation, as is often encountered in coke reactivity tests.

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1 Stanton-Redcroft, n.l.c., Copper Mill Lane, London
Appendix 3

Society of Chemical Industry: Industrial Carbon and Graphite Group
SURFACE AREA CHANGES IN RELATION TO REACTIVITY OF COAL DURING OXIDATION

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ABSTRACT

Changes in surface area, porosity and rate of oxidation have been studied
for coal burnt in air at different temperatures.

Gas adsorption isotherms, determined gravimetrically on the solid residues
of the partly-combusted coal, show that there is considerable development of
surface and porosity as the oxidation proceeds, especially during the first
half of the burn-off. However, most of the new surface developed is located
in micro- or meso-pores where access to oxygen (from air) is restricted by
slow diffusion. Hence the oxidation of the coal is only slightly accelerated,
so that the diminution in oxidation rate according to the ideal two-thirds
order law (for the contracting sphere model) is just compensated enough to
make the earlier stages of oxidation approximately linear with time. This is
found also for oxidation of the coal in air, oxygen or carbon dioxide (oxidation
reaction) under dynamic (gas flow) conditions. There is some sintering of the
coal ash during the later oxidation stages, especially at the higher
temperatures, which tends to inhibit oxidation.

Results obtained are analogous to those found for the oxidation of zinc
used in zinc-lead processing (ref. 1-3) and in steel-making (ref. 4).

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1072.
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VACUUM MICROBALANCE STUDIES ON THE COMBUSTION OF SARAJI COAL

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ABSTRACT

Samples of Saraji coal have been oxidised in air at various temperatures and for different times. Products have been examined by a gravimetric gas sorption technique. Results are presented for changes in surface area and porosity with carbon burn-off and discussed in relation to kinetics of the oxidation.

There is considerable development of surface and porosity as the oxidation proceeds, especially during the first half of the burn-off. However, oxidation of the coal is only slightly accelerated, since most of the new surface is located in micro- or meso-pores where access to atmospheric oxygen is restricted by slow diffusion.

INTRODUCTION

Saraji coal is an Australian prime coking coal of rank 30la. It is a Gondwana Permian coal formed under temperate conditions showing distinct ring structure. In contrast, European coking coals, e.g., British and Polish, have been formed under hot, steamy tropical conditions (ref.1). Thus British coking coal is a high volatile, strongly caking coal of rank 501, but having an indistinct ring structure.

In earlier research (ref.2), the behaviour of Horden coal on oxidation has been examined and in the present research it is compared with the oxidation of Saraji coal. Gas sorption isotherms have been determined gravimetrically (ref.3) on the solid residues of the partly-combusted coal and likewise show considerable development of surface and porosity for the faster burn-offs. These changes are correlated with the oxidation kinetics.

EXPERIMENTAL

Samples of Saraji coal at various degrees of burn-off were prepared isothermally in a furnace at 100, 400 and 500°C, using lumps of approximately 3-6mm diameter. Surface areas were determined by a gravimetric BET method (ref.3), using nitrogen gas sorption at -196°C recorded on a CI Electronics Mark 1B microforce balance. Samples of up to 200mg weight could be examined, using balance ranges of 0.1, 1mg, 10mg and 100mg for measuring the gaseous adsorption. The adsorption isotherms also provided data on the micro- and meso-porosity of...
the materials (ref. 4). Information on the macroporosity was obtained from density measurements by gas or liquid displacement.

RESULTS AND DISCUSSION

Surface activity and kinetics during coal oxidation

Variations in surface area during oxidation of Saraji coal in air at 300, 400 and 500°C are presented in Fig. 1 and Fig. 2.

![Graphs showing surface activity and kinetics during coal oxidation](image)

**Fig. 1.** Oxidation of Saraji coal in air at 400 and 500°C.
As oxidation proceeds at each temperature, the specific surface area, $S$, of the partly-combusted coal progressively increases, reaching a maximum in the later stages of burn-off. Similar maxima are shown for the changes in total surface area, $S'$, (rather than specific surface, $S$) of initial lg-samples of coal at various degrees and times of burn-off. However, these maxima all occur at about 50% burn-off. The increases for the more rapid burn-offs at 400 and 500°C are considerably greater than that for the slow burn-off at 300°C, rising to 170 m$^2$ at 400°C and 125 m$^2$ at 500°C. Increases to 125 m$^2$ and 83 m$^2$ respectively were recorded for Horden coal in earlier research (ref.2). The smaller increases at 500°C compared with 400°C were ascribed to the tendency of the coal residue to form small globules, suggesting that the rate of energy transfer was insufficient to maintain an even temperature and hot spots were formed. The temperature of 500°C is well above the softening temperatures of the coals (Horden, 346°C, Saraji, 406°C) facilitating loss of volatiles and just above resolidification temperatures, 449, 487°C (ref.5). Saraji coal burns more slowly than Horden coal, particularly in the later stages of oxidation, cf. Fig.1. Nevertheless, the increases in surface are correspondingly larger for Saraji than Horden coal, which is in line with the higher temperatures for Saraji coal. At 300°C, a temperature below the softening points, the increases in surface are much smaller, cf. Fig.2, but the maximum for the Saraji coal (11.1 m$^2$) is about twice that for the Horden coal (5.6 m$^2$) for practically equal oxidation rates during the first half of the burn-off. Initially the Saraji coal ($S = 0.5 m^2 g^{-1}$) is more compact than the Horden coal ($S = 2.0 m^2 g^{-1}$) and evidently is subjected to greater strain during the loss of its volatile...
Fig. 3. Combustion of Saraji coal in air at 300, 400 and 500°C.

matter (19.6-27.5 dry mineral matter free %) compared with Horden coal (32.1-36.0 dmmf %): the Saraji coal shows a tendency to flake on combustion, thereby forming more new surface.

There is evidently formation of pores at the coal surface, including opening of initially closed pores as the oxidation proceeds. Thus although the original coal samples have mainly macroporosity and some mesoporosity, they develop full ranges of mesoporosity (pore sizes 2-50nm diameter) and some microporosity during the burn-offs. This is shown by the nitrogen isotherms developing adsorption hysteresis in the relative pressure range 0.37-0.96 corresponding to mesopores and then at relative pressures below 0.37 (micropore range), cf. Fig. 4 and ref. 4, which shows examples of Saraji coal approximately half-burnt at 400°C and at 500°C. Thus there is considerable development of surface and porosity as the oxidation proceeds, especially during the first half of the burn-offs. However, most of the new surface is located in the micro- or meso-pores where access to oxygen (from air) is restricted by slow diffusion. There are not the large increases in oxidation rate which are suggested by the plots of $S'$ against time in Figs. 1 and 2 (where $S'$ should be proportional to rate of oxidation and the oxidation-time curves should be acceleratory and sigmoidal). In practice, the oxidation of the coal is only slightly accelerated, so that the diminution in oxidation rate according to the

A xxii
Ideal two-thirds order law (for the contracting sphere model) is just compensated enough to make the earlier stages of oxidation approximately linear with time, cf. Fig.3. This is found also for oxidation of the coal in air, oxygen or carbon dioxide (Boudouard reaction) under dynamic (gas flow) conditions.

Formation and sintering of the coal ash

Although the surface area changes and combustion rates were considerably different at 300, 400 and 500°C, yet the surface areas of the ashes were approximately the same. In Fig.4(b) nitrogen adsorption isotherms are shown (i) for the ash formed when the coal combustion at 500°C was just complete (in 2h), and (ii) when the ash had been sintered at 500°C for a further 8h. The isotherms for the ash are of type II (BET classification, ref.6) in contrast with those of the partly-burnt coal which are of type I, cf. Fig.4(a). The surface area of the newly-formed ash (i) was 30m²g⁻¹ which decreased to 18.5m²g⁻¹ on 2h heating at 500°C and remained practically constant during a further 8h heating (ii), S = 18.1m²g⁻¹. The main components of the ash were silica, alumina or alumino-silicates and iron oxides, Fe₂O₃ and Fe₃O₄. Since the Tammann temperatures (half m.p. in K) correspond to 890°C for alumina, 730°C for silica and 650°C for ferric oxide (ref.7), there is no possibility of
ash sintering proceeding by crystal lattice diffusion at the lower temperatures of 300-500°C. Therefore sintering is possible only by surface diffusion, which becomes appreciable above about one-third of m.p. in K, i.e. 500°C for alumina, 400°C for silica and 340°C for ferric oxide. Since only the lower-temperature mechanism is available, sintering is restricted, i.e. some initial loss of surface is followed by comparatively slow sintering, as was found earlier for Horden coal ash (ref.2). The nitrogen adsorption isotherms on the ash in Fig.4(b) indicate a small amount of mesoporosity and no microporosity and the surface areas indicate average crystallite sizes of approximately 0.1-0.2μm. The surface areas are somewhat higher than those found for the ashes of metallurgical cokes oxidised in air at 500°C (ref.8), where there will have been some sintering produced by the higher temperatures used in the initial coking of the coals.

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REFERENCES

DEVELOPMENT OF POROSITY DURING THE COMBUSTION OF COALS AND COKE

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ABSTRACT

Coal samples of European and Australian origin have been oxidised in air at 300, 400 and 500 °C for different lengths of time. The combustion causes formation and opening of pores in the remainder of the coal. Products have been examined by a gravimetric gas sorption technique. Results are presented for changes in surface area and porosity with carbon burn-off and discussed in relation to kinetics of the oxidation.

There is considerable development of surface and porosity as the oxidation proceeds, especially during the first half of the burn-off. However, oxidation of the coal is only slightly accelerated, since most of the new surface is located in micro- or meso-pores where access to atmospheric oxygen is restricted by slow diffusion.

When samples of Polish Weglokoks coal are coked in flowing nitrogen at 1000 °C, most of the volatile matter is lost within 1 hour and there is some increase in surface area to give a coke of about 8 m² g⁻¹. On further coking up to 24 hours, the surface area decreases to about 4 m² g⁻¹, becoming comparable with commercial metallurgical cookes (up to 4 m² g⁻¹). Oxidation of the Polish coke occurs in carbon dioxide at 1000 °C by the Boudouard reaction viz., C + CO₂ → 2CO, and the surface area of the residue increases from 8 up to about 30 m² g⁻¹ at about one-third burn-off. These increases are not so large as those found for the rapid combustion of the coal in air at lower temperatures (400 or 500 °C) of up to 120 m² g⁻¹ at just over half burn-off, when accompanied by loss of volatile matter. However, the ten-fold increase in surface area for the coke is similar to those found previously for the commercial cookes and the earlier stages of the burn-offs also give approximately linear kinetics.
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Signed... K. Adams...