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The deterioration of Gieseler fluidity with time

P. D. Ruffle

University of Wollongong

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THE DETERIORATION OF

GIESELER FLUIDITY

WITH TIME

by

P. D. RUFFLE
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The chemical and petrographic characterisation and the special empirical tests used for evaluating coals for metallurgical coke manufacture are of vital importance to the coal mining industry. Of these tests, the Gieseler Plastometer is one of the most closely monitored by customers for Australian coals, particularly the Japanese steel industry.

In the process of coke formation, particles of crushed coal pass from a solid, granular material through a fluid, or plastic state to become a fused porous solid. The temperature range over which the coal exists in this fluid state, and the viscosity of that fluid state are critical factors in the blending of coals from different sources for coke manufacture. These characteristics are commonly measured by the Gieseler Plastometer.

The fluidity of soft coking coals particularly measured by the Gieseler Plastometer decreases dramatically with time. The cause of this deterioration has long been attributed to the process of oxidation.

Recent work suggests that the loss in fluidity accompanying this apparent oxidation reaction occurs due to an oxygen cross-linking mechanism. This theory attributes the formation of a plastic fluid to the rupture of oxygen cross linkages and the stabilisation of the fluid by the transfer of hydrogen to free radical sites. Since oxidation reduces the availability of transferable hydrogen (through the loss of aliphatic C-H groups) and produces oxygenated functional groups (which increases the potential for oxygen crosslinking during thermal reactions), the resulting plastic mass is affected, leading to an apparent loss of
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fluidity. Internal friction measurements appear to substantiate this crosslinking mechanism but Fourier transform infrared measurements on coal, as a function of time, failed to discern any loss of C-H functional groups.

Samples of freshly cut medium rank Borehole seam coal were collected and taken to C.R.L. In the laboratory, the samples were crushed to minus two millimeters and placed in controlled environments so that the effects of oxidation, outgassing and freezing on their maximum fluidity could be measured using a Gießeler Plastometer.

Laboratory carbonisation tests, proximate and ultimate analyses, maceral counts and reflectivity measurements were also made on the samples. Analysis of gas given off from the samples stored in sealed bombs was done using chromatographic equipment.

The results obtained from the experimental program indicated that the samples that outgassed differed little in their rate of maximum fluidity drop off when compared to those which were prevented from outgassing. The maximum fluidity of the samples that were frozen remained relatively high for the duration of the experiment. This suggests that moisture may play a role in an oxidation process.

Since oxidation is initially a surface phenomena it would be expected that crushing the coal should rejuvenate the fluidity back to near its original value. Crushing the coal down to 0.425 mm did not restore the fluidity to the initial values.
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Gieseler fluidity is one of the principle tests used to determine the suitability of coals for use in coking coal blends. Gieseler fluidity is well known to be sensitive even to low levels of oxidation (Moxon and Nicol, 1987), especially in the case of the lower rank coking coals. The present study examines possible causes for changes in fluidity and examines the effects of storage under a range of conditions. The experimental work was concentrated upon the possible effects of outgassing of adsorbed gases on Gieseler fluidity.

Although coal is visibly heterogeneous there are many regular and repeating features which have definable physical or chemical structure. A thorough knowledge of these features is necessary for understanding the behaviour of coal in various physical and chemical processes such as crushing, conversion to liquid and gaseous fuels, combustion, carbonisation and weathering.

Since coal consists mainly of carbon, hydrogen and oxygen (its nitrogen content is low (1 - 1.5%) and relatively constant, early classifications were based on elemental analysis. As early as 1839 Regnault developed a system of classification based on the oxygen content of coals. In 1899 Seyler designed a classification, using carbon and hydrogen content as parameters, which was published in 1933.

The relationship between the elemental composition and the technological properties of coal is complex. It was therefore necessary to develop a classification based on the parameters that provided direct information on the
behaviour of coals as a fuel and as a basic material for the manufacture of gas and coke.

In combustion technology interest is mainly directed towards the specific energy (S.E.) value. This is despite the fact that it is becoming apparent that coals with the same S.E. value characteristics may perform very differently in the furnace (Shibaoka, et al., 1985).

Besides the S.E. value, the behaviour on heating is also of importance in combustion technology. Whereas some coals cake together, others swell to such a degree as to interfere with the passage of air, while a third category is burnt to ash as a granular mass.

Experiments have shown (Shibaoka, et al., 1985), that coal combustion occurs in two main steps - devolatilisation to produce char, followed by char combustion. Softening, devolatilisation, swelling and resolidification are closely related. These phenomena depend, however, to a very large degree on the heating rate. This has been clearly demonstrated by Duinhunty and Harrison, (1953), who found that all coals, irrespective of their rank, can be devolatilised without showing any swelling provided the heating rate is sufficiently slow. Goodarzi and Murohisor, (1988), showed that although the size and pattern of the mosaic is essentially rank dependent it can be greatly influenced by the heating rate.

It has become clear that the quality of coke depends upon the typological, petrological and granulometric composition of the coking coal blend, which in its turn, determines the rheological behaviour in the plastic state and the mechanical behaviour immediately after
resolidification. The porosity of the coke is mainly determined by the transient plasticity, the structure of the cracks formed during the resolidification process, and the mechanical strength, whereas the hardness depends principally on the final heating level.

The influence of the composition of the coking coal blend was studied systematically by van Krevelen, et al. (1960). They found that the potential coke quality depends both on the nature of the coal blend and on the granulometric distribution of its components.

In a coke oven the heat is supplied from the oven walls. The crushed coal particles pass from a solid, granular material through a fluid, or plastic stage to become a fused porous solid. The evolution of a gaseous phase during the coke formation, in addition to the solid and liquid phases, renders the system on which the measurements of plasticity have to be made very complicated. For this reason, the method used for measuring plasticity of coal must, of necessity, be empirical in character.

The normal behaviour of coals undergoing carbonisation may be affected by oxidation or hydrogenation of the coal, (Boyapatti, et al., 1984), as well as by the presence of mineral matter (particularly sulphides) in the coal (Moxon, et al., 1986). Higher heating rates increase fluidity and swelling, and the temperature range over which the coal is plastic is extended. Some coals, which show no softening when heated slowly, soften and may swell when heated more rapidly. It has been shown that oxidation affects plasticity adversely, and deoxygenation has been reported to enhance plasticity (Rembashevski, et al., 1960). Although selected studies (Boleslaw, et al., 1974; Wachowska, et al., 1974) have
led to some insight, the role of oxygen is still not well understood.

As soon as coals are exposed to air, they begin to interact with oxygen and undergo a series of profound chemical changes. These include deterioration of their coking properties and softening characteristics. Maximum fluidity and solidification temperatures tend to be lower, and the fluid range becomes narrower. Spontaneous ignition and a progressive loss of specific energy may also occur.

The inclusion of oxidised coal in most coal products detracts from their value. Therefore, the methods and tests for detecting oxidized coal and characterization of the degree of oxidation of coal are valuable. Several tests and techniques have been developed for this purpose. These include; free swelling index, phase inversion, flotation recovery, Gieseler plasticity, dilatometry, volatile matter, pH of coal slurries, alkali solubility, electrostatic charge, oxygen content, observation of the microscopically discernible changes in the oxidised coal and the coke made from it such as reflectance, evidence of cracks and oxidation rings and evidence of isotropy in the coke (Pines, et al., 1973).

Several other techniques have also been developed in recent years for the detection and characterization of oxidised coal such as: high temperature nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy (FTIR), (Painter, et al., 1980), carbon $^{13}$ nuclear magnetic resonance (Pines, et al., 1973), comparison of the differences in reflectance or bireflectance between chars from fresh and weathered vitrinites, (Shibaoka, et al., 1985), alkali extraction
test and the presence of the minerals geothite and basanite.

The Gieseler plastometer is a type of viscometer that monitors the fluidity of a crushed coal sample as it undergoes the process of carbonisation. In order for a coal to make good quality metallurgical coke, the reactivess must become fluid enough to flow around the inerts and thus bind them together, but it must not become so fluid that a weak, spongy coke is produced.

Fluidity measured by the Gieseler plastometer is not a real measure of fluidity, but a measure of the resistance to the rabble arms. In high volatile coals this lack of resistance may be due to high rates of gas emission because resistance to the mixture of gas and solids is low. The Gieseler unit does not solely measure the viscosity of the non-gaseous phases.

When coals are to be blended to form a coking blend, the individual coals must become fluid at much the same temperature. Coking coals become fluid over a temperature range, having a low fluidity at the lower and upper ends of the temperature range and a maximum fluidity in the centre of the temperature range. For the various individual coals in the blend to flow and mix properly, their ranges of fluidity (or plastic ranges) must overlap to a high degree.

The fluidity properties, like other coking characteristics, depend very heavily on the petrographic properties of the coal. Only coals in the rank range of vitrinite reflectance ($R_o \text{ max}$) 0.9 to 1.6 are capable of producing blast furnace quality coke when coked on their own.
The coals in this rank range contain those reactive components (vitrinite + exinite + low reflecting semi-inertinites) which become sufficiently fluid in the plastic phase so as to completely 'wet' the inert particles and then form a strong and coherent bond between these inert particles upon solidification.

Apart from coal rank, coal type is also of importance in coke production. The exinite group of macerals produce much more gas on heating than the other maceral groups, this contributes to both fluidity and swelling properties of the coal but the rapid degassing may produce unfavourable structures within the resultant coke.

Coals with a high and with a low fluidity may be blended to obtain optimum coking characteristics, but the plastic ranges of the various components in this case should generally be compatible with each other. More so than most other properties, the degree of maximum fluidity is sensitive to oxidation of the coal, and care must be taken in storage of samples for such tests.

The Gieseler fluidity of a coal measured in dial divisions per minute (ddpm) decreases with oxidation. Under controlled oxidation at 80°C, the granular fraction of a high volatile (low rank) bituminous Australian coal (less than 3.18mm) was found to lose all of its Gieseler fluidity characteristics after only 20 hours in laboratory conditions (Guyot and Pollard, 1974). However, the same size fraction of a low volatile (high rank) bituminous coal lost only 50% of its fluidity under equivalent conditions. The effects are less severe for coarser size fractions and much less severe at lower temperatures. At 20°C, for example, both high and low rank materials retained some residual fluidity even after twelve weeks of oxidation. Mitchell (1963), found only a
slight decrease in fluidity for two American coals after 18 months outdoor stockpile storage.


The former study established that the crucible swelling number (C.S.N.) and the Gray-King coke type tests are relatively insensitive to changes in ash level at low concentrations (less than 15% [dry] for the coal studied). At high ash concentrations a decrease in the C.S.N. was observed, and this possibly resulted from the dilution of the coal by the ash forming minerals. Further studies were not continued on this aspect as practically all coking coal specifications require an ash figure below 10% [dry].

The results observed from the Gieseler and Dilatometer tests showed that ash variations had a significant effect. The conclusion reached was that the reduction in Gieseler fluidity and dilatation is most pronounced for ash levels less than 10% [dry]. The mineral matter increases the viscosity of the coal during the plastic stage, therefore reducing its fluidity as measured by the Gieseler Plastometer and the expansion as measured by the Dilatometer. This then reduces the attractiveness of the coal in the market place.

In the latter work, Moxon, et al., (1987), established that the laboratory carbonisation properties of the samples from the Borehole and Dudley seams are affected
by prolonged exposure to the atmosphere. The C.S.N. and
the Gray-King coke type tests showed only slight
decreases over time. The dilatometer results decreased
gradually over the study period, whereas the Gieseler
fluidity of coal decreases dramatically with time
particularly over the initial 30 to 50 days, (Figures 1
and 2). The cause of this deterioration has been
attributed to the process of oxidation of the coal
surface.

Preliminary investigations at C.R.L., (Moxon and Nicol,
1987), have supported the theory that surface oxidation
may not be the major mechanism responsible for the
deterioration of the laboratory carbonisation properties
of coal with time. The desorption of gas from the coal
has been cited as a possible alternative mechanism which
might be able to explain this effect. This project was
formulated to consider the question of gas desorption.
Fig 1.
Dudley seam simulated bore samples showing the variations in laboratory carbonisation properties as a function of time. The ash level is also shown plotted against time. (Moxon et.al., 1987)
Fig 2.
Borehole seam simulated bore samples showing the variations in laboratory carbonisation properties as a function of time. The ash level is also shown plotted against time. It should be noted that the large variations in ash recorded were probably due to some lump material being collected in the original sample. (Moxon et al., 1987).
CHAPTER TWO
THE CHEMISTRY OF COAL

It is generally agreed that coal originates primarily from plants. Through a series of chemical changes the primary products of the original decomposed plant material, (biopolymer), is then sequentially transformed into peat, lignite, (geopolymer), sub-bituminous coal, bituminous coal, and finally to anthracite. With these transformations, the carbon content increases and the oxygen content decreases. The calorific values of coals with carbon contents below about 92% exhibit a marked relationship to their rank. A slight decrease in calorific value occurs in the anthracites.

The chemical structure of coal began to attract the interest of coal chemists shortly after the end of World War I and was for many years pursued by studying the composition of solvent extracts and the nature of coal oxidation products resulting from partial oxidation. Solvents used included strong solvents for polyaromatic systems, such as pyridine. Infra-red spectroscopy proved useful for the study of functional groups (Retcofsky, 1977).

Attention was also given to "model compounds", which in some respects appeared to display coal-like behaviour. However these studies were limited by inadequate analytical techniques.

In these circumstances, real progress in elucidating the chemical structure of coal became possible only with the development of better investigational tools, at first X-ray diffraction (Ergun and Tiensuu, 1959), (Cartz and Hirsch, 1960), and later electron spin resonance spectroscopy (Retcofsky, et al., 1981), mass spectrometry
and nuclear magnetic resonance (N.M.R.) spectroscopy (Pines, et al., 1973), especially C\textsuperscript{13} "magic" angle spinning techniques (Miknis, et al., 1979). These new methods of enquiry did not simplify the exploration of coal chemistry, but they offered means for studying coal without chemically altering it as much as previous techniques, provided valuable new information, and for the first time allowed verification of some of the conclusions drawn from earlier experimental data on chemically altered and unaltered coals.

The major elemental components of coal are carbon, hydrogen and oxygen; the minor elements include sulphur, nitrogen, silicon, aluminium, iron, calcium, potassium, sodium, magnesium and titanium. Essentially all of the remaining elements occurring in the earth's crust have either been identified in trace amounts or are likely to be present in coal, many of these occurring with minerals of non-organic origin (Ward, 1984). Carbon is by far the most abundant element present and, as various molecular groupings, combined with small amounts, by weight, of hydrogen and oxygen, provides the structural integrity and most of the heat content and reducing power of coal.

The elements are combined to form chemical compounds which are either organic or inorganic in nature and thus form the two coal subdivisions; the organic coal matrix and the mineral matter (crystalline inorganic compounds). The elemental composition of the mineral matter includes all the elements listed, while the organic matrix consists mainly of complex and irregular polymers of carbon, hydrogen and oxygen, with small amounts of sulphur and nitrogen.

Much of the work reported in the literature on coal chemistry relates specifically to vitrinite which, apart
from being the most abundant component of sub-bituminous and bituminous coal, is also the most homogeneous maceral (Berkowitz, 1975). Nevertheless, heterogeneity within vitrinite is well established. The differences in reflectance of the vitrinite, (Brown et al., 1964), are due to different original plant materials and to different degrees of preservation of the plant substance (Stach, et al., 1982). The composition of this vitrinite is believed to be the result of the coalification of either cellulose or lignin dominated structures, which constitute the majority of the plant components. It has been shown by Exarchos and Given, (1977), however, that cellulose undergoes very rapid biodegradation in plants which are decomposing today. The same is true for protein. Plant constituents which are most resistant to bacterial attack are waxes, resins, tannins, lignins, flavonoids, and possibly alkaloids.

These structures are present in plants today, and are probably similar to those of plants of prehistoric times, but they do not survive intact over the long periods of time required for their transformation to coal beyond the brown coal stage (Teichmueller, 1967).

However, some of the structural features can be recognised even in bituminous coal and anthracite. Just as the peat-forming process acts variably on the various plant tissues, for example on lipid rich parts such as cuticles and resins versus woody tissues rich in cellulose and lignin, coalification affects different components in different ways.

Among the major physical changes coalification brings about are a reduction in the bed moisture content, a decrease in density, a decrease in porosity and an increase in refractive index in later stages. Chemical
changes which occur are condensation, polymerization, and loss of functional groups, i.e., of functions containing oxygen, sulphur and nitrogen linked to the molecular structure of coal. Polymerization and condensation occur as an extension of the humification process that takes place in lower-rank coals. The net result of these changes is a continuous but nonlinear enrichment of carbon with increasing rank.

The general nature of the coal molecule has been suggested both from chemical (Given, 1960, 1961; Cooper and Murchison, 1969) and from X-ray evidence (Cartz and Hirsch, 1960). Models derived from these studies are illustrated in Figure 3. Given's model embodies the essential features of the Cartz-Hirsch model, but can more easily be brought into better accord with NMR data on hydrogen forms in coal by making the basic aromatic unit a dihydrophenanthrene- rather than a dihydroanthracene-like configuration (Berkowitz, 1979).

For most geological purposes, the rank and type of coal, as determined by petrographic methods, provide an adequate basis for the comparison of different materials. However, in industrial usage of coal, many of the chemical parameters are more significant, and a number of schemes have been drawn up to classify coals for academic and industrial purposes.

The classification of coals published by the American Society for Testing and Materials (A.S.T.M. 1979) is used extensively in North America and many other parts of the world. It is based on two fundamental properties of practical significance, the fixed carbon (and hence the volatile matter) content and the specific energy. Further classification for some coals is then based on their agglomerating or coking properties, expressed by the
FIG. 3 - Chemical and physiochemical evidence of the general nature of the structures of coal.

a) X-ray data for vitrinite with a carbon content of 84.5% (Cartz and Hirsch, 1960)

b) Chemical structure with a vitrinite content of 82% (Given 1960, 1961)

c) Vitrinite at various rank levels (Teichmueller et. al., 1968)
nature of the residue after carbonisation of small amounts of granular coal in conical crucibles (Free Swelling or Crucible Swelling Index) or in a cylindrical vessel (Gray King Coke Type).

A generally accepted definition of rank states that rank is related to the temperature attained during burial and the time at that temperature. There is no definite line of demarcation between the several ranks and the analyses, properties and characteristics of one group merge into those of the next group. In general, the coking properties of coal are at an optimum in the higher rank bituminous coals e.g. 89% carbon (d.a.f.) (Coal Glossary, 1980). Many groups and authors have attempted a more specific definition, for example the word "rank" is defined by the A.S.T.M. standard to represent the "degree of metamorphism, or progressive alteration, in the natural series from lignite to anthracite." The use of the word rank in this sense is acceptable but the parameters (volatile matter and specific energy) used in the ASTM standard to assess rank are less than desirable because petrographic composition of coals can vary greatly, greatly affecting the volatile matter yield and specific energy of a coal (Tschamler and de Ruiter, 1966; Ting, 1969). A high inertinite content will cause a decrease in volatile matter yield from a coal, and a high liptinite content (particularly resinite and alginate) will effectively increase the specific energy of a coal. In general, petrographic composition of a coal is determined in the peat swamps at the time of peat accumulation. Work done by various authors but particularly Teichmueller, have indicated that the maceral micrinite may form from liptinites and usually appears first in the bituminous-coal stage (Teichmueller, 1974). Thus minor changes in maceral composition and volume will occur during progressive metamorphism or
alteration but will not change the maceral composition of a coal in any meaningful way. Thus, rank as determined by the A.S.T.M. standard does not represent, in a strict sense, the degree of metamorphism of a coal.

Of the numerous "scientific" coal classification systems that start with carbon-oxygen or carbon-hydrogen correlations the best known is that proposed by Seyler in 1899 and progressively extended and refined by Seyler (Seyler, 1948). It is based on the percentage of carbon and hydrogen present in the coal, calculated to a dry, mineral-matter-free basis, as shown in Figure 4.

Alternative criteria, shown by other axes superimposed on these, are the percentage of volatile matter and the specific energy, both also on a d.m.m.f. basis.

Most coals plot on the curved band indicated in Figures 4 and 5. Low rank coals have higher hydrogen and lower carbon contents than high rank coals, and plot to the right of the graph. At the other end of the scale, anthracites, with almost no hydrogen present, plot in the lower left-hand sector. Variations in coal type are expressed, to some extent, by the use of the terms "perhydrous" for hydrogen-rich material, "sub-hydrous" for hydrogen-poor samples and "orthohydrous" for samples lying close to the mid-line of the coalification band.

A very simple means for obtaining an insight into the course of the processes occurring during coalification is the "atomic H/C versus O/C diagram". The main constituents of coal are the elements carbon, hydrogen and oxygen. The elementary constitution of any term of the coalification series may be represented graphically by plotting its H/C ratio versus its O/C ratio. The H/C versus O/C diagram also shows the development lines of
FIG. 5 - Seylers chart simplified (Francis 1961)

All results are given on a dry mineral free basis.
the various macerals (Figure 6).

Presentation of hydrogen contents on an atomic H/C ratio basis, demonstrates that hydrogen is an important component of the coal structure (Table 1). The atomic hydrogen/carbon ratio decreases with increasing rank. The H/C ratio changes slowly at low ranks, but changes are more marked in the higher rank range. This is illustrated in the Seyler diagram Figure 4 and Figure 5 and van Krevelen diagram Figure 6.

<table>
<thead>
<tr>
<th>Coal Rank</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>Organic S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracite</td>
<td>100</td>
<td>50</td>
<td>2-5</td>
<td>1-2</td>
<td>1/2-1</td>
</tr>
<tr>
<td>Bituminous</td>
<td>100</td>
<td>70</td>
<td>4-8</td>
<td>1-2</td>
<td>1/2-1</td>
</tr>
<tr>
<td>Sub-bituminous</td>
<td>100</td>
<td>80</td>
<td>10-20</td>
<td>1-2</td>
<td>1/2-1</td>
</tr>
<tr>
<td>Lignite</td>
<td>100</td>
<td>80</td>
<td>20-25</td>
<td>1-2</td>
<td>1/2-1</td>
</tr>
</tbody>
</table>

Table 1. Atomic Ratios by Rank (after Meyers, 1982)

In van Krevelen's diagram, (Figure 6), the oxygen/carbon ratio decreases with increasing rank. As the rank of coal increases the oxygen content will drop as does the density of the coal. At about 87% carbon content the coals density begins to rise due to the hydrogen gas being given off. This is seen in Figure 6 in the flattening of the lignin vitrinite line of the diagram, whilst the wood to fusinite line drops relatively smoothly.
Fig. 6. The convergence of maceral properties during the geochemical stage of coalification based on atomic $\frac{H}{C}$ versus $\frac{O}{C}$ ratios. Modified after van Krevelen (1961). A = alginite; C = cellulose; E = exinite (except alginite); F = fusinite; L = lignin; V = vitrinite; W = wood.
The new International Classification of Hard Coals (1987) is cumbersome but may be adopted as the limitations of single parameters are stated more carefully than is the case for most other classification systems.

The proportions of nitrogen and sulphur atoms are always small and thus although often critical in determining coal use, these elements are not important in the basic structure of coal. The atoms are bonded together to form various organic ring structures, aliphatic chains, and functional groups. Unfortunately, the complexity of coal causes a great deal of "noise" in the results from the spectroscopic methods which provide non destructive coal analysis data eg., infrared and nuclear-magnetic-resonance (Dormans, et al., 1957; Tscharmler and de Kuijer, 1966), ultraviolet and fluorescence spectroscopy (Teichmueller and Wolf, 1977).

There are two important aromaticity values to be considered: the percentage of hydrogen atoms directly bonded to aromatic carbons and the (much more important) percentage of aromatic carbon atoms. The carbon aromaticity is one of the more important structural parameters of coal.

The primary criteria used to infer aromaticity have been the similarity of C-C bond lengths, infrared and electron-spin-resonance spectra, selective chemical behaviour of coals and model "aromatic" compounds. The most recent analytical method developed is cross-polarisation carbon-13 N.M.R., developed by Pines, et al. (1973). It has been applied to coal by a number of investigators, including Retcofsky and Vanderhart, (1976), Bartuska, et al. (1977), Miknis, et al. (1979), and Tarki, et al. (1979). While the conditions for the
combined use of cross-polarisation, strong proton decoupling, and magic angle spinning (CP-SD-MAS) to obtain quantitative information in clearly defined model compounds are well understood, there is some disagreement about whether those conditions are satisfied in the application of such combined procedures to coals. These conditions have been discussed by Vanderhart and Retcofsky, (1976).

In 1954, van Krevelen proposed a structural model for an average vitrinite macromolecule, which contains around the groups of condensed aromatic nuclei (6, 9 or 11 rings) side radicals and connecting bridges—the naphthene, heterocyclic and aliphatic groups (van Krevelen, 1981). Ultraviolet (UV)-visible spectrophotometry was used by Friedel, (1959). Friedel and Queser, (1959) and by de Ruiter and Tschamler, (1958) in coal aromaticity studies, and it triggered perhaps the first controversy over aromatic versus diamond-like structures in coal.

Hirsch, (1958), reported that coal was from 50 to 80% aromatic, with primarily 89% ordered structure. Ergun and Tiensuu, (1959), using X-ray scattering, concluded that coal is less aromatic and contains large quantities of amorphous regions.

According to Kroger, (1956), exinites contain more hydrogen and less oxygen and are less aromatic than vitrinites. Given, (1960), showed that spore-rich exinites have less hydroxyl groups than the associated vitrinites but probably more hydroaromatic groups.

The liptinite macerals contain the most strongly aliphatic organic components, whereas the inertinite macerals contain the lowest proportion of aliphatic
structures. This has been shown by infrared spectroscopy, X-ray diffraction, physical constitution analysis and broadline \(^1\)H nuclear magnetic resonance (N.M.R.) spectrometry (Dormans, et al., 1957; Cartz and Hirsch, 1960; van Krevelen, 1961; Tschemlner and de Ruiter, 1966). More recently, Retcofsky and Vanderhart, (1978), concluded from C\(^{13}\) cross-polarisation (C.P.) N.M.R. that the fusinite from a high volatile bituminous coal was more aromatic, and the liptinite in that coal less aromatic than the vitrinite. They also estimated that the number of rings per mean structural unit of vitrinite high volatile A bituminous rank was 3 - 4, whereas fusinite had the largest polynuclear aromatic ring system with five rings. The aromaticities of macerals increase with increasing rank (Dormans, et al., 1957; Retcofsky and Vanderhart, 1978).

In 1961, van Krevelen concluded that "the average structural unit in coals from the lignitic stage to the low volatile bituminous stage contains about 20 carbon atoms and about 4 - 5 aromatic rings. The aromaticity of the carbon in this range increases from 0.7 to 0.9. In the anthracite stage the size of the clusters, and hence the number of rings per cluster, increases rapidly; the aromaticity goes up at the same time from 0.9 to 1.0."

The second major controversy over the high aromaticity of coal occurred in 1974 (Chakrabartty and Kretschmer, 1974) and was based upon the analysis of products resulting from hypochlorite oxidation of coal. This led Chakrabartty and Berkowitz, (1976) to consider that bridge tricyclo-alkanes (eg. polyamantanes) attached to the individual benzene rings were the dominant motif of the coal structure.
Work carried out by Whitehurst, (1978), and by Bartuska, et al. (1977), does not bear out van Krevelen's statement that the aromaticity in the range of lignite to low-volatile bituminous increases from 70-90%. It would appear that whereas the higher value may be correct, the figure for low-rank coals is less than 70%.

The understanding of the aromatic ring structure in coals is still incomplete. Most of the recent studies have indicated that the condensed units in coal are fairly small, typically not more than four rings. These values can be obtained by reducing ring structures from elemental composition and aromaticity data or by degrading coal and identifying the products. These low figures contrast with the values suggested by van Krevelen and also by Hirsch, (1958), on the basis of X-ray scattering. These X-ray results have been re-evaluated by Scaroni and Essenhigh, (1978). They suggest that the number of condensed rings is constant at four or five up to about 90% carbon, after which it rapidly rises with rank.

Recently, a number of studies has focussed on the aliphatic components of coal. Batts, et al. (1986), report significant yields of saturated hydrocarbons from mild hydrogenation of vitrinite-rich brown coal and contrast this yield with the dominantly naphthenic hydrocarbons obtained from liptinite-rich coal. Crick, et al. (1988), using pyrolysis, have found significant yields of straight chain alkanes from suberinite, cutinite and desmocollinite but note that sporinite dominantly yields naphthenic compounds.

There is also a problem in understanding what is meant by the "molecular weight" of coal. One can consider the molecular weight (MW) of each macromolecule in coal or
the molecular weight of the fragments between cross-links in the coal structure (the constituent molecules). There is not a great deal in the published literature that is directly relevant to the molecular weight distribution in solid coal. This point is particularly important since most studies of the molecular weight of coal provide the average molecular weight or number of coal fragments rather than the relative distribution and frequency of those fragments within the coal. Most methods of determining molecular weights of coal depend on converting the largely insoluble coal into soluble substances under mild conditions to ensure that the coal molecules remain unchanged as far as possible. The main problem is to avoid the cracking reactions which take place over 350°C.

The concept of a unique structure or a simple repetitive structure cannot be justified given the extensive heterogeneity of coals. However, the fact that coals are heterogeneous as a group and, indeed, heterogeneous mixtures individually, does not mean that there cannot be a concept of a basic macromolecular structure to which coals will converge to a greater or lesser extent. This basic skeleton of the coal structure should be limited to the vitrinite in coal or to vitrinite-rich coals. As pointed out by Aczel, et al. (1975), there are currently three models which claim to represent the organic structure of coal. They are:

1. the aliphatic/polyamantane model, which resulted from the sodium hypochlorite oxidation studies of Chakrabartty and Kretschmer, (1972, 1974), and was proposed by Chakrabartty and Berkowitz, (1976)
2. the aromatic/hydroaromatic model of Given, (1960)
It would be unacceptable to point to any of the models presented and choose one as the representation of the molecular structure of coal. The idea of regular polyamantane structures can be discounted. The molecular sieve model of coal structure considers coal as consisting of relatively light, hydrogen-rich molecules trapped in a hydrogen-poor carbon matrix (Aczel et al., 1975). The basis for this model is the work reported on the low molecular weight compounds of coal. A corollary of the presence of large numbers of these low molecular weight "trapped" compounds is that since they are relatively hydrogen-rich and "light", the macromolecular skeleton must consequently be hydrogen-poor and of high molecular weight. This could imply that, in the matrix, the ratio of naphthenic to aromatic rings is higher or that there are bridged structures present. Marzec et al. (1979), have reported studies on the solvent extraction of high-volatile bituminous coal at ambient temperature with various solvents. It is unfortunate that the models tend to be seen as competing interpretations. The "classical" hydroaromatic view is largely the result of earlier studies on the relatively high-rank coals of Britain and Germany, and it should be no reflection on its success as a model to suggest that, at least in the low-rank coals, other structures such as bridged tricycloalkanes ought to be considered. Certainly the molecular sieve model has to be modified for different ranks of coal and the work by Marzec et al. (1979), can be interpreted in the light of a macromolecular network containing an amount of smaller volatile or extractable molecules. The macromolecular network is considered to be a linked, three-dimensional molecule as proposed by Larsen and Kovac (1978). This macromolecular network binds the trapped molecules by "donor-acceptor" bonds. The aromatic/hydroaromatic model of coal structure does
contain possible centres of this type, for condensed aromatic systems have electron-acceptor properties.

The study undertaken at C.R.L. whilst examining the deterioration of Giesler fluidity with time, had to take cognisance of the chemical and physical structure of the coal.

Chemistry as a science has largely responded to problems posed by single molecules of whatever size or complexity but having a semblance of regularity. The lack of regularity in coal means that the coal chemist is forced to extend the boundaries of chemical techniques and knowledge to examine coal. It is to be expected, therefore, that a subject which has not yet been incorporated into the body of an established discipline should be in a state of confusion, disarray, and promise. Nevertheless, there has been worthwhile research and valuable results, some of which are reported in this thesis.

Even if all the research work carried out was of a consistently high quality and the nature of the coals used was always fully documented, there would remain the virtually insurmountable problem of comparing the results of experiments performed on different coals. The complexity and heterogeneity of coals is the most persistent "problem", and partly because of this a truly coherent picture has yet to emerge.
CHAPTER THREE
OXIDATION OF COAL

Oxidation of coal has aroused the curiosity of many coal researchers. One of the principal goals of their research has been to explain the occurrence of autoignition and the deterioration of the technological properties of coal in stockpiles.

A second area of interest has been the destructive oxidation of coal as a method for gathering structural information. A third type of coal oxidation work has to do with conversion to coal acids or humic acids, intended for use as a fertilizer or soil conditioner.

In 1945, C. Geogiadis produced an important thesis which covered oxygen in coal and its effects on the coal properties. This was published in 1951.

Early investigators found that the process of oxidation occurs in several stages, the exact number being a matter of dispute. At least two stages of oxidation were observed by van Krevelen, (1961). D. Carpenter and Giddings, (1964), distinguished three stages in the initial phase of oxidation. Four stages including the combustion stage were proposed by Schmidt and Elder, (1940). The latter expressed the mechanism of the reactions as follows:

\[
\text{coal} + \text{oxygen} \rightarrow \text{coal surface} \rightarrow \text{coal-oxygen complex} \rightarrow 2. \text{CO}_2, \text{CO} \text{and H}_2\text{O} \\
\text{coated on} \rightarrow \text{coal surface} \rightarrow 3. \text{coal-oxygen complex} \rightarrow 4. \text{CO}_2, \text{CO} \text{and H}_2\text{O}
\]

They stated that at low temperatures, the first stage is extremely rapid compared to the succeeding stages.
Consequently, the rate of reaction is controlled by one or other of the later stages. It is clear that at least three stages result progressively in increased production of gases and changes in the nature of the solid residue.

Below 70°C (which has been found to be a distinctive transition temperature) rates of oxidation are generally low enough to be independent of coal rank; oxidation does not proceed much beyond forming acidic functional groups and peroxides; and for all practical purposes the reaction ends when the hydrogen content of the coal has fallen to 3%. Further oxidation proceeds so slowly that significant concentrations of humic acids develop only over long periods of time.

In the second range, 70-150°C, the above pattern is only modified by thermal instability of peroxides and by the fact that oxidation rates are now sufficiently high to be controlled by oxygen transport to the inner coal surfaces. Overall oxidation rates therefore become progressively more dependent on coal porosity and tend to fall with increasing rank or particle size. Peroxides form only transiently or not at all. Because of the greater instability of functional groups other than peroxides, there is also a reversal of the CO:CO₂ ratio in the off-gas, with CO₂ now more abundant than CO. In the third range above 150°C rapid generation of humic acids occurs. It is not until over 250°C that rapid (secondary) destruction of these humic acids is seen. Both reaction rates are dependent on oxygen partial pressures and temperature.

The kinetics of coal oxidation has been a subject of investigation by several workers and several kinetic equations have been proposed. The rate of reaction of oxygen with coal at low temperatures has been found to
depend, apart from coal properties, on several variables such as temperature, particle size (Speight, 1983), partial pressure of oxygen, humidity, total pressure and flow-rate of oxidising gas (Berkowitz, 1979). There has been, however, no consensus on the rate controlling step or a general kinetic expression of rate data. This difficulty is due, not only to the wide differences in the properties of coals used, but also to the different methods used for determining and interpreting the rate data.

It is now generally accepted that the oxygen of the air is first adsorbed on the coal (physical and chemical adsorption) (Walker, et al., 1968). Interaction between the coal substance and adsorbed oxygen produces an unstable coal-oxygen complex. As the temperature and/or time increases, the decomposition of the oxygenated complex occurs and carbon dioxide, carbon monoxide and water are released, their relative proportions depending on the conditions of the oxidation process. The oxidation of coal results in the introduction of oxygen into the coal mainly as phenolic hydroxy (OH), carbonyl (-C=O) and carboxyl (-COOH) groups and also seems to bring about some molecular degradation. If moisture is present or is generated from chemically combined hydrogen in the coal, some chemisorbed oxygen will also form peroxide or hydroperoxide complexes, which are capable of oxidizing ferrous thiocyanate (Jones and Townsend, 1946). These reactions can be used to estimate the concentrations of peroxides in the coal. However, given enough time, oxidation will gradually reach deeper and begin to degrade the coal substance itself, first converting it into alkali-soluble but otherwise still coal-like solids (humic acids) and then breaking those substances down into progressively smaller molecular species.
After causing a slight transient weight gain, (due to incorporation of additional oxygen without concurrent loss of volatile oxidation products), these processes gradually lower the carbon and hydrogen contents of the coal (toward limiting values of 50 to 65% carbon, 2 to 3% hydrogen) (Speight, 1983; Barkovitz, 1979), through abstraction of CO, CO₂ and H₂O and thereafter steadily convert the residual solids into water-soluble benzenoid acids and carbon oxides without further change in its elemental composition. Unless prematurely interrupted, this will continue until all available coal material has been effectively "consumed".

All coals other than anthracites and all coal components other than high reflectance inertinites are so sensitive to oxidation that even minute additions of oxygen, too small to be detected by conventional "wet" methods, will alter their properties. In extreme cases, exposure of freshly mined coal to air at ambient temperatures for as little as a few days will not only cause marked deterioration of caking properties (Neavel, 1982), but also adversely affect its solubility, tar yield (Wachowska and Pawlak, 1977), heating value, and other properties. Although details of the chemical changes responsible for such deterioration are, for the most part, still uncertain, there is agreement that they are ultimately connected with progressive oxidative destruction of non-aromatic configurations in the coal "molecule".

Different ambient conditions leave the course of events of oxidation qualitatively unchanged. Higher temperatures and/or oxygen partial pressures will usually accelerate the process. However, due to the thermal instability of some of the primary oxidation products at greater than 70°C, there are important quantitative differences between
Effects of Oxidation on Coking Properties of Coal

The coking properties which are affected due to oxidation are:
1. reduction of free swelling index;
2. a reduction of maximum dilatation in the dilatometer;
3. a decrease in Gieseler maximum fluidity and
4. softening, maximum fluidity and solidification temperatures tend to be lower and the fluid range becomes narrower.

Control of bulk densities in coke ovens when using oxidised coal becomes poor; oxidised coal does not fuse well and the coke produced from it is more granular than that from fresh coal. Coke rates in the blast furnace increase because of higher reactivity of the coke made from oxidised coal, coke stability (strength) is reduced. The danger of pressure exerted on coke ovens during carbonisation is increased and in most cases coke breeze generation increases (Gibson, 1979). These factors contribute to increased costs in both coke oven and blast furnace plants.

The majority of coals show serious impairment of coking properties before they are oxidised enough to decrease the heating value by one per cent and before their ultimate and proximate analyses show changes that are greater than the experimental error of analysis (Moxon and Nicol, 1987).

While the mechanism of the deterioration in coking properties due to oxidation and the precise role of oxygen in causing this deterioration are not well understood, previous work by Berkowitz, et al. (1974);
Painter, Snyder, Pearson and Kwong, (1980), suggests that ether-type oxygen cross-linkages formed in the course of oxidation are indirectly responsible for the deterioration of coking properties. This may occur due to condensation reactions involving the hydroxyl groups during the subsequent pyrolysis of the oxidized coal.

This theory attributed the formation of a plastic fluid during carbonisation to the rupture of oxygen cross-linkages in the coal (Goodarzi and Murchison, 1972; Neavel, 1982). The plastic fluid is stabilised by the transfer of hydrogen to the free radical sites. Since oxidation reduces the availability of mobile hydrogen (through the loss of aliphatic C-H groups) and produces oxygenated functional groups (which increases the potential for oxygen crosslinking during thermal reactions), the resulting plastic mass is destabilised leading to an apparent loss of fluidity. Internal friction measurements by Wert and Weller, (1985) appear to substantiate this surface crosslinking mechanism.

The factors causing deterioration of coking properties and other technological properties of coal and self-heating are known qualitatively, but the mechanism of the low temperature oxidation process leading to this behaviour is poorly understood. Much basic scientific research is needed on the pore structure characterization of different coals and the fundamental understanding of the mechanism of low temperature oxidation and the precise role of oxygen in the deterioration of the coking properties. The potential economic benefits of this work are considerable.
CHAPTER FOUR
CARBONISATION

Carbonisation is the process of decomposing coal by heating in a mainly reducing atmosphere to form:-
a) a carbon-rich solid, "coke" if vesicular and fused, "char" if not fused with no semi-graphitic structure developed, or a partly graphitised carbon, this last being a product from the carbonisation of anthracitic coals;
b) liquid products, made up of a mixture of hydrocarbons termed "tar" and aqueous solutions containing a variety of dissolved materials termed "ammoniacal liquor"; and
c) hydrocarbons and other components that remain in the form of gas on cooling to normal temperatures.

Coal carbonisation processes are customarily regarded as low-temperature (LT) operations if the final temperature is less than 700°C or as high-temperature (HT) ones if the final temperature is above 900°C (Speight, 1983). Although arbitrary, this distinction reflects the pronounced physical changes that the solid products of carbonisation undergo at temperatures between 600 and 800°C.

Low-Temperature Carbonisation
LT carbonisation was mainly designed to provide "town gas" for residential use and street lighting and/or to manufacture substantially devolatilized "smokeless" solid fuels that were sufficiently reactive to be burned on domestic grates. Great economic importance attached, however, to the by-product tars which were essential feedstocks for the chemical industry and were refined to motor spirit, heating oils and lubricants (Berkowitz, 1973).
The preferred coals for LT carbonisation were, as a rule, lignites or sub-bituminous and most especially high-volatile bituminous coals, which, when pyrolyzed at temperatures between 600 and 700°C., yield porous semicoke with reactivities which are typically not very much lower than those of their parent coals. Higher-rank (caking) coals, unless pretreated to destroy their caking properties, were less suitable because they formed residues that tended to stick to the walls of the carbonization chamber and thereby impeded fast discharge of the char. Numerous LT processes were also developed for the carbonisation of briquettes, which were in some cases manufactured from blends containing caking coals (Gibson, 1979; Speight, 1983; Schinzel, 1981).

Commercial LT carbonisation evolved and flourished principally in industrialized European countries (whose energy economies were founded on coal) and was even there gradually abandoned after 1945 as cheap oil and natural gas became widely available and demands for solid fuels dwindled. Subsequent rapid escalation of oil and gas prices, environmental constraints on combustion of "raw" coal (especially in urban areas), and a growing interest in the recovery of gaseous and liquid hydrocarbons from coal before burning it are, however, beginning to redirect attention to LT processes (Shires, 1981; Schneiderman, 1982).

High-Temperature Carbonisation
If carbonized at temperatures above ~650-700°C, LT chars and cokes become progressively less reactive through devolatilization and loss of porosity and, as a result, tend to lose the properties that make them attractive domestic and industrial boiler fuels. Several kinetic studies on carbonisation have been made (van Krevelen,
1950; Fitzgerald and van Krevelen, 1959; Berkowitz and Muiin, 1966). In practice, HT carbonisation is therefore largely restricted to production of metallurgical coke which is used in the blast furnace for the reduction of iron ores and in the cupola furnace for the melting of pig iron. However, small amounts of high temperature chars are used in some metallurgical plants for the reduction of iron ores. The coke is required to be of constant quality to be high in carbon and low in ash content to assist in the chemical reactions within the blast furnace. Many authors (Stach et al., 1962; Diessel, 1985; Warbrooke and McLellan, 1987; Shapiro, Gray and Eusner, 1961) consider a vitrinite content of approximately 50% gives maximum stability to the coke made from a medium volatile bituminous coal. However, there are some cases where 50% vitrinite is sufficient to produce a hard and strong coke (Cook and Edwards, 1971). The coke must also be relatively strong to help support the burden and maintain burden porosity, thus ensuring high wind volumes and high reaction rates. The importance of these properties increases with blast furnace size. Reactivity properties are also of considerable importance and are related to the rank of the coals used to produce the coke but are also influenced by coal type and by the abundance of inorganic components. Factors such as ash yield, sulphur content and coke yield are very important in relation to the value of a coal as a component in an oven blend but they are not the greatest overall factors affecting the demand for reserves of coking coal. The main limitation on the range of coal reserves which can be considered as suitable for coking is that imposed by the mechanical specifications on the coke. A particular coal, or coal blend will, because of considerations of coal type and coal rank, make coke which has physical properties which can only be changed by carbonisation conditions in normal coking practice within relatively
narrow limits (van Krevelen, 1981; Gibson, 1979). Major extensions of the availability of suitable coke come from appropriate blending schemes.

The Plastic Properties of Coal
Coking coals, by definition, are coals that when heated to sufficiently high temperatures pass through a plastic stage in which they successively soften, swell, and resolidify into a coherent cellular coke. The temperature interval over which these changes occur coincides roughly with the interval of primary devolatilisation (van Krevelen, 1981). Methods of measuring the plastic range of coals form one of the methods used to determine coking potential.

Prime coking coals have volatile contents in the range 20-32% (d.m.m.f.) (Gibson, 1979), and are restricted in both type and rank. Coals with a volatile matter yield between 20 and 32% (d.a.f.) (equivalent to approximately 1.2 to 1.5 maximum vitrinite reflectance), produce a high stability coke if they contain sufficient vitrinite. With lower rank coals, the cokes are increasingly frothy and weak, whereas cokes made from higher rank coals lack physical stability and reactivity and are relatively unreactive chemically (Cook and Edwards, 1971).

The temperature interval between onset and termination of plasticity is normally of the order of 50°C to 75°C, (dependent primarily on rank) and occurs between 250°C and 500°C (Zimmerman, 1979). The recognition by Wiser in 1968 of the relationship between coal pyrolysis and coal liquefaction built upon the suggestion of Brown and Waters, (1966), that low molecular weight, hydrogen-rich compounds (the bitumens) serve as the initiators of plastic behaviour. These materials, which may begin to melt at temperatures below 200°C, solvate (or
alternatively lubricate as suggested by Berkowitz, et al. (1974), the coal micelles as they become thermally loosened.

Coal is far from being a homogeneous substance (Davidson, 1982; van Krevelen, 1981; Ward, 1984). Examination of thin sections or polished blocks under the microscope reveals that it is a complex mixture of plant debris which has undergone transformation into coal in the course of geological time.

The major part of the coals used for carbonisation is made up of "reactive" material, i.e. material which, on heating in the coke oven, reacts to the increase in temperature with a distinctive sequence of events as the temperature rises. The reactive components are liptinite (a minor constituent of most coals) and vitrinite. Except for a few coals, only the vitrinite in coals of bituminous rank develops plastic properties. At a submicroscopic level, vitrinite is composed of packets (micelles) of more or less aligned molecular units (lamellae) of variable structures typified by condensed ring systems connected by bridging atoms. Attached to the rings are various functional groups (=O, -COOH, -OH, -C\(_n\)H\(_{2n}\)). Some of the ring carbons may be saturated with hydrogen (hydroaromatic structures). The model attributed to F.H. Given, (1960), (Figure 3b), is the generally most accepted representation of a "typical" micellar unit, although it is important to recognise that among vitrinites from coals of different ranks (and even within a given vitrinite) there are significant variations on this theme. Lamellar size, degree of condensation, aromaticity, heteroatom content and functional group characteristics all vary. The "reactive" components of the coal undergo the softening stage in the 400-500°C range, and act as the binder for the "inert" material.
The "inert" material does not soften, nor does it undergo subsequent contraction to the same extent as the "reactive" components; it does, however, lose volatile matter and suffer internal structural chemical change (Gibson, 1979; Neavel, 1982). The role of the "inert" material in the coking process is to reduce the overall swelling and contraction. If good quality coke is to be produced, a balance in terms of content and size grading between the "reactive" and "inert" composition of the charge to the oven must be achieved.

In Gondwana Permian coals the inertinite group of macerals generally shows some plasticity on heating (Diessel, 1985). Vitrinites and liptinites seldom show plastic behaviour if their carbon content is below 80.5% or above 91% (van Krevelen, 1981). Liptinites that show plastic behaviour show high fluidities, while vitrinites of similar rank become less fluid. In general, plastic properties are evident in coals when the content of volatile matter exceeds 12-15%, become more pronounced as the volatile matter increases to 30-35%, become less pronounced at higher content yields of volatile matter and are not present in most coals of less than 80.5% carbon (Diessel, 1985; Gibson, 1979), (an exception to the lower boundary occurs with some coals having a very high content of organic sulphur) (Titheridge, 1988). In the same general way, the plastic properties are correlated (inversely) with coal porosity. The most plastic coals (88-89% carbon in vitrinite) are also the least porous. Exceptions are found to these generalizations, as to virtually all others concerning coal. Loison, et al. (1963), suggests that neither volatile matter nor porosity provides a better correlation with plastic properties than does coal rank. As stated previously, the ASTM 1979 classification of
coal is based on the fixed carbon (i.e., volatile matter) content and specific energy.

Evidence seems to show that when samples of coal, including samples of strongly caking coal, are brought slowly to increasing temperatures as high as 500-600°C and cooled rapidly, their surface areas and microporosity change only slightly (Grimes, 1982). This suggests that some characteristics of the fine structure of coal are little modified by fusion (Brown et al., 1958). However, heating to the 500-600°C range causes a marked change in optical properties, and therefore, by inference in the degree of aromaticity. This fact, as well as the effect of system pressure on coal plasticity, contradicts the suggestion by Audibert, (1926), that the softening of the coal is similar to a physical melting process.

As coalification progresses there is also a related increase in aromaticity but the development of aromaticity due to coalification differs in many respects from that due to carbonisation.

In a sub-bituminous or high volatile bituminous coal, the aromatic ring systems (micelles) are small and widely separated by aliphatic and other non-aromatic compounds. The porosity of the coal is high, many pores are large and interconnected which results in relatively unimpeded degassing during carbonisation (Diessel, 1985; Berkowitz, 1979). In contrast, the structure of a medium to low volatile bituminous coal displays a considerably tighter stacking of the aromatic clusters. The internal pore space has been reduced and the pores are small and commonly isolated. On heating, the gas produced from the cracking of the intermicellar and perimicellar aliphatic and other volatile compounds exerts an increasing pressure on the pore walls causing them to yield. As the
weak bonds break down and the bitumen fraction melts the coal becomes converted to a quasi-liquid. According to this mechanism plasticity in coal would seem to require the presence of at least a minimum quantity of low molecular weight bitumen. It has long been known that removal (by extraction with chloroform or benzene) of these bitumens removes the plastic properties of coal. However, they are not sufficient to explain the process. Berkowitz, et al. (1974), has drawn attention to the fact that during isothermal pyrolysis the chloroform solubles disappear before maximum fluidity is reached. However, other features are also necessary. The requirements include the presence of lamellae-bridging structures capable of thermal rupture, a supply (both in the bitumen and the balance of the coal) of hydroaromatic hydrogen, and an intrinsic potential for micellar and lamellae mobility not associated with the chemical bond rupture (Heavel, 1976).

During the plastic stage the coal is in a fluidised condition which is supported by the evolving gases, vapours and tars. High mobility associated with this fluid or plastic phase leads to widespread molecular-ordering and mesophase formation similar to the growth of liquid crystals (Taylor, 1961; Patrick and Shaw, 1972).

A polished section through a coke made from a medium-rank coal, when examined between crossed polarizers, presents an appearance which is described as a mosaic texture, with each unit area having an extinction direction different from those of its neighbours.

The texture of the mosaic depends on the rank of the coal (Abramski and Mackowsky, 1952). A prime coking coal gives a mosaic size usually of the order of 1 micron, and with decreasing rank, caking coals have progressively smaller
sized mosaics. Coke made from low-rank coal appears isotropic, but it is not known whether it is truly isotropic or has a mosaic size too small to be resolvable by an optical microscope. In a coke made from a high-rank coal the mosaic effect is replaced by lamellar texture and in anthracite cookes/chars there is overall anisotropy but most of the original textures of the coal are preserved (Goodarzi and Murchison, 1988).

In a random mosaic, strong and weak regions will alternate along any line and the material will be equally strong in all directions. Sometimes, however, the mosaic texture develops a preferential orientation (while remaining essentially a mosaic) and then the coke will be weak in one direction. Examples of preferential orientation frequently occur adjacent to boundaries with pores and in these cases the coke is better able to withstand tensile forces parallel to the boundary than perpendicular to it.

Since the gases supporting the plastic stage seek to leave the coal, gas bubbles (coke cells or pores) are formed and the mass becomes essentially rigid when the remaining gas can no longer sustain a sufficiently high internal pressure to distort the pore walls. The result is a well caked semi-coke which will continue to de-gas as a solid on further heating to high temperatures.

According to Marsh and Cornford, (1975), the degree of plasticity of the mesophase is related to the aromaticity of the parent substance because aromatic molecules form planar, hexagonal ring systems which slip easily and can be stacked to produce pre-graphitic crystallites. The mobility, aided by molecular shape is enhanced by the relatively low chemical reactivity of aromatic compounds.
This spreads the temperature range over which mesophase retains its plasticity.

As the temperature is raised after the plastic mass resolidifies, the solid contracts but at a rate which is non-uniform and dependent upon the rate of devolatilization and reorientation processes in the solid, varying from coal to coal. If the rates of contraction measured in a high temperature dilatometer are plotted against temperature (Gibson, 1975), two peaks are observed; the first occurs just after resolidification (~500°C) and the second in the region of 750°C (Figure 7). Because the coefficient of contraction is a large number it is necessary to multiply it by 10^-4 for the purpose of the graph (Figure 7).

In a coke oven, the heat is supplied from the oven walls and the plastic layer travels through the coal charge from each wall leaving behind it an apparently solid but initially visco-elastic semi-coke undergoing further solidification and contraction. While the moving plastic layer is generating swelling pressures and forming the porous semi-coke structure, the already solidified semi-coke nearer the oven wall is undergoing further decomposition and contracting unevenly to form the denser, strong, higher temperature coke characteristic of the completion of high temperature carbonisation (usually in the range of 900-1050°C). Thus sequential compressive and tensile forces are produced in the semi-coke. Differential strains are set up and result in the formation of fissures which break up the coked mass. A primary fissure network is associated with the rapid contraction at about 500°C and it has been shown, (Gibson, 1975), that the size of coke discharged from the oven is related to the height of the first peak in the contraction curve. A secondary fissure network is
Fig. 7. Contraction of coal in high temperature dilatometer (after Gibson) (Coal Rank Codes are from the N.C.B. classification)
apparent if the coke pieces are sectioned. On impact these secondary fissures extend to break up the coke into smaller pieces. The impact strength of coke is seen to be related, therefore, to the height of the second peak in the contraction curve (Gibson, 1979). The swelling measured in the dilatometer is a maximum for a volatile matter yield of about 25 to 28%. For coals with 15 to 18% volatile matter, as for those with 35 to 40%, the dilatometer tests show contraction without swelling. The fluidity measured with the Gieseler plastometer reaches a maximum at a volatile matter yield of about 28 to 32%, as does the Gray-King index. The swelling index determined by the crucible Swelling Test shows a very flattened maximum because the majority of vitrinite-rich coals with a volatile matter yield of between 21 and 32% have an index near the maximum value. Some New Zealand workers recognise 9+, 9++, and 9+++ in order to give more discrimination (Suggate, 1959; Toyubee, 1974).

In evaluating the coking properties of a coal, it is important that the condition or treatment of a sample be completely known. A fresh, unexposed sample of coal may possess suitable coking properties, but if tested after oxidation through exposure to the atmosphere for various lengths of time, may give inferior results.

Another factor that must be taken into consideration in testing a sample of coal for its coking properties is the amount of extraneous impurities (such as shale partings or other non-coal material) it may contain. The presence of such extraneous materials may be sufficient to lower or destroy the natural coking characteristics of the coal.

The sequence of phenomena (softening, swelling and resolidification), which is obviously interrelated with
decomposition and devolatilisation, can be considerably affected by changes in ambient conditions.

a) Increasing heating rates increase the maximum Gieseler fluidity and extent of swelling, and simultaneously raise the temperatures at which maximum fluidity and the onset of swelling are observed (Meavel, 1976).

b) Preheating the coal in a protective (inert) atmosphere at temperatures as low as 200°C for extended periods of time progressively diminishes fluidity, swelling and related caking indices (Dulhunty and Harrison, 1953).

c) A similar, if less marked, diminution of all aspects of plasticity is observed when the coal is increasingly finely comminuted. Even a strongly caking coal (with FSI 6-7) will yield only a barely coherent coke button if sufficiently finely ground and heated very slowly (Dulhunty and Harrison, 1953; Wenger and Neubaum, 1969).

d) Plastic properties of weakly and moderately caking coals with high ash contents (e.g., coals with FSI 3-5 and >10% ash) can be substantially enhanced by reducing the mineral matter contents of the coals (Meavel, 1976; Moxon, et al., 1986).

e) Oxidation quickly and progressively narrows the plastic range, reduces the maximum fluidity, and eventually completely destroys any caking propensities. Slight oxidation will, in some cases, increase the FSI of a coal. This is attributed to reduction of fluidity and to the consequent increased tendency of the coke button to expand without, at the same time, tending to collapse upon itself (Berkowitz, 1979).

f) Mild hydrogenation, which does not significantly alter the molecular structure of coal, broadens its plastic range and increases fluidity and swelling (Kawa, et al., 1955).

g) Plasticity can be suppressed, or partially suppressed,
by pyrolyzing the coal under a vacuum and enhanced by heating it under high pressure (Loison, et al., 1963).

This dependence of coal plasticity on ambient conditions has been utilized in industrial operations to destroy caking properties where they would be deleterious, or to improve them where, as in coke making, they are critical for commercial success. But it has also created difficulties in formulating a comprehensive, self-consistent theory of the causes of plasticity. Although earlier views which envisaged homogeneous melting and concurrent decomposition of the melt, (Audibert, 1926), have now been discarded in favour of hypotheses that regard softening and swelling as consequences of thermal decomposition (Berkowitz, 1979), there is still some disagreement about mechanisms (which must account for softening and swelling in individual small particles as well as in closely packed assemblages of such particles).

The dependence of plastic properties on both rank (characterised by carbon content) and petrographic composition has been investigated with Australian coals (Cook and Wilson, 1969). Measurements of the fluidity in the Gieseler plastometer, the dilation, the swelling indices, and the Gray-King coke type were statistically evaluated (Brown, et al., 1964).

More than 60 coals with ranks between 81 and 89% carbon (maf) were tested by Brown et al. (1964). Thermal decomposition was also studied by means of thermogravimetric methods. The results show that some properties of these coking coals depend mainly on the rank and others on the vitrinite content, still others depend in different measure on both these factors. Rank strongly influences the temperature of maximum fluidity and resolidification. These properties are directly
related to the thermal decomposition process, and are therefore determined more by the chemical structure of coal as a whole than by the petrographic composition. The only properties of the coking coals investigated that depend almost entirely on the petrographic composition, not on the rank, were those related to physical softening. These are the temperatures of the beginning motion in the Gieseler plastometer (at 0.1 dial divisions/min) or in the dilatometer.

The MOF diagram (Figure 3) illustrates how the Gieseler fluidity of reactive coals increases very rapidly with rank and passes through a peak. Coals with a low inerts content (<25%) lie close to the curve, whereas those of higher inerts content lie below this curve. It should be noted that most coals represented lie off the curve rather than on it. The shaded area indicates the range of properties preferred in Japan for coking blends. This fluidity range can be attained by balancing high fluidity components with coals of higher rank. Other tests of caking properties show a similar variation with coal rank.

It can be seen from the description above that the mechanism by which certain coals, soften, swell and then resolidify is still not fully understood, and is open to discussion and further research.
FIG. 8 The MOF Diagram: Gieseler Maximum Fluidity versus Coal Rank by Reflectance (after Miyazu, et al., 1971)

LEGEND:
V.M. denotes% Volatile Matter dry, ash free basis.
L.V. denotes Low Volatile
M.V. denotes Medium Volatile
H.V. denotes High Volatile
Inerts are % by Volume
CHAPTER FIVE
MEASUREMENT OF PLASTICITY BY PLASTOMETERS

The 1956 International Classification System for medium and high rank Bituminous Coal uses testing methods that, in some form, measure the softening properties of the coal. Thus the caking ability is characterised by the swelling index or by the agglutinating coefficient according to the Roga method and the coking ability by the dilatometer or by the Gray-King test.

This system was replaced in 1987 by a classification based on mean random reflectance, maceral content, swelling index, volatile matter, ash content, total sulphur and gross calorific value (International Classification System, 1987).

Many other test methods have been developed, some of which are still in use. Of significance among these methods are those for the determination of plastic behaviour: the Gieseler plastometer, the Brabender plastograph, the Sapozhnikov plastometer and the Penetration plastometer.

Plastometers are used to study the resistance offered to the rotation or penetration of a movable unit into a mass of coal subjected to a particular rate of heating. Rotation plastometers can be placed in two categories: Constant-torque plastometers in which the movable unit is subjected to a constant couple and the rate of rotation is measured; and the variable-torque plastometers in which the movable unit is rotated at constant speed and the torque opposing its rotation is measured.
The Constant-torque Piastometer is represented by the Gieseler plastometer developed by Gieseler in 1934. Descriptions of a variety of this unit were published by the ASTM in 1954. The original testing equipment was manually operated (Figure 9) and some laboratories still use this type of operation. Greater accuracy is obtained and fewer man hours are required with the constant-torque automatic apparatus.

The automatic Geiseier plastometer (Figure 10) consists of the following main components:
- Molten metal bath and heater
- Plastometer head
- Sample retort
- Automatic counting system
- Automatic temperature programmer

The automatic Geiseier has an electric motor of constant rpm with a shaft having a brake, which controls the torque. The drum is directly connected to the shaft and the stirrer, and now it has 100 divisions instead of the previously used 360° dial. Each full rotation is counted photoelectrically.

The sequence of events for the operation of the automatic Geiseier plastometer are set out below.

The temperature of the bath is adjusted to approximately 300°C. The freshly prepared sample is packed according to one of the methods described in Australian Standard 2137-1981. The sample retort is then assembled, the packing is checked by switching on the fixed speed motor and noting whether the dial of the plastometer head rotates or not. The fixed speed motor is switched off and the sample retort is lowered into the molten metal bath to a depth of 76mm. The fixed speed motor is again switched on along
Fig 9.

Gieseler plastometer. (after Loisson et.al., 1963)
FIGURE 10. Automatic Gieseler Plastometer (after Burke 1973)

1. Fixed Speed Motor
2. Adjustment Screws
3. Permanent Magnets
4. Dial (ferro-magnetic material)
5. Light source and detector unit
6. Retort barrel, upper section
7. Metal bath
8. Molten metal
9. Retort crucible
10. Electric furnace
11. Base
with the automatic counting system and the molten metal bath stirrer. When the temperature of the bath returns to its original temperature (approx. 300°C) the temperature programmer is switched on.

At this stage the operator can leave the instrument while it continues with the test on a completely automatic basis. The automatic counting system does not start operating until the plastometer head dial has moved a distance of one dial division. At the completion of the test, a pre-set buzzer signals the operator that the test is completed.

The manual Geiseler plastometer consists of the following main components:
- a) Molten metal bath and heater
- b) Plastometer head
- c) Sample retort

As with the automatic Geiseler plastometer, the bath is maintained at an initial temperature of approximately 300°C. The assembled sample retort is screwed on to the plastometer head and then inserted into the metal bath. The cord, with the 40 g mass attached, is placed over the dial pulley and the brake on the drum pulley is taken off. The temperature of the metal bath should regain the original temperature of approximately 300°C in ten minutes. The temperature at which there is the first continual movement of the pointer is noted. Thereafter, the temperature and position (in dial divisions) of the pointer is noted and recorded every minute until the pointer ceases to move, indicating the completion of the test.

As the rate of movement of the pointer increases, the brake can be applied to the drum pulley, the cord rewound
and then the brake released and the time taken for a given number of dial divisions to be completed is noted. The number of dial divisions per minute is then calculated.

The rate of temperature rise during the test is also 30° per minute.

A variable-torque plastometer was first described by J. Davis in 1931. In the Davis plastometer, 16g of (-650 micron) coal are placed in a horizontal cylindrical retort which is rotated at a uniform speed of 2 rpm by means of a synchronous motor. A shaft with rabble arms, fixed to the framework of the apparatus by means of a spring, is located inside the retort. The coal is set in motion by the retort and, itself, tends to move the shaft; the deformation of the spring, which is very slight, enables the torque acting on the shaft to be assessed. The retort is placed inside an electric furnace with a constant rate of heating. Until the coal softens, the resistance remains low and then increases rapidly as the particles adhere together. As the plasticity of the coal increases, the torque decreases and passes through a minimum which is sometimes not much greater than the corresponding torque in cold coal. The reduction in the plasticity preceding solidification is accompanied by a very considerable increase in the torque; the semi-coke formed then breaks up, and the torque falls rapidly, the second maximum of the curve corresponding to the resolidification point. The maximum value of the torque attained at the moment of resolidification also gives an idea of the mechanical resistance of the semi-coke. The Davis plastometer allows the softening point, and the resolidification point to be determined with a high degree of accuracy. The difference between these two
temperatures, (the plasticity range), is greater than that determined with the Gieseler plastometer because the torques produced by the Davis plastometer are much higher.

Two other types of variable-torque plastometer differing in design from the Davis plastometer have been developed; these are the Brabender plastograph, modified by Echterhoff, (Echterhoff, 1954), and the Cerchar plastometer, (Boyer and Lahouste, 1954).

The Brabender plastograph, (Echterhoff, 1954), is used in Germany and in Italy and has found wide application in industry to determine the viscosity and grinding hardness of coal. It has not been accepted for testing coal samples in other countries, although in comparison to the Gieseler plastometer it has several advantages: the test procedure is simpler, the result of the experiment is independent of the investigator, and the results have excellent reproducibility. Also, the curves obtained supply more information about the softening behaviour of the coal than those of the Gieseler plastometer.

Echterhoff modified the Brabender plastograph to adapt it for the study of coals. In contrast to the Davis plastometer, the retort is fixed and the shaft with the rabble arms moves. The latter is moved at constant speed by a motor mounted on pivots. A mechanical device allows the torque, which acts on the shaft with rabble arms to be measured and recorded. The rabble arms fixed on the movable shaft and on the walls of the retort are arranged in such a way that the whole mass of coal is stirred and set in motion. Because the retort is large, holding 10 g of coal, the coal need not be ground to less than 1 mm. The curve recorded has a shape similar to that given by the Davis plastometer.
The following disadvantages of the Gieseler plastometer and the Brabender plastograph should be mentioned:

a) The stirrer arms in these units produce a complex system of shear stresses.

b) An expansion of the softened coal may occur in a part of the stirred steel retort, which is not disturbed by the rabble arms.

c) The rabble arms produce grooves in the coal mass through which the blades of the stirrer may move with far less resistance, giving an inaccurate record of the actual viscosity of the coal in the steel retort.

d) Due to the escaping gases, a foam structure may develop in the steel retort.

The mobility of the stirrer in the Gieseler depends not only on the true plasticity of the coal but also on the character of the foam structure within the steel retort. Because of the foam structure phenomenon, viscosities measured are often much lower than those actually present in the coal/semi coke in the range of maximum fluidity.

For these reasons a fully automatic viscosimeter was constructed (Stevens, 1963), in which the shearing velocity gradient is almost constant. It represents a concentric cylinder viscosimeter without end effects, in which the coal under test is contained in a 4 mm annulus between an outer rotating cylinder and a solid copper inner cylinder with milled surface. The surfaces of the two cylinders are kept at approximately the same temperature, so that volatile products do not condense on them. The outer cylinder rotates at 2 revs/hour. The torque necessary to secure this speed of rotation is measured. This unit has not found wide application, although it was used successfully with Australian coals (Stevens, 1963).
The Cerchar plastometer, (Boyer and Lanouste, 1954), was specially devised to determine the resolidification point to within $\pm 2^\circ C$. As with the Brabender apparatus, the retort is fixed and the movable shaft is rotated by a motor mounted on pivots. This manner of installation permits the torque exerted on the shaft to be measured after mechanical or optical amplification. The retort and the shaft with rabble arms are similar to those of the Gieseler plastometer, the shaft having been reinforced to support higher torques. In addition, the retort has a square section in order to prevent the whole mass of coked-coal being carried around bodily as the plastic mass nears the resolidification point. This apparatus differs from the two preceding types by having a much slower rotation, of the order of 1 rev/hour. It is only set in motion when the coal is already in the plastic state, the total displacement of the shaft is, therefore, very low, being in the order of 1/4 to 1/2 of one revolution.

In addition to the fluidity measurements, the temperature ranges of plasticity and the temperatures marking the onset and the end of fluidity during this period are equally important as these have to be taken into account to ensure the effectiveness of blending with other coals. Obviously, the longer the period of plasticity is, the wider the potential for blending with other coals will be.

In Eastern Europe, the Sapozhnikov plastometer, (Donkov, et al., 1971), which is used permits automatic recording of the conventional indices of this plastometer, that is the thickness of the plastic layer, and the shrinkage, of the coal sample. In addition, it automatically measures the force needed for penetration of a needle into the
plastic coal layer, which is proportional to the relative viscosity of the plastic mass.

A penetration plastometer was developed at the B.H.P. Central Research Laboratory (Calcott and Innes, 1962). They developed a method of determining fusion and resolidification temperatures, by lowering a probe onto the top of the plastic layer, the electro-motive-force of the probes thermocouple was then read 45 seconds later from a potentiometer. The probe was then gently pressed through the plastic layer until the firm resistance of the semi-coke was met. At this point the electro-motive-force of the thermocouple was again measured. After the bottom of the layer had been probed, the probe was withdrawn above the coal for approximately seven minutes before the operations were repeated. Probing continued until the top of the plastic layer ceased to rise and the bottom temperature had been measured a sufficient number of times. This gave values from which a series of graphs were plotted and from these the average values of temperatures at the top and bottom of the layer were obtained.

The penetration plastometer is particularly suitable for study of the relationship between the effects of common coking factors on plastometric properties and the effects of these factors on coke quality. Factors such as the size consist of charges, or charge density, or heating rates can be used; the levels for these factors being the same as are attainable in plant scale coking.

The relationship between carbonisation parameters measured with the Gieseler plastometer, the Audibert-Arnu dilatometer and the penetration plastometer are of interest. The former instruments use much finer coal than does the penetration plastometer and all three tests
detect plastic characteristics in differing ways. Various
measurements of the plastic stage characteristics (e.g.,
the resolidification point) largely depend on the levels
of arbitrary and instrumental factors. The effects on
such parameters (e.g. resolidification temperatures) of
changes in the levels of the arbitrary factors are not
the same for all the plastometric tests. The dependence
of the parameters on the levels of the test factors
varies from coal to coal.

In practice, these features show up the lack of precise
relations between the values recorded with the different
instruments.

It is thus suggested that the empirical parameters of
carbonising tests lack the precise physical meaning that
would enable their direct substitution for the
corresponding values from another type of test in a plant
coke oven.

These methods of investigating the plastic behaviour of
coals were developed not so much to obtain information
about the properties of the plastic mass itself, but
rather to be able to predict the properties of the coke
that will be produced. Since the softening of coal is an
important prerequisite to the formation of metallurgical
coke, it seems necessary to assume at first that the
properties of the coke are closely correlated with the
properties of the plastic mass. It has been shown,
however, that such a close correlation does not exist and
that the coke properties depend on a number of parameters
connected with the raw material and the process which do
not all correlate with the plastic properties. Therefore,
a variety of methods was developed to determine the
properties of the solid product (Cook and Edwards, 1971;
Mackowsky and Wolff, 1966; Gibson, 1970; Brown et al.,
1964). This permits more or less accurate conclusions concerning the properties of the coke produced in a commercial plant.

It is not possible to obtain quantitatively valid correlations between the results from different plastometric methods for different coals and different test results to the extent that one method can be replaced by another. However, qualitative correlations are recognizable. For example, the maximum fluidity measured in the Brabender plastograph, (Echterhoff, 1954), is inversely proportional to the maximum fluidity according to Gieseler, (1934), which in turn increases with the thickness of the plastic layer \( y \). (Sapozhnikov and Bakun, 1932). Nevertheless, the maximum thickness of the plastic layer determined in the Sapozhnikov plastometer, (Donkov, et al., 1971), is not by itself sufficient to describe the coking properties of coals. A close relationship exists between the thickness of the plastic layer measured in the Sapozhnikov plastometer and in the large laboratory-scale oven (Donkov, et al., 1971). Therefore, measurements in the larger unit are not necessary. Similarly, the plastic range measured in the Brabender or Gieseler plastometer increases but shows a relatively large scatter with the thickness of the plastic layer.

The plastic range becomes larger as the coal becomes more fluid during heating. With an increasing coal rank the fluidity becomes less related to the crucible swell (C.S.). This is shown by very fluid (liptinite-rich) coals which give a collapsed coke button under the C.S. test but exhibit high fluidities (Jones, 1988).

No generally valid answer can be given to the question of which test method is most useful with regard to coke oven
practice. The best selection of the test method depends largely on the purpose for which the coal will be used and on the process in which it will be used, as well as a degree of customer preference. It further depends on whether the coal properties will remain unchanged over long periods of time or whether there will be frequent and considerable fluctuations in coal quality.
This experiment was designed to study the possible effects of outgassing of adsorbed gases on the Dieselcr fluidity.

It was essential that during the experimental period no contamination of the coal samples or the outgassed products from the samples occurred. Once the fresh coal sample from the Borehole seam was collected its rate of degassing had to be immediately recorded. The sample collecting cylinders (bombs) were designed to be portable, robust and easily sealed (Plate 1).

As crushing the sample in the laboratory atmosphere was not acceptable due to the oxidising conditions present, all samples were crushed under a nitrogen-rich atmosphere.

The apparatus for the gas collections was designed so that the gas flowed in from the top of the cylinder thereby displacing the liquid. If the pipe had been fed into the liquid from below a pressure drop in the bomb would have caused liquid to be sucked back into the bomb. Fluctuating pressures in the bomb (attributed to diurnal temperature variations) were recorded during the study.

It was expected that carbon dioxide would form a proportion of the outgassed product. An acidic solution was used in the measuring cylinders and plastic trough (Plate 2), to prevent the carbon dioxide going into solution and being lost from the total gas flow measured.

The Gresham handpumps and gas cylinders (Plate 3), had
PLATE 1: GAS MEASURING EQUIPMENT, SHOWING THE FOUR GLASS MEASURING CYLINDERS, THE PLASTIC TROUGH AND THE COAL BOMBS.
PLATE 2: GAS MEASURING EQUIPMENT SHOWING THE PLASTIC TROUGH AND THE FOUR GLASS MEASURING CYLINDERS.
PLATE 3: GAS SAMPLING EQUIPMENT SHOWING THE PUMP, GAS SAMPLE CYLINDER AND PRESSURE GAUGE.
been used sucessfully at the B.H.P. steelworks to obtain flue gas samples for analysis by chromatography. For the Gieseler experiment, it was decided to purge the gas cylinders with argon to reduce the possibility of contamination of the outgassed products.

The samples stored under the controlled environments had to be easily accessible and resealable. It was decided to use a standard laboratory autoclave (Plate 4). To prevent sample contamination by outgassing or oxidation the autoclave was pressurised to 5000 kPa with nitrogen gas. The samples stored under oxygen and nitrogen at atmospheric pressure were kept in standard glass desiccators for ease of access and quick, efficient resealing. A desiccator was chosen for the same reason for the vacuum samples (Plate 5).

Results from Gieseler Flatometers do vary depending upon laboratory conditions and the skill of the personnel conducting the experiments. For this reason an automatic Gieseler Plastometer and highly experienced operators were chosen. Duplicate samples were analysed using the Gieseler Plastometer and their results had to be within acceptable laboratory tolerances.
PLATE 4: THE PRESSURISED AUTOCLAVE WITH NITROGEN CYLINDERS
PLATE 5: SUBSAMPLES IN THE DESICCATORS, STORED UNDER THE EXPERIMENTAL ENVIRONMENTS.
Coal Bombs

These are plastic cylinders 530 mm long with an external diameter of 120 mm. The bombs are moulded at the base and are sealed at the top by a screw threaded lid into which has been fitted a brass pipe and valve assembly. The bombs are all pressure tested before being used. Once the bombs are filled, the lids are secured using a chain wrench, preventing any ingress of air into or egress of gas from the bomb. A plastic pipe connects the bomb to the measuring cylinder (Plate 1).

Gas Measuring Equipment

This consists of a plastic trough 1.0 m long, 105 mm wide and 80 mm deep. Four glass 1000 ml measuring cylinders are inverted in the plastic trough. Into the base of each measuring cylinder has been glued a two way glass stopper valve. One valve was connected to the individual bombs and the second was utilised to sample the outgassed product from the measuring cylinders. The liquid in the trough consisted of diluted H₂SO₄ with a rhodabin B indicator and a pH of two. The trough was fitted with an overflow pipe to accommodate the volume of liquid displaced by the outgassing.

Gas Sampling Equipment

This consists of a hand operated pump, a pressure gauge reading up to 35 kg/cm² and a gas sample cylinder. All the components were manufactured by Gresham and Co. Ltd. of England.

The Autoclave

In a chemical engineering sense an autoclave may be described as a heated pressure vessel for carrying out chemical reactions involving the use of liquids. The particular autoclave selected for the experiment was
manufactured by Autoclave Engineers of Erie, U.S.A. It was extensively modified to facilitate the holding of ten metal dishes each containing 150g of the subsample. Nitrogen gas fed from a cylinder was used to pressurise the autoclave to 5000 kPa. This pressure was periodically checked from the gauges mounted on the cylinder (Plate 4). A spare nitrogen gas cylinder was held in reserve.

Desiccators

These are standard laboratory desiccators. The desiccators held the samples stored under nitrogen gas, oxygen and those under vacuum. They were taped over to avoid shattering should the pressure inside accidentally be raised too high (Plate 5).

The Gieseler Plastometer

This equipment is a fully automatic Gieseler Plastometer manufactured by Yoshida Seisakusho Co. Ltd. of Japan (Plate 6). The device indicates and records the time, temperature and fluidity simultaneously by measuring automatically the change in revolutions per minute of the pulse producing plate (which has 100 divisions). The plate movement is triggered by the revolving mixing rod set in the coal sample.
PLATE 6: THE GIESELER PLASTOMETER
CHAPTER SEVEN
EXPERIMENTAL PROCEDURE

Description

A sample of approximately 20kg of freshly cut coal was collected from the upper and middle portions of the Borehole seam in the Newcastle Coal Measures. The samples were bagged and carried 150m to the nearby "crib room" where two sealable plastic bombs (A and B) of 55 cm³ capacity were opened. Coal lumps of various shapes and dimensions was inserted into the bombs until they were full. The bombs were then sealed using the screw lids. The remainder of the coal sample was left in the collection bags and the ends sealed over. The flow of gas from each bomb was measured by running a tube from the "T" pieces in the bomb lid through a container of water and into an inverted measuring cylinder (Figure 11). After approximately one hour the valve was closed and the measuring apparatus dismantled. The quantity of gas that had outgassed in this one hour period was used to calculate the quantity that would have outgassed in the time taken to travel from the "crib room" to the C.R.L. at Shortland [some 20km from the colliery].

On arrival at the laboratory the two bombs (A and B) were immediately joined by plastic tube to the inverted 1000ml measuring cylinders (Plate 1). The taps on the bombs were then opened, and further outgassing measurements taken. The time was recorded for every 10ml drop in the liquid level in the measuring cylinders.
Figure 11. The apparatus used underground to measure the degassing of the coal sample.
The bagged samples were unloaded, weighed and the top sizes measured. The whole sample was then crushed to minus two millimeters. To prevent oxidation occurring the crushing was carried out in a nitrogen-rich atmosphere. This gave 20.865kg of -2mm crushed sample which was rotary sampler divided (R.S.D.) into twelfths (approximately 1739g).

The -2mm samples were then allocated as follows:

a) 1739g to gas bomb C
b) 1739g to gas bomb D
c) 1739g kept for sizing
d) 1678g kept in reserve
e) 1500g in ten subsamples to be kept in the autoclave under pressure.

This left 7/12ths of the -2mm sample (approximately 12.7kg), which was subdivided into samples of 1014g, and these were finally subdivided into samples of eighty four grams each. A portion of these 84g samples were made up into forty 200g subsamples and allocated to the following controlled environments:

a) Ten subsamples were stored in desiccators under nitrogen gas at atmospheric pressure.
b) Ten subsamples were stored in a desiccator under oxygen gas at atmospheric pressure.
c) Ten subsamples were placed in plastic containers open to the normal laboratory atmosphere.
d) Ten subsamples were placed in a desiccator under vacuum.

From the remaining original crushed coal in the 94g samples, six subsamples of 300g each were made up and allocated to the following:

a) Five subsamples were taken for storage in a freezer at -12°C.
b) One subsample was taken for:


ii) Proximate analysis involving the calculation of percentages of ash and volatile matter yield (AS1038 Part 3 - 1979).


The sampling procedure is summarised in Figure 12.

The gas bombs C and D were connected to outgas into the measuring cylinders (Plate 1) and their valves opened. Measurements were initially taken every ten to twenty millimeters of liquid displaced but, as outgassing decreased, this was reduced by day twenty nine to once per day for all four bombs. As outgassing proceeded it became necessary to extract the gases for analysis. This was done by noting the measuring cylinder reading and closing the feed valve one from the bomb. The pump was attached to valve two which was then opened and a sample sucked into the gas cylinder (Plate 3) which had been purged with argon. The cylinder was disconnected from the pump and sent for chromatographic analysis at the B.H.P. steelworks laboratory.

In the autoclave (Plate 4) the nitrogen was fed via a pipeline into the top of the cylinder. When a sample was required the feed was shut off and the nitrogen slowly released to atmosphere via the lower valve. After the pressure was relieved, bolts securing the upper and lower
FIG 12: SAMPLE PREPARATION PROCEDURE

INITIAL WEIGHT
20.865 kg.

CRUSH TO -2mm.
IN CHIPMUNK AND
THEN COFFEE MILL
(N₂ over sample)

R.S.D. 1/12ths.
(1739g)

Reserve in
Freezer 1678g.

1739g.
For Sizing

Gas test in
"Bomb" C ≈ 1739g.

Gas test in
"Bomb" ≈ 1739g.

12.2 kg.
R.S.D. 1/12ths.
(1014g)

Each 1014g-
R.S.D. 1/12ths.
(84g)

10 samples ≈ 150g
under N₂ gas in
Autoclave

10 samples ≈ 200g.
each under vacuum

10 samples ≈ 200g.
each under N₂ in
desiccator

10 samples ≈ 200g.
each under O₂ in
desiccator

5 samples ≈ 300g.
each in plastic
bags in Freezer

10 samples 200g.
each in plastic
containers open
to lab. atmosphere

1 sample ≈ 300g.
full lab. carb.
maceral count
reflectivity
moisture, ash and
volatile
Ultimate analysis
parts of the autoclave were released. When the subsample had been removed, the autoclave top was relocated with the base and the bolts inserted and tightened. The autoclave was then repressurised with nitrogen, allowing a slow bleed to atmosphere. This ensured all the air had been expelled from the autoclave. The valve to atmosphere was then shut off and once the pressure reached 5000kPa the nitrogen feed valve was closed.

The Gieseler fluidity test was carried out by the laboratory staff and me in compliance with AS2137 - 1981. A brief summary is given below:

5 grams of coal crushed to pass a 425 micrometer sieve is compacted into a closed steel crucible containing a stirrer, fitted with rabble arms. The assembled crucible is then screwed into the plastometer head fitting the top end of the stirrer into the slotted end of the axle drive. The drive will apply a constant torque of 100g per cm to the rabble arms. The motor drive is switched on as is the printer and programme controller. The crucible and contents are then lowered into the solder bath at 300°C. The solder bath temperature is then raised at the rate of 3°C/minute.
The chemical analysis of the coal sample is given in Table 2.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Result</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>% air dried (%a.d.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>% dried basis (%d.b.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>35.1</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>&lt;0.005</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.048</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>75.13</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>4.93</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>6.12</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Chemical Analysis of Borehole Coal Seam Sample
The sample had an ash yield of 10.9% (d.b.) which correlated closely with the ashes of the randomly selected samples in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H₂O%</th>
<th>Ash %a.d.</th>
<th>Ash %d.b.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 3 Pressure</td>
<td>2.16</td>
<td>10.82</td>
<td>11.05</td>
</tr>
<tr>
<td>Day 4 Pressure</td>
<td>2.23</td>
<td>10.72</td>
<td>10.96</td>
</tr>
<tr>
<td>Day 5 Nitrogen</td>
<td>2.16</td>
<td>10.59</td>
<td>10.81</td>
</tr>
<tr>
<td>Day 5 Vacuum</td>
<td>2.04</td>
<td>10.56</td>
<td>10.78</td>
</tr>
<tr>
<td>Day 5 Pressure</td>
<td>2.18</td>
<td>10.32</td>
<td>10.55</td>
</tr>
<tr>
<td>Day 5 Oxygen</td>
<td>2.22</td>
<td>10.88</td>
<td>11.13</td>
</tr>
<tr>
<td>Day 5 Atmosphere</td>
<td>2.19</td>
<td>11.05</td>
<td>11.30</td>
</tr>
<tr>
<td>Day 7 Atmosphere</td>
<td>2.14</td>
<td>10.39</td>
<td>10.42</td>
</tr>
<tr>
<td>Day 9 Atmosphere</td>
<td>2.18</td>
<td>10.59</td>
<td>10.82</td>
</tr>
</tbody>
</table>

Table 3. Analysis of Random Coal Samples From The Borehole Coal Seam Used in the Gieseler Experiment.
A significant variation in the ash yield affects the carbonisation properties particularly the Gieseler fluidity (Moxon, et al. 1986). Chemical analysis of the ash is given in Table 4.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>% d.b in ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>33.50</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>1.73</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>4.00</td>
</tr>
<tr>
<td>$\text{K}_2\text{O}$</td>
<td>0.90</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>0.77</td>
</tr>
<tr>
<td>$\text{Mn}_3\text{O}_4$</td>
<td>0.02</td>
</tr>
<tr>
<td>$\text{Na}_2\text{O}$</td>
<td>0.62</td>
</tr>
<tr>
<td>$\text{P}_2\text{O}_5$</td>
<td>1.00</td>
</tr>
<tr>
<td>$\text{SO}_3$</td>
<td>0.11</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>55.30</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>1.26</td>
</tr>
<tr>
<td>$\text{BaO}$</td>
<td>0.05</td>
</tr>
<tr>
<td>$\text{SiO}_2/\text{Al}_2\text{O}_3$</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Table 4. Ash Analysis (% d.b. in ash) of Borehole Coal Seam Sample.
The laboratory carbonisation results are collated in Table 5. The results are all consistent with other coal samples obtained from the Borehole seam at this location.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSN</td>
<td>71/2</td>
</tr>
<tr>
<td>GKCT</td>
<td>g₆</td>
</tr>
<tr>
<td>Dilatometer</td>
<td></td>
</tr>
<tr>
<td>c%</td>
<td>30%</td>
</tr>
<tr>
<td>d%</td>
<td>112%</td>
</tr>
<tr>
<td>T1 °C</td>
<td>370°</td>
</tr>
<tr>
<td>T2 °C</td>
<td>410°</td>
</tr>
<tr>
<td>T3 °C</td>
<td>470°</td>
</tr>
<tr>
<td>Gieseler</td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td></td>
</tr>
<tr>
<td>Fmax ddpm</td>
<td>6000</td>
</tr>
<tr>
<td>Tfm °C</td>
<td>440°</td>
</tr>
<tr>
<td>Ti °C</td>
<td>400°</td>
</tr>
<tr>
<td>Ts °C</td>
<td>470°</td>
</tr>
<tr>
<td>Tr °C</td>
<td>70°</td>
</tr>
</tbody>
</table>

Table 5. Laboratory Carbonisation properties of Borehole Coal Seam Sample.
The coal petrographic analysis was conducted at C.R.L. by K. Hall and Table 6 indicates a normal maceral composition for the Borehole seam at this location.

<table>
<thead>
<tr>
<th>Summary</th>
<th>Inc.</th>
<th>Volume %</th>
<th>Exc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitrinite</td>
<td>69.7</td>
<td></td>
<td>74.0</td>
</tr>
<tr>
<td>Exinite</td>
<td>6.4</td>
<td></td>
<td>6.8</td>
</tr>
<tr>
<td>Inertinite</td>
<td>18.2</td>
<td></td>
<td>19.2</td>
</tr>
<tr>
<td>Minerals</td>
<td>5.7</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>TOTALS</td>
<td>100.0</td>
<td></td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table 6. Maceral Analysis of Borehole Coal Seam Sample

The sample has an average random reflectance for vitrinite "A" of 0.85, an average maximum reflectance of 0.91 and standard deviations were 0.0541 and 0.0577 respectively. The Australian Standard AS 2486-1981 states:

"In both rank determinations and analyses for technological purposes the number of measurements made depends upon the range of reflectance values encountered in the sample. The required number of measurements may be estimated from the following formula:

\[ N = \left[ \frac{\text{Range}}{0.04} \right]^2 \text{ or } N = \left[ \frac{s}{0.01} \right]^2 \]

where:

\[ N = \text{number of individual reflectance readings} \]
\[ s = \text{standard deviation} \]"
The two formulae give differing figures for the required number of measurements. The standard recommends a minimum number of thirty measurements (which are summarized in Table 7).

<table>
<thead>
<tr>
<th>Average random reflect</th>
<th>0.85</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min. reading of random reflect</td>
<td>0.73</td>
</tr>
<tr>
<td>Max. reading of random reflect</td>
<td>0.95</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.0541</td>
</tr>
<tr>
<td>Average Maximum reflectance</td>
<td>0.91</td>
</tr>
<tr>
<td>Min. reading of max. reflect</td>
<td>0.78</td>
</tr>
<tr>
<td>Max. reading of max. reflect</td>
<td>1.01</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.0577</td>
</tr>
</tbody>
</table>

Table 7. Vitrinite Reflectance of Borehole Coal Seam Sample.

The Gieseler maximum fluidity (m.f.) results are summarised in Table 8 and represented graphically in Figure 13.

From the graph it can be seen that the m.f. of the subsamples kept under atmospheric conditions (A) dropped from 6000 ddpd on day zero, to 3000 ddpd by day seven, 900 ddpd by day forty, and by day one hundred and sixty six it had reduced to 220 ddpd. The subsample stored under an oxygen atmosphere (O) followed a similar trend to the (A) subsample, dropping to 190 ddpd by day one hundred and sixty six. This trend has been well documented by researchers and is attributed to oxidation taking place. The significant trends from the experimental view point were those of the subsample kept
### Tables 8

Summary of Gieseler Maximum Fluidity and Log of Maximum Fluidity results over the duration of the experiment.
Figure 13. Gieseler Maximum Fluidity measured over time for the various subsamples. Points A, B, D are the Gieseler fluidities measured on day 173 from the coal samples contained in the bombs.
under vacuum (V), pressure (P), nitrogen (N) and freezer (F) conditions.

From Figure 13 it can be seen that the m.f. of the (V), (P) and (N) subsamples had dropped from 5000 ddpm on day zero to approximately 4600 ddpm by day three. (No figures are available for (F) subsamples until day twelve. The trend for this subsample has therefore been interpolated.)

The trend for the subsamples (V), (P) and (N) had levelled out by day nine to 4600; 4300 and ~4250 ddpm respectively. By comparison, the m.f. for the (A) subsample had dropped to 2600 ddpm on day nine.

On day forty four (Table 9) the figures for the (V), (P), (N) and (F) subsamples were 3400; 2500; 2400 and ~3800 ddpm respectively.

These figures indicate a slowing down in the rate of m.f. reduction when compared to the (A) subsample figures for the same day. The final Cieseler results obtained for the (V), (P) and (F) subsamples reinforced the earlier trend (a slow decline). The (F) subsample maintaining the highest m.f. at 3300 ddpm (recorded on day one hundred and sixty seven).

The (V) subsample m.f. value dropped to 2600 ddpm by day one hundred and sixty eight. This result is midway between the corresponding m.f. values obtained for the (F) and (P) subsamples and therefore raises doubts about the role of outgassing in the reduction of the m.f. value.

The trend of the m.f. values was plotted on a Log f against time basis but the resulting graph (Figure 14)
TABLE 9: Results of the gas analyses using chromatographic methods.
FIG. 14 Graphical representation of Log Maximum Fluidity plotted against time. (The oxygen plot was similar to that of Air and therefore, it was left off for clarity)
gave no indication of a linear relationship. The oxygen sample followed a similar path to the air sample and therefore was not included on Figure 14.

The trends for the m.f. values for the (V), (F) and (H) subsamples are therefore best studied with reference to the graph in Figure 13. This scales the time periods between the Gieseler results. The m.f. value obtained for the (N) subsamples when compared indicated a significant drop from day forty eight to day eighty two. This trend is continued, the m.f. value reducing to 270 ddpm by day one hundred and sixty seven. Air contamination of the nitrogen atmosphere was suspected after the result on day forty eight, but the continued downward trend would indicate an, as yet, unidentified factor influencing the m.f. value.

The Gieseler m.f. results obtained from the samples stored in the gas bombs A, B and D on day 173 averaged ~3600 ddpm, and this was similar to that obtained from the freezer subsamples on day 167. The result obtained from bomb C was considerably higher at 4200 ddpm. There was visible evidence that during the course of the experiment bomb C had leaked and therefore the result from bomb C, being unreliable, was ignored.

The chromatograph analyses are given in Table 3. Only the air free results will be discussed as they are likely to give a more accurate trend. (Some air contamination of the gas cylinders may have occurred affecting the non-air free results.) Suspect readings were obtained for sample A on day three, sample C on day twenty three, and sample D on days three and twenty three. Their results will therefore not be considered.
The reasons for these erroneous results is not clear. Each gas cylinder was fitted with inner tube valves at each end and these were pressure tested under water for leaks before each use. The gas sample cylinders were also purged with argon gas to reduce the likelihood of contamination.

The hydrogen outgassed varied in quantity but followed a general downward trend. Sample B outgassed less hydrogen at the start of the experiment but had attained the overall sample average by the end of day one. Some hydrogen may have been outgassed from sample A and B whilst underground.

The methane quantities outgassed climbed slowly making up ~99.8% of the analysis by day seventy two (results based on sample B). It is possible that some methane may have been preferentially outgassed during the crushing process.

Samples A, B and C followed a similar downward trend in ethane outgassed. The trend from sample D was less consistent rising and falling at random. However, these quantities are so small that individual variations are not necessarily significant.

The quantities of carbon dioxide outgassed from all samples dropped consistently from day zero. The early results from samples A and B indicated that some carbon dioxide had been outgassed underground into the mine atmosphere.

The relationship between oxygen and the oxygen plus nitrogen outgassed percentages is shown in the final column of Table 3. Ignoring the result for day three and twenty three, the results are random and fail to conform
to a recognisable trend. Contamination of the gas cylinders by air or leakage into the bombs are possible causes of variation, the latter being the less likely as the seals on the bombs were checked regularly. The trend of outgassing from the bombs is shown graphically in Figure 15. The first days of the experiment show a steep rise which flattens after day ten continuing a slower ascent to day one hundred.

The amounts outgassed from the samples can be seen from Table 9 and Figure 16. Plotting the graphical trends of the various gasses added little clarification. It was therefore decided not to include these in this thesis.
Figure 15. Amount of Gas liberated over time from the gas bombs A, B and D.
Observation of the trends plotted in Figure 13 reveals that the subsamples under all conditions of storage are characterised by a sharp drop off in m.f. from day zero to day nine. (The trend for the (F) subsample was interpolated as no results were available before day twelve). The simplest explanation for the decrease in m.f. is that, despite all the precautions taken, oxidation processes were still able to affect the subsamples.

The samples crushed under a nitrogen-rich atmosphere may have been able to outgas. Work done by McCulloch and Diamond, (1976), showed that the initial gas emissions from the coal are the largest. This puts pressure on the researcher to attempt to minimise the time interval associated with the "lost gas" factor. Gas composition analyses conducted by Battino and Doyle, (1983), showed that CH₄ gas is emitted earlier than CO₂ gas. This effect was attributed to the differing molecular weights of the gases. Crushing the subsamples under vacuum should, therefore, be considered for future experimental work. This will accelerate early degassing of the coal but will avoid the lost gas factor. Solomon and Mains (1977), found that conventional grinding processes are harsh and the production of heat and the increase of reactive surfaces in an oxidising environment modify the coal. They ground coal in liquid nitrogen and their work suggests that the liquid nitrogen ground coal surface more accurately represents the macroscopic structure of the coal.

A second factor may have been an incorrect measurement of the initial m.f. (6000 ddpm). This too is unlikely as
other fresh borehole seam samples from this locality have given similar m.f. results. It has been shown (Figure 13), that the samples were outgassing for the duration of the experiment. There is, therefore, currently no simple explanation of how oxygen could have entered the subsample unless it was already chemically combined within the coal.

The downward trend in the m.f. for both (A) and (O) subsamples is evident from Figure 13 and Table 5. They follow a similar path and oxidation is the assumed cause of this decline in m.f. The subsamples stored under (V), (F), (N) and (F) conditions, by contrast, indicate a different graphical trend to that of the (A) and (C) subsamples. The subsamples stored under vacuum should be unable to oxidise normally due to the removal of the oxygen. The moisture content in the subsample may also be affected due to the vacuum applied. The subsample should outgas consistently as indicated by the samples in the bombs. The subsamples stored under freezing conditions maintained a high proportion of their initial m.f., remaining approximately at 3600 ddpm until day seventy eight and only dropped to 3300 ddpm by day one hundred and sixty seven - the final days of the experiment. No (F) subsamples were tested before day twelve. It is, therefore, not possible to interpolate accurately the initial rate of decrease in their m.f. The (F) subsamples should have experienced no oxidation from the atmospheric oxygen, nor should they be affected by moisture which will be frozen and therefore can be assumed to be relatively inert. Outgassing too may be reduced under the freezing temperatures.

The subsamples stored under pressurised nitrogen gas in the autoclave will neither be able to oxidise from
atmospheric oxygen nor cutgas. The moisture in the coal may also be affected by the high applied pressure.

The plots of these three ((V), (P) and (F)) subsamples are similar and the m.f. on day seventy six for the (V) and (F) subsamples was approximately 3600 ddpm, whilst that for the (P) subsample was 2800 ddpm. This difference is unlikely to be significant as it is close to the maximum fluidity replicate tolerances (m.f.r.t.) in Table 10.

The subsample stored under nitrogen at atmospheric pressure maintained a similar trend to the subsample under (V), (P) and (F) conditions until day eighty two. The m.f. reading for the nitrogen subsample on that day showed a marked decrease to 1100 ddpm. The decrease in the m.f. value for the (N) subsample continued and dropped to 270 ddpm by the end of the experimental period. This last m.f. value corresponds to those of the (A) and (O) subsamples taken at the same time.

The nitrogen atmosphere should have prevented oxidation taking place, unless leakage or contamination occurred. Leakage is unlikely, but if the drop in m.f. value had been caused by outgassing alone, a similar trend should be evident in the results from the (V) subsamples. This is not the case. The results for the (N) subsamples cast doubt on the role of both outgassing and atmospheric oxygen in reducing the m.f. values.

The (V) subsamples maintained a relatively high m.f. value throughout the experiment dropping to 2600 ddpm in the last Gieseler test. Although this value is less than the corresponding (F) subsample the difference is not considered significant as it lies within the m.f.r.t. given in Table 10.
TABLE 10. - Maximum Fluidity replicate tolerances for use with the Gieseler Plastometer.

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It is believed that the constant opening and closing of the sealed desiccators would have led to some leakage which may have caused the decrease in m.f. towards the end of the experimental period.

The m.f. results from the bombs indicated that although outgassing had been taking place throughout the experimental period, there had not been a significant lowering of the Gieseler m.f. values, when compared to the other subsamples.

The results indicate that the subsamples that were able to outgas most readily ((N) and (V)), differed little initially in their maximum fluidity (m.f.) drop off to those which were prevented from outgassing ((P) and (F)). The (V) subsample maintained high (m.f.) results throughout the experiment whilst the (N) subsamples (m.f.) dropped sharply after day 48, but if outgassing is not the cause of the drop in Gieseler m.f. then other mechanisms have to be examined.

The role of oxygen in the self heating of coal has been known for over sixty years. Investigations by T. Winmill and Graham, (1914), at Bentley Laboratory of the Doncaster Coal Owners' Cobi Fires Committee led to the conclusion that "Self heating of coal is mainly due to the absorption of oxygen by the coal resulting in the generation of heat".

It was demonstrated (Winmill, 1915), that all coals when powdered, had a certain capacity to absorb of oxygen at ordinary mine temperatures, but that this capacity varied considerably with different kinds of coals. The rate of oxidation is a function of the exposed surface area of coal, the smaller the particle size the higher the rate of oxidation. If 25 mm coal, for example, is crushed to
250 microns, the specific surface area increases approximately one thousand fold.

While the explanation for this relationship is still unproved, empirical evidence suggests that coal rank, inherent oxygen and inherent moisture are all correlated with high reactivity to oxygen and to the potential of coal for spontaneous combustion (Kelly, 1985).

Laboratory carbonisation properties of coals are also affected by prolonged exposure to the atmosphere particularly the maximum fluidity measurements (Moxon, et al., 1987). The cause of this deterioration has been outlined above (Neavel, 1982). Since adsorption of gases on microporous coals is often diffusion-controlled, rates of adsorption can be generally enhanced by decreasing the particle size. It was concluded by Walker, et al. (1968), that grinding of the coal in air resulted in the closure of some micropores due to the overheating and plastic flow during grinding.

Unless the oxidation taking place on the coal surface is very rapid, the crushing of the samples should have restored the fluidity. As reported above this did not occur.

It has been stated that how much surface moisture a coal retains and how long it is retained are functions of the size consist of coal. Large pieces hold a minimum of surface moisture by virtue of the capillary forces in the small interices between the particles (Kelly, 1985).

Lebedev, et al. (1979), have reported that the water content associated with the coal during particle size reduction has a marked effect on subsequent surface area. They ground three coals - a brown coal, a hard coal and
an anthracite - associated with different amounts of water in a vibromill in air and measured specific surface area of the resultant coal sample by argon adsorption. Results showed that an increase in water content during grinding had an adverse effect on surface area. Since no attempt was made by Lebedev, et al. to measure the particle size distribution in the ground coal samples, it is not clearly evident why the water content during grinding has an affect on surface area.

The evidence from the bombs showed that outgassing was maintained for the duration of the experiment. If gas is issuing under pressure it is difficult to understand how oxygen could enter the coal sample. Water associated with coal occurs as inherent moisture, surface moisture and gaseous water vapour. Inherent moisture is water that is physically trapped and chemically combined with the organic and mineral molecules and occurs within the pore structure of the coal.

If the water content of coal is below its equilibrium level, the material will seek water from its surroundings and in replenishing its equilibrium water, will give off heat - the heat of wetting.

The equilibrium value for moisture content varies with the relative humidity. As a result, coal can be continuously experiencing heat of wetting or cooling as the weather changes. When a coal containing less-than-equilibrium moisture absorbs water, it can and does obtain it from the surrounding air. When this happens, additional heating occurs as the water in the vapour state condenses and changes state.

In the experimental conditions described, the (V), (F), (N) and (F) subsamples theoretically were isolated from
the outside atmosphere. The equilibrium value could therefore not be balanced from this source. In the (V), (F) and (F) environments the effects of any moisture in the subsample will be reduced. In the (N) and (O) environments the gases will be relatively dry and of constant humidity, whereas, the subsample stored in the laboratory (A) will be affected by changes in humidity. However, if moisture does play a role in the drop off in m.f. the reasons for the sharp initial drop in m.f. in all subsamples will need to be researched. If moisture does break down to supply oxygen, then some evidence of substantial hydrogen outgassing should be present unless the hydrogen is chemically recombined.

The chromatograph results show a reduction in the percentage of hydrogen outgassed against time, which suggests that the hydrogen is not a product of oxidation.
CHAPTER TEN
CONCLUSIONS

The samples of coal that were studied were kept under the following controlled environments.
1. Storage in desiccators under nitrogen gas at atmospheric pressure (N).
2. Storage in a desiccator under oxygen gas at atmospheric pressure (O).
3. Storage under normal laboratory atmospheric conditions (A).
5. Storage in a desiccator under vacuum (V).
6. Storage in a freezer at -12°C (F).

Because of the continuing uncertainty about what contributes to the coking properties in the first place, little is known about how a deterioration due to oxidation could be caused; nor is it known why otherwise seemingly identical coals can deteriorate at greatly different rates. Indeed, the very basic process of softening-fusing-resolidification of coal is still a subject of study which has resulted in a variety of differing viewpoints.

The chemical, physical and technological properties of the coal depend on its rank and its maceral composition. The properties of the macerals generally change during coalification. The macerals themselves are not chemically uniform substances, even at a given level of rank. An investigation of the influence of the petrographic composition on the softening behaviour of the coal must consider the possibility of an overlapping of the influences of rank and maceral composition.
It has been shown (Brown, Hesp and Waters, 1964), that some properties of Australian coking coals depend mainly on the rank and others on the vitrinite content, the latter which is the main parameter in petrographic composition that influences the coking ability of the coal; still others depend in different measures on both of these factors. Rank strongly influences the temperature of maximum fluidity and resolidification. These properties are directly related to the thermal decomposition, thus are determined more by the chemical structure of the coal as a whole than by the petrographic composition.

The selection of the test method for a coal depends on the purpose for which the coal will be utilised and on the process in which it will be used. It further depends on whether the coal properties will remain unchanged over long periods of time or whether there will be frequent and considerable fluctuations.

In addition to the information obtained from the swelling index test, the dilatometer test supplies data about the softening and resolidification temperature of the coal and about the interval of the plastic range.

The plastometers and plastographs were developed not so much to obtain information about the properties of the plastic mass itself, but rather to be able to predict the properties of the coke that will be produced.

The dilatometer and plastometer methods must be viewed critically. The dilatometer and plastometer curves show some relationship exists between the measured variables and the strength of the coke, but no relationship to the structure of the coke. For the formation of a coke of suitable quality, next to the amount and nature of the
bitumen in the coal, the amount and nature of the remaining residue of the coal is a determining factor. The participation of this remaining residue is insufficiently visible in the measured curves. They characterise, more or less, only the melting parts of the coal (bitumen) and how they are influenced by the gas formation (dilatation) or by splitting and condensation reactions (plasticity).

It is not possible therefore, to arrive at definite and quantitatively valid correlations for different coals and different test results in the sense that one method can be replaced by another.

The series of experiments I carried out at Central Research Laboratories (C.R.L.) attempted to isolate the role that outgassing plays in the reduction of Gieseler maximum fluidity. It would appear that outgassing is not a major contributor to the deterioration of the Gieseler m.f. but I suggest that further research is required into the following areas:

a) The effect that freezing conditions have on outgassing from a crushed coal sample.

b) The effect that storage under nitrogen gas and vacuum conditions have on the maximum fluidity of crushed coal.

This will substantiate whether or not the drop in maximum fluidity for the nitrogen and vacuum subsamples was due to leakage or to some factor so far not recognised.

I further suggest that all samples for this type of experiment could either be crushed under vacuum or ground under liquid nitrogen (Solomon and Mains, 1977).
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