Coking pressure and coke structure

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COKING PRESSURE AND COKE STRUCTURE

by

ELENI PSOMIADOU

A Master’s Thesis
Submitted in partial fulfilment of the requirements
for the award of

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ABSTRACT

The carbonization of some low volatile matter coals for the production of metallurgical coke in slot type ovens is accompanied by the exertion of pressures on the walls which can be dangerous and destroy the walls. It is generally accepted that coking pressure originates from the volatile matter released from the coal being retained as pressurized vapours trapped within the plastic layer of the carbonizing coal charge.

Pressure during carbonization also influences the nature of the carbon texture and the porous structure of coke is strongly dependent on volatile matter release during the plastic stage of the carbonization process. There is therefore a possible association of coking pressure, coke porous structure and coke carbon texture.

Seven coals giving a variety of wall pressures, as measured in a movable-wall oven, ranging from safe to dangerously coking, were carbonized in a small laboratory oven. The textural compositions of the resultant cokes were assessed by polarized light microscopy while pore structural parameters were measured by computerized image analysis.

The textural compositions varied with volatile matter content of the coals while the porosities varied linearly with the internal gas pressures measured in a single plastic layer.

In an attempt to investigate possible relations between the pore structure development and internal gas pressures generated in a single plastic layer, polished surfaces showing the coal-to-coke transformation were prepared after quenching carbonized single-wall oven charges. These surfaces were studied by image analysis techniques to obtain measurements of the pore sizes as carbonization proceeded. Pore sizes generally rose to a maximum within the plastic temperature range before falling to the almost constant value seen in the semicoke. No systematic variation between the pore structure development and the internal gas pressures could be established.
I am grateful to my supervisor Professor John W. Patrick for his help and encouragement during this project.

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I wish to thank British Coal for providing the coals used in the experimental study.

I thank my husband, Ioanni, for his support throughout this study.

Finally, I am grateful to the European Coal and Steel Community for their financial support.
Dedicated to

my mother, Theodora
my husband, Ioanni
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1 INTRODUCTION

Metallurgical cokes are porous carbon-rich solids produced by the carbonization of crushed coals in slot-type ovens with vertical heating walls. During this process, coking coals soften to become plastic, decompose, swell, agglomerate and finally resolidify. The plastic temperature range is usually between 350-500°C. Thus in the coking process two vertical plastic layers are formed parallel to the heating walls which proceed towards the centre where they coalesce. During carbonization some coals generate internal gas pressures and exert measurable wall pressures, sometimes dangerously high, on the oven walls. These two pressures are manifestations of the coking pressure phenomenon.

The present study is a part of a wider investigation designed to obtain a better understanding of the processes involved in the generation of coking pressure.

It is known that two processes occur during the plastic temperature range. The pore structure of the coke develops and the coal carbon becomes organized into graphite-type layer planes the ordering of which results in the optical anisotropy of the coke. The variations in size of the anisotropic units give rise to textural components in the coke. The proportions of the various components present being the textural composition of the coke. Since the coking pressure arises in the plastic range, the object of the present study was to investigate whether these two processes were linked to the generation of the coking pressure.

In a previous study a small double heated-wall oven had been developed and for a series of seven coals the internal gas pressures generated in the centre of the oven were measured. In the present study, the cokes produced in the above oven were used and attempts have been made to relate the tensile strength, textural composition and pore structural data of the cokes to the internal gas pressures.

Also, an oven with a single vertical heated wall has been used to set up a temperature gradient along the length of a coal charge. After cooling and fixing the relative positions of products, using epoxy resin, horizontal sections were polished for microscopic examination and for studying the pore structure development by image analysis. The aim of this study was to examine possible association of variations of internal gas pressure and differences in the manner of pore development.
After this introduction, the thesis is divided into the following sections: 2) Literature review, 3) Experimental, 4) Results, 5) Discussion, 6) Conclusions and Recommendations for Future Work and, 7) References. Finally the Figures and the Tables referred to in the text are arranged in numerical order at the back of the thesis, on unnumbered pages.
2 LITERATURE REVIEW

The total world coke production remained virtually stable at 367-376Mt in the last twenty years since the decline of 70Mt in the industrial countries was counterbalanced by an expansion of 140% in the developing countries and 45% in the centrally planned economies.²

The international trade in coking coals showed an increase from 130Mt in 1970 to 187Mt in 1990 due to the fast growing steel industries in Asia and Latin America.

In Europe the production of hard coal in 1990 was 11.2 million tonnes less than in 1989 while net imports increased by almost 13Mt. About 22% of the hard coal was delivered to coking plants and about 88% of the coke plant production was delivered to the iron and steel industry.³

Metallurgical coke is mainly used as a fuel in the blast furnace for the production of pig iron and in cupolas.

In the blast furnace, coke performs three functions⁴:
1) to generate by combustion most of the heat required by the process.
2) to provide the necessary carbon monoxide for the reduction of iron oxides.
3) to provide a permeable bed for the ascent of gases and the descent of molten iron and slag.

In order to fulfil these roles coke must possess high strength and low porosity. Its chemical impurities such as ash and sulphur should be as low as is economically feasible. The physical and chemical properties, especially size and strength should be as uniform as possible. The size in particular should be compatible with the sizes of the other burden materials in order to obtain optimum gas permeability.⁵

There are variations in the specification for coke due to differences in the coals used for coking and to differences in the size and design of the blast furnace.

Coke is produced by the carbonization of coking coals. The feed to essentially all coke ovens is a blend of several coals, most commonly based on high volatile bituminous coals for bulk and medium or low volatile bituminous coals for strength.⁶ Techniques have been developed for effective blending because of the limited supply of prime coking coals.⁶
The literature review consists of the following parts: i) production of metallurgical coke in slot-type ovens where a description of coke oven and operation practices are concisely given, ii) brief description of the science of coke-making which considers the nature of coals (coking coals) and the process of coal-to-coke transformation through the two important processes that occur within the plastic temperature range, i.e., the pore structure and the optical anisotropy development, iii) review of the methods developed to measure the coking pressure and of the various parameters known to influence its development, iv) finally a review is given of the existing theories regarding the development of coking pressure which leads to an outline of the research programme.
2.1 PRODUCTION OF METALLURGICAL COKE

Metallurgical coke is produced by high temperature carbonization (temperatures in excess of 900°C) which aims primarily at the manufacture of hard coke for use in cupolas and blast furnaces.\(^7\)

Coal blends are commonly carbonized in narrow slot-type chambers constructed of silica brick. These chambers are built in batteries of up to 100 ovens per battery in order to conserve heat and space. The walls between the ovens have heating flues in which gas, usually part of the gas production of the plant, is burnt to provide heat for the carbonization.

The ovens vary greatly in capacity. Newer ovens have chamber dimensions of up to 7.8m in height, 18m in length and 0.62m in width.\(^8\) Both ends of the oven are closed with removable self-sealing doors. Each oven has 3 to 5 charging holes on top for filling the oven with coal. Larry cars filled with coal travel on top of the battery and discharge the coal into the selected oven through the charging holes. A long leveller bar is inserted through a small opening in the door at one end of the oven to level the coal. Some oven batteries have used pipeline charging systems by means of which dried or preheated coal is conveyed through a pipe as a dense phase fluid in steam and charged into the appropriate oven. At the top of one or both ends of the oven, refractory lined standpipes conduct the volatile carbonization products to the chemical recovery plant.

Once heated, an oven battery is usually maintained at or near operating temperature for the life of the ovens. The life of an oven battery is considered to be approximately 25 years although much older batteries are still in operation. In U.S.A. 40 out of 79 batteries in use are 30 years old or older and due for either replacement or major rebuilds.\(^9\) The average life expectancy of the tall batteries is estimated to be considerably lower than the above (12-18 years).\(^10\)

The number of the heating flues (25-33) contained in an oven wall depend upon its length and other design factors. The gas flow to the heating flues is controlled with a reversing machine by turning on the gas in half the flue system of an oven and shutting off the gas to the other half.

The flue temperature, oven design and characteristics of the coal blend influence greatly the time required for the completion of the carbonization. The flue temperature and the resultant coking time are different for blast furnace and the foundry coke manufacture. Generally, the coking time for blast furnace coke is 16-22h and for foundry coke 24-36h.
The coal blend is charged into hot ovens and coke is pushed out of them according to a planned schedule. A pusher ram on rails along the pusher side of the battery removes the coke from the oven into a quenching car for transport to a quenching station. There the coke is sprayed with water to cool it below its ignition temperature. After draining, the quenched coke is deposited on an inclined brick wharf where it is further cooled to ambient temperature. Afterwards the cooled coke is conveyed from the wharf to the screening station for separation into desired sizes. An alternative to quenching coke with water is dry quenching. This technique is in almost general use in Japan and besides producing dry coke, the ideal for the blast furnace, it also allows the sensible heat of the fuel to be recovered and the environmental protection standards to be observed."11

2.1.1 Further blend treatment.

The growing demand for metallurgical coke of specified quality and for conservation of the rapidly depleting reserves of good coking coal have motivated much research on the treatment of coal before carbonization in coke ovens. A number of pretreatment methods such as oil addition, selective crushing, thermal treatment, addition of tar, briquette blending and stamp charging have attained an improvement in the coking characteristics of a coal blend containing weakly coking coals.

The most widespread operating procedure used throughout the world is charging by gravity at a moisture content between 6-10 %. However additional benefits are achieved if the coal charge is preheated before entering the oven. The advantages of charging preheated coal include the following: a) enables lower rank, poorer coking coals, to be used without loss in coke quality b) the charge is much more uniform, c) the bulk density increases, d) the coking time may be reduced by as much as 20-35%, e) preheated charges are self-levelling and f) preheated coals improve the consistency of coke quality and increase the oven output.11

The stamp charging of coals which was found to improve the coking properties of low rank coals,7 is conducted as follows11: coal is compacted in a metal box the dimensions of which are slightly smaller than those of the oven chamber and is then charged horizontally through one doorway. With this technique the charge density is greatly increased. This procedure brings about a significant improvement in the cohesion of the coke, as characterized by the M10 index, but on the other hand tends to increase the fissuring and thus results in a reduction of lump size. However, this drawback is easily
overcome by the addition of suitably crushed coke breeze (antifissurant). This way of charging is recommended for weakly coking coals (low rank, high volatile matter content). However if high rank coal is used, the pressure exerted on the oven walls during carbonization could be very dangerous because of the high charge density.

Preliminary control of any potentially hazardous increase in coking pressure of coal blends charged, either preheated or by stamp charging, should take place because of the increased danger due to the increased bulk density of the charge.

2.2 THE NATURE OF COAL

Coal is a heterogeneous and complex organic rock and is the most abundant fossil fuel. It consists mainly of carbon, hydrogen and oxygen with minor amounts of nitrogen, sulphur and varying amounts of water and mineral impurities.12

The origin of coals is attributed to the accumulation and burial of partially decomposed vegetation in previous geological ages. Biochemical changes and subsequent effects of pressure and especially temperature converted these deposits to coal. This evolution follows a complicated procedure going from peat through lignite, subbituminous coal, bituminous coal to anthracite and is simultaneously accompanied by physical and chemical changes among which the most important ones are: a) enrichment in carbon through the reduction of the hydrogen and oxygen contents, b) reduction in volatile matter content and c) increase in reflectance.

Generally coalification is more advanced in the older coal deposits. The most important bituminous coal reserves were deposited in the Carboniferous (approximately 200-300 million years ago) and Upper Cretaceous and early Tertiary (60-120 million years ago) periods.

In coal seams, petrographers have distinguished with the naked eye more or less lustrous thin beds and regular accumulations which can be divided into four well defined classes called lithotypes, the bright vitrain and clarain, the dull granular durain and the powdery fusain.

The usual technique employed in coal petrography is the observation of polished surfaces of crushed coal embedded in epoxy resin with reflected light under oil immersion.11 Observations using this technique established the presence of organic constituents that comprise coals which are called macerals and which are divided into three basic groups:
vitrinite, exinite, inertinite. In each of these groups there is a great similarity of properties. These macerals in certain cases are dispersed among one another forming preferential associations called microlithotypes.

2.2.1 Classification of coals.

Before the 19th century, coal was classed by its appearance as bright coal, black or brown, but with the spread of the industrial revolution it became apparent that a more detailed definition of fuels should be adopted.

Since then many systems of classification have been put forward to meet particular requirements. Most coal producing countries have their own coal classification system. All these systems generally combine a measure of coal rank with some indicator of the agglutinating properties of coals.

In the U.K. the NCB (National Coal Board) Classification Scheme is used in which the volatile matter content on a dry, mineral-matter-free basis is used as a measure of coal rank, while the agglutinating properties are assessed by the Gray-King assay. In this test, 20g of finely crushed coal are heated in a silica tube at a heating rate of 5°C/min between 300 and 600°C. The appearance of the residue is classified by comparison with a series of reference cokes.

With this scheme coals are divided into classes each of which is given a Coal Rank Code number (Fig. 1). These range from 100 for high rank anthracites up to 902 for low rank coals. Coals important for the coking industry range in rank from 204 to 602, with volatile matter content from 17.1 to over 36%. The best coking coals are to be found in classes 301a and 301b.

A variety of testing methods has been developed to determine the quality of coals for coke-making. The most extensively used are dilatometry and plastometry.

There are different kind of dilatometers. In the International Classification System, the dilatometer test of Audibert-Arnu using coal pencils was chosen in addition to the Gray-King test as the final method for determining the coking ability.¹¹ The dilatometer used in U.K. is the Ruhr dilatometer¹² which is a further development of the Audibert-Arnu dilatometer. In this instrument two pencils made of finely ground coal are placed in tubes and simultaneously heated at a heating rate of 3°C/min. The axial changes of the lengths of the samples are transmitted to a plunger which rests on top of
the coal. This is connected to a device that records on a drum the change in pencil length(%) versus temperature. In general the dilatometer curve shows an initial contraction of the coal pencil followed by an expansion as the plastic coal swells. Finally the plastic mass is converted into solid semicoke and the curve remains parallel to the abscissa. The maximum decrease in length is defined as the maximum contraction, the distance of the final value from the zero line is called the dilatation and the limits of the plastic range are the temperatures of softening and resolidification.

The plasticity of coals is evaluated using plastometers. The Gieseler plastometer, which is widely used, has a metal crucible in which about 2g of finely crushed coal can be heated in the absence of air. A small stirrer bearing rabble arms is located in the coal, actuated by a constant torque produced by a weight attached by a wire around the axis. This torque is small so that the stirrer is not rotated when the coal is in the solid state. The test is carried out by heating coal at a fixed rate between 300-550°C. In the curve produced, the rate of rotation of the stirrer (degrees of arc/min) is given as a function of temperature. The rate of rotation rises to a maximum before falling to zero. The stirrer continues to rotate at temperatures higher than the resolidification temperature as measured by the dilatometer.

2.2.2 Effect of rank and petrographic composition.

Some of the plastic properties of coals depend mainly on the rank others on the petrographic composition while others depend in different degree on both these factors. A study of Australian coals showed that the temperature of the initial softening which is a reversible physical process depends almost entirely on the petrographic composition. On the other hand the temperature of resolidification and maximum plasticity rise continuously with rank. These properties are related to the thermal decomposition and so are determined more by the chemical structure of the coal.

The swelling and agglutinating properties show a characteristic maximum in the middle of the rank range (approximately 87% C, 30% VM).

Among the macerals of coking coals, exinites show the greatest fluidity and dilatation, inertinites do not soften and show no plasticity while vitrinites exhibit an intermediate behaviour.
2.3 COAL TO COKE TRANSFORMATION

During the coking process powdered coal is transformed into a porous, fissured, silver-black solid, coke. Microscopically coke consists of a solid matrix, organic and inorganic inclusions in the matrix, pores and microfissures.

The processes of the development of the porous structure and the microtexture of coke take place essentially within the plastic range.

The structure formed in the coke by the gas bubbles occupies almost half its volume and influences two properties of coke, the mechanical strength and the bulk density.\(^{11}\)

The solid material forming the pore walls consists of optically-anisotropic entities which are usually observed using polarized light microscopy (PLM). The coke microtexture influences the coke properties which are essential for its use in the blast furnace.

In the following sections first there will be a description of the porous structure development as it was described and investigated by researchers at the British Carbonization Research Association\(^{17,18}\) (BCRA) using a small, single-wall oven and secondly, a description of the study of coke optical anisotropy using PLM followed by a discussion on the development of the optical anisotropy in cokes.

2.3.1 Pore structure development.

The mechanism and the principal factors influencing the formation of pores in semicoke were investigated at the BCRA.\(^{17,18}\) A series of coals was heated at 3.5K/min from one side in a small box into which four thermocouples were inserted to lie parallel to the heating wall. As soon as the coolest thermocouple indicated 320°C the box was drawn away from the hot wall and allowed to cool down to room temperature. Thus a coal/semicoke box with temperature variation from 700-300°C was obtained.

Microscopic examinations were made using blocks taken from the above boxes as follows. The relative positions of the materials carbonized at different temperatures were fixed with an epoxy resin and the resulting block was cut horizontally 3 mm above the level of the thermocouples to expose two surfaces. The lower surface was then polished to a standard suitable for microscopy. A Ruhr dilatometer and a Gieseler plastometer were used for the determination of the plastic properties of the coals. These studies
showed that the pore structure of coke is largely determined within the plastic temperature range of the carbonization process. The microscopic observations of all coals fitted into a single general pattern when related to experimentally determined temperatures resulting from the Ruhr dilatometer curve.

As can be observed from Figure 2, initially pores appeared in large particles at a temperature near the softening point, while the medium size particles became porous at higher temperatures. No pore formation was detected at any temperature within particles <125μm in size. An increase in temperature induced an increase both in the number and the size of pores. More particles were observed to have pores and the large particles became multipored. With increasing temperature particles became more rounded and swelled into the interparticulate voids.

In the case of coals of zero fluidity, the above mentioned stage marked the end of the observed changes. However, for coals of higher fluidity, an increase in temperature, reaching eventually the temperature of maximum contraction, resulted in the continued swelling of the larger particles and the concentration of the small ones in the diminishing void spaces. The swelling of the more fluid coals continued until all the small particles were incorporated within the expanding cell walls of the larger particles thus leading to the loss of their separate identity. Above this temperature of complete fusion, the mean pore size increased reaching a peak value before it finally fell to a size which was practically unaltered at higher temperatures. The increase in the number of pores with temperature was interrupted by a transitional minimum at the temperature which corresponds to the maximum pore size. The size of these large pores was reduced before the resolidification temperature, thus leaving a more coherent structure. The growth of small almost spherical pores and fusion of the matrix near this temperature must have resulted in the formation of interconnected pores.

Above the resolidification temperature insignificant changes were observed apart from a slight reduction in the mean pore size. The compaction of the completely fused structures which occurred near the resolidification temperature aroused a great interest. The explanation that was given was that the large expansion of the slightly colder zone may press the compacting layer against the more rigid semicoke. An interconnection of pores possibly occurring at this stage may facilitate this process. This suggested explanation was further supported by the observation of a development of anisotropy in pore shape, with the largest dimension lying along the temperature isotherms.
A further study of the influence of charge density and particle size on the pore structure development showed that both mean pore and pore-wall sizes attained maximum values within the plastic zone. The new experimental findings were explained by the suggestion of two further processes: a) the rupture of some thin pore-walls during the post fusion expansion stage and b) a secondary pore nucleation occurring at higher temperatures during the compaction process.

It was shown that an increase of the charge density reduced the porosity, mainly the mean pore size of the resultant coke, whereas the mean pore-wall size showed negligible variation. The effect of charge density was attributed to the restriction of the expansion along the horizontal direction which is perpendicular to the oven wall.

No evidence was found for any systematic variation in the coke pore structure resulting from variations in the coal particle size distribution within the range considered.

Juranek et al. also studied microscopically the transformation of coal to coke and carried out a study of the morphology of the plastic layer as a function of coal rank.

They observed that for coals with volatile matter content between 25-30% the first step in the transformation was the formation of a continuous medium from the viscous deformed coal particles which was characterized by the absence of bubbles. The second step was the devolatilization which was obvious by the presence of a highly porous zone. In their view, the formation of the pores begins suddenly when the borders of individual particles are not identifiable. In addition to the melting zone with lack of pores there was another one rich in pores with very thin walls which was described as a froth zone.

In similar studies, Hautkappe found a difference between the high and medium rank coals. He observed that, in the case of medium-volatile-matter coals, during resolidification the compaction of the bubbles dominated their formation while the opposite happened during the preceding zone of maximum fluidity. There existed a mass transport in the plastic layer from the region of maximum fluidity to the semicoke which is expressed in the high porosity measured in the centre of the plastic layer. In the case of high rank coals no similar maximum was observed and this indicated that for these coals a different mechanism for the elimination of bubbles might exist.
2.4 POLARIZED LIGHT MICROSCOPY

The microtexture of metallurgical coke is characterized by a unique anisotropy of the organic substance as observed by optical microscopy. Microscopic examination, is carried out by viewing polished coke sections in plane polarized light.

Linearly or plane polarized light is the light in which the electric wave fluctuates in a single plane.\(^{21}\) Optically isotropic materials have the same values of optical properties in all directions whereas the properties of optically anisotropic crystals are direction dependent and these materials will have at least two values of refractive index (birefringent). The directions in which the maximum and minimum refractive indices are observed are called the slow and fast directions respectively.\(^{22}\)

The polarizing microscope has two polarizing filters, the polarizer and the analyser, which are usually set with their planes of polarization perpendicular to one another (crossed polars).\(^{21}\) Under these conditions isotropic materials appear grey. Anisotropic crystals appear black under polarized light when their slow direction is either parallel or perpendicular to the direction of vibration of the polarized light. If it is perpendicular then minimum reflection occurs and when it is parallel then reflected light is blocked by the analyser. When the slow direction is at 45° to the polarizer the surface appears light. Intermediate alignments appear grey. Coke samples would appear as a range of dark greys.

From this variation of shading with orientation of the carbon layer planes relative to the vibration direction of incident polarized light it can be deduced that the appearance of a carbon composed of small graphitic areas randomly orientated with respect to one another will be as illustrated in Figure 3.\(^{23}\)

With the insertion of a retarder plate into the optical system the orientation of the lamelliform structures can be assessed because different orientations adopt different colours (reflective interference colours).\(^{24}\) The thickness of the retarder plate is so chosen that a phase difference exists for linearly polarized light passing in the fast and slow directions. A \(\lambda\)-plate or \(\lambda/4\)-plate is used with the crossed polars and it is usually positioned so that its slow and fast directions lie at 45° to the polarizer.

If the carbon is ordered on a scale above the resolution of optical microscopy, it will appear yellow, purple or blue, depending on its orientation and if the sample is rotated those colours change in sequence. Purple colour originates at a surface of isotropic carbon or when the basal planes are parallel to the polished surface. With rotation of the specimen
stage the colour remains unchanged. Yellow and blue colours appear when a prismatic edge is presented at the surface. A rotation of the stage by 90° will change a yellow into blue through an intermediate purple. For anisotropic crystals the purple is light when the slow direction of the crystal is aligned parallel to the incident polarization and dark when the crystal is rotated through 90°.

The effect of using a λ-retarder plate with crossed polars is shown in Figure 4.23 The result is that varying orientations of the prismatic edges are now indicated by variations in tint rather than shading. Thus, when the surface of carbon or graphite is viewed under these conditions each visible isochromatic area is composed of aligned layer planes, the colour depending upon their common orientation relative to the polarizer and analyser. Changes in orientation over the surface can be assessed by noting how the colours change.22 Cokes can be characterized by the colour, shape and size of the isochromatic areas.

The highest degree of alignment is seen in natural graphite crystals, which consist of extended layers of fused hexagonal rings of carbon atoms. Depending on their behaviour when heat-treated, carbonaceous solids can be classified as graphitizing or non-graphitizing.7 Graphitizing carbons are formed generally from substances (including coking coals) which are inherently rich in hydrogen and poor in oxygen. In the early stages of carbonization as they pass through the plastic stage, the crystallites retain mobility and cross-linking is relatively weak. This leads to a compact, highly ordered structure in which neighbouring crystallites align themselves as near as possible and parallel to each other.

2.5 DEVELOPMENT OF OPTICAL ANISOTROPY IN GRAPHITIZING CARBONS

Early experimental evidence about the formation of anisotropic carbon was given by Taylor in his initial study of a thermally metamorphosed coal seam in Australia.25 Several studies followed including the carbonization of different kinds of materials which on heating pass through the fluid or plastic stage. It was found that their behaviour follows a general pattern.26
Their preliminary decomposition results in an isotropic pitch-like material. The general features of carbonization can be outlined in terms of the behaviour pattern of a typical material such as a petroleum pitch.

The first chemical process is the rupture of weak bonds followed by cyclization, aromatization and polymerization. Thus with increasing temperature, products of increased molecular mass and size are formed. When the essentially planar aromatic molecules reach a critical concentration and size (molecular weight >1000amu) van der Waals forces become sufficiently strong to establish parallel orientation. A process of homogeneous nucleation is considered responsible for the separation of the optically-anisotropic, nematic liquid crystals from the isotropic fluid phase in the form of spheres. The formation of these spheres is a reversible physical process. These anisotropic spheres are observed under polarized light as pin-pricks of light in the isotropic matrix.

A progressive increase in heating temperature leads to further polymerization within the liquid crystals resulting in their irreversible transformation into mesophase spheres. Brooks and Taylor showed the characteristic structure of the simple spherules formed in an extracted coal tar pitch. The layers are aligned perpendicular to the polar diameter but curve to meet the interface of the isotropic matrix at a high angle. The poles constitute anomalous regions but this is not clearly reflected since only slight departure of the droplet from spherical geometry is observed. An increase in the size and number of nucleated spheres at the expense of the isotropic phase is caused by further increase in temperature. Under favourable conditions the growth of the mesophase spheres leads to contact and coalescence thus forming large domains of ordered regions (bulk mesophase) which eventually solidify to semicoke. The mechanism of coalescence appears to be a simple process of interleaving of the mesophase layers.

The structure established on coalescence of the liquid crystals is maintained essentially in the resultant coke product, modified to a degree by further heat treatment. The characteristics of optical anisotropy of resultant cokes are controlled by the fluidity and the chemical reactivity of the system. The texture of the resultant carbon is mainly determined by both the extent of mesophase coalescence and by the deformation of mesophase. The latter may be caused by bubble percolation and also by mechanical means or convection currents.

The existence of non-fusing components within the plastic phase affects the growth and coalescence by congregating at the mesophase-matrix interface. Changes in the mesophase development can be also brought about by the presence of sulphur or oxygen...
which leads to a reduction in the size of the anisotropic units in the resultant coke. Heteroatoms inhibit mesophase formation by cross-linking reactions, which impair planarity, reduce viscosity and lead to small mosaic structures in the coke.

2.6 OPTICAL ANISOTROPY IN METALLURGICAL COKE

The development of optical anisotropy during carbonization of coals at atmospheric pressure was investigated by Patrick et al. In these studies hand-picked samples of vitrains were carbonized in open boats at 5K/min to various temperatures selected to cover the plastic temperature ranges of the coals and to 1000°C. Polished surfaces were examined using crossed polars and a retarder plate. The anisotropic entities observed in the polished surfaces were allocated according to size or shape into various categories termed fine, medium, coarse mosaic, granular flow and flow-type. The term flow type refers to components with extensively elongated isochromatic areas and does not necessarily imply flow during carbonization.

Their results showed that the development of the different types of anisotropy was strongly dependent on coal rank (Fig. 5). Low rank vitrains remain isotropic on heating. With increasing rank, fine, medium, coarse mosaic and granular-flow anisotropic components appear progressively in cokes. The cokes from prime coking coal vitrains contain granular flow as the major component but also small proportions of material in the other classes including flow type. Higher rank vitrinites exhibit basic anisotropy and their cokes contain flow type components and some granular flow. As the rank increases an increasing proportion of material exhibiting basic anisotropy, unaltered in form from that in the vitrinite but more intensely coloured becomes evident in their cokes.

The results showed that the development of optical anisotropy occurred within the plastic temperature range. In contrast to studies of an Australian coal, at no stage in the carbonization of U.K. coals was any clear evidence of spherical bodies as a precursor to the anisotropic entities observed. However it was recognized that such units could be present in a size range below the limits of resolution of the optical microscope. However, as Brooks and Taylor noted, mosaic structures could be formed during the carbonization of a range of materials without any indication of the intermediate stage prescribed for the carbonization of pitch. They concluded that in some instances there was a direct conversion into mesophase without the formation of spheres.
Nevertheless a role of liquid crystals was not excluded and it was suggested that the loss of volatile matter and the retention of fluidity are two significant factors in the development of optical anisotropy during carbonization of coals. The degree of structural order was considered to be dependent upon the balance attained during the plastic temperature range between the loss of volatile matter required to enable the necessary molecular rearrangements to take place and the retention of sufficient plasticity, when appropriate molecular constituents are available, to allow the formation of the liquid crystals which form the anisotropic bodies.  

In general, fine mosaic was the first stage in the formation of anisotropic textures. The initial fine grain mosaic was followed by progressively coarser grain mosaics.

A re-examination of high rank cokes led to the subdivision of the flow-type and basic categories into new types termed broad and striated flow, patterned anthracitic and plain anthracitic and to a suggestion of different development routes for the granular flow and the flow type components. Thus the granular flow components are formed through the intermediate formation of fine, medium and coarse components. While flow type is considered to be formed from basic anisotropic vitrinite either directly or via the intermediate formation of a kind of fine mosaics. The classification scheme described above is the modification of the system developed by Patrick et al. and is given in Table 1. Several classification schemes of coke textural components exist and Coin has given details of about fourteen of them.

Marsh developed a theory of coke formation from coals in terms of a process of liquid crystal development, from observations of the formation, growth and coalescence of spherical anisotropic liquid crystals during the carbonization of pitch-like materials and in the carbonization under high pressure of many other organic substances. He noted that with coals the anisotropic liquid crystals do not coalesce as observed in pitch carbonization, but maintain their identity. They do grow to position of close proximity and may fuse. This process provides a more coherent structure and further decreases fluidity.

The important properties of cokes, including mechanical strength and reactivity, are governed by the arrangement of the constituent carbon atoms. The principal features of the atomic arrangement are the alignment and size of carbon crystallites. The size of textural components is regarded as indicative of their chemical reactivity.
2.7 COOKING PRESSURE PHENOMENA

Coking pressure is a phenomenon which became important with the use of the double-heated wall, vertical, slot-type coke ovens. In the round beehive ovens, extensively used for coke production in the previous century, the coal could freely expand upwards and thus the swelling of the charge was accommodated by this free expansion. On the contrary in slot-type ovens the expansion of the coal horizontally to the heated wall is restricted.37

As early as 1915 Koppers and Jenkner38 reported that a coke battery in the U.S.A. had to be completely repaired because all the oven walls had been damaged due to carbonization of unsuitable coals.

The erection of the new, larger considerably higher ovens was accompanied by undesirable occurrences of distorted walls due to coking pressure and so the expansion of coal was more thoroughly investigated. The efforts were focused on developing a reliable test so that coal blends could be tested for safety prior to their use in the ovens.

2.7.1 Early studies.

Laboratory tests were first conducted in order to ascertain the safety of coal blends. In these tests, a small quantity of coal, placed in a small crucible, was heated from one side either at constant pressure or at constant volume.

A test developed by Korten in 1920 is considered as the first attempt to determine the swelling pressure that coals generate.39 In this test, 100g of coal were heated in a vertical, cylindrical iron crucible under standard conditions, in a gas-fired furnace. A perforated piston was placed on top of the charge. The movement of piston was recorded appropriately, and the significant measurement was the change in the volume expressed as a percentage.

This test was further developed in two directions and resulted on the one hand in the constant-pressure Koppers test and on the other hand in the constant-volume Damm and Hoffmeinster test.
Fowxell\textsuperscript{40} and Mott and Spooner\textsuperscript{41} were among the first workers who used modifications of the Koppers apparatus. Further developments of the Damm-Hoffmeinster test are the Baum-Hauser and the Nedelmann tests.

In the Koppers test, 80g of air-dried coal are placed in a steel crucible. A load of 1kg/cm\textsuperscript{2} is applied to the coal charge and both expansion and contraction of the charge are recorded as changes in the volume.

In the Nedelmann test apparatus, which in contrast to Koppers test is carried out at constant volume, 120g of air-dried coal are carbonized in a steel crucible and the pressure required to keep the coal at constant volume is recorded.

Furthermore, a number of larger scale tests which used several kilograms of coal have been devised. Their concept is similar to the smaller scale tests. A representative example is the large Koppers test which differed from the smaller test mainly in size and had a charge capacity of approximately 5kg.\textsuperscript{40} Only pressures generated in the coal charge greater than 8kPa were measured. This pressure was regarded as the maximum permissible limit on a coke oven wall. Another large laboratory test is the 'sole-heated' oven which constitutes an ASTM standard.\textsuperscript{42} In this test, a charge of approximately 35kg is heated unidirectionally from the sole and is subjected to a pressure of approximately 14kPa. The movement of the upper slab is followed by means of a cathetometer. Since heating in the above described tests is single-sided, the phenomena remain quite different from those occurring in a large oven.

Due to the difficulty of recording the wall pressure in a coke oven, early investigators felt that they should try to simulate the carbonization conditions occurring in a commercial oven as closely as possible by adopting double-wall heating.

Koppers and Jenkner designed a large-scale oven chamber in which both heating walls were movable.\textsuperscript{38} By fixing one wall the pressure exerted on the other wall during carbonization could be measured with the aid of a hydraulic system. This oven is considered to be the prototype of the movable-wall oven allowing a direct measurement of the coking pressure.

2.7.2 Movable-wall ovens.

Numerous movable-wall ovens exist throughout the world. All designs, without exception, are based on heating from two sides. One of their walls is mounted on a trolley
so it is free to move and the coking pressure developed during carbonization is expressed as a force exerted on the wall and is measured by means of a suitable device and is called the wall pressure. They are either gas or electrically heated and take coal charges ranging from 250-500 kg. As in the full-scale ovens, two vertical, plastic layers are formed, during carbonization, and progress gradually towards the center of the oven where they merge.

The Koppers or Russell oven is one of the oldest designs of movable-wall oven and it is fairly widespread in the USA. In this oven, approximately 250 kg of coal are carbonized in a coking chamber which measures 300x700x1100 mm. One wall is mounted on rollers and is equipped with a lever weight system for measuring the pressure developed against the wall. Soth and Russell used this oven to study the coking pressures developed by American coals. They conducted about 300 tests in which the coal was crushed 80 wt% below 3 mm and charged with low moisture content at bulk densities ranging from 785-850 kg/m³. The curves obtained by plotting pressure against coking time were classified into six types according to several characteristics of the tested coals.

Figure 6 shows examples of each of the types of pressure curves. Pressure curves of types I to III are all for coals or blends normally safe to use in commercial ovens. Coals which give curves II or III may give higher pressures when charged at higher bulk densities. Types IV to VI are pressure curves of coals that are dangerous to use in coke ovens.

In the U.K., the Pontypridd Test Plant Committee used a modified Russell type oven to study the behaviour of some 70 British coals and blends with volatile matter content in the range of 13-36%. A broad classification of coals into three types i.e., α, β, and γ (Fig. 7) was suggested according to their results. They also compared their results with those obtained using laboratory tests i.e., Koppers and Nedelmann tests. They concluded that there was no clear association of dangerous character as assessed by the Koppers test with high wall pressure in the test oven. The results in the Nedelmann test reflected qualitatively the maximum pressure developed in the movable-wall oven test but there were many exceptions.

A larger 400 kg movable-wall oven was employed in the Centre de Pyrolyse de Marientau (CPM), for an extensive investigation of the coking pressure phenomena. In this oven, the two walls were of corundum construction which allowed operation at higher temperatures and offered more strength and resistance to thermal shock. The force exerted on the movable wall was measured by a strain gauge balance which was mounted
at the exterior of the wall at the geometric center of the useful surface of the heating wall. They found four main types of coking pressure - time curves which are the most frequently encountered in their tests (Fig. 8).

By analysing the form of the curves they concluded that these resulted from the superimposition of two basic curves, each one of them corresponding to one of two phases. The first phase reflects the formation of the plastic layers parallel to the oven walls and their movement towards each other, and the second phase reflects the coalescence of the plastic layers at the ovens centre. Curves of types 1 and 2 were given by coals developing high pressures. Type 3 was characteristic of the stamped charges whatever the magnitude of the pressure, while type 4 was recorded for coals giving low pressures. Coals which give high pressures showed similar type of curves in the above mentioned work (Figures 6, 7, 8).

In the case of low-volatile coals, the pressure rises regularly from the start to the maximum. The other type of curve typical of high coking pressure shows a rapid rise in the pressure during the first hour. Then the pressure remains relatively constant during the course of the carbonization. When the plastic layers meet a further increase occurs until the plastic coal disappears.

Another approach to the problem of coking pressure is the measurement of the pressure of the gas at the centre of the plastic layer. These measurements were made both in the movable-wall and industrial ovens thus allowing comparisons to be made between the two sets of results. The gas pressure is measured by means of tubes introduced through holes either in the oven doors or in the charge hole lids.

Many investigators have reported studies of simultaneous measurement of gas pressure and wall pressure in test ovens. They found that the maximum gas pressure in the centre of the charge is related to the peak wall pressure. The gas pressure increases with the distance from the oven wall and attains its maximum value in the centre of the charge at the time of meeting of the plastic layers. This maximum gas pressure usually coincides with the peak of the wall pressure and is always greater. Different values were given for the ratio of gas pressure to wall pressure by different investigators.

Russell et al. used a test oven which had a silicon carbide thermocouple block in the back wall. This block contained 13 holes into which pressure probes were inserted, after the coal was charged and levelled, along the ovens width at 25mm intervals to lie parallel to the heating walls. The probes consisted of 6mm outside diameter steel tube, closed at the inner end, but containing seven holes drilled in a row, or alternatively a narrow
slit, as gas inlets which extended back from the end about 25mm. The outside ends of the tubes were connected to manometers containing water or mercury. Thermocouples were inserted into the pressure tubes to record the temperature. Readings of wall, internal pressure and temperature were taken at frequent intervals. They carried out 28 tests using coal blends from a wide variety of coals. Figure 9 illustrates the course of the pressures in a typical test. As carbonization proceeds and as the plastic layer passes the end of each probe there is a sudden rise in the gas pressure. When the plastic layer moves beyond that point the gas pressure drops quickly and that probe does not record again any gas pressure. When the plastic layers met at the oven centre, the recorded gas pressure was higher than the pressures at other points in the oven. The ratio of gas pressure to wall pressure in their experiments varied from less than one for low pressures to up three for high pressures. The gas pressure peak at different distances from the heated wall lasted longer the closer was the probe to the centre of the oven.

At the BCRA similar tests were carried out but they used a specially designed probe through which a stream of nitrogen could be passed. The internal gas pressure was taken to be the pressure necessary to maintain a slow flow of nitrogen. The flow also kept the probe unblocked. They carried out about 150 tests on a modification of their movable-wall oven in which they had increased the width, the wall thickness and improved the flue design. Figure 10 gives representative graphs from coals of types a, b, c. They also studied the influence of both charging and carbonization conditions on the internal gas pressure and it was found that internal gas pressures were influenced by the same variables as the wall pressures.

Similar technique was used by Janssen et al. for the measurement of gas pressure in the movable-wall oven.

BCRA, Russell et al. and Janssen et al. all reported measurements of internal gas pressures in full-scale ovens. They found that gas pressures measured in the centre of the full-scale oven were similar in magnitude to the maximum internal gas pressures recorded in the movable-wall oven. They concluded that the gas pressure recorded in the centre of the full-scale oven is a good indication of the wall pressure provided that the pressure probes accurately recorded the pressure when the plastic layers meet.

M. te Lindert claimed that pressure probes distort the plastic layer too much so thin probes should be used to measure internal gas pressures. By using three modifications of thin probes, one with outer diameter 1.4mm, in a 20kg oven internal gas pressures much higher than those in a 300kg oven using heavy probes, were recorded.
At the CPM, ordinary steel tubes (6-10mm) were used which were inserted horizontally into the charge through holes in the oven door and connected to transducers thus allowing continuous electrical recording. These pressure probes, equipped with thermocouples, were closed at the end with contact with the coal but had two slits 1mm wide by 20mm long diametrically opposite and in the vertical plane. Due to small differences in temperature between the heating walls the thermal centre and the geometric centre of the charge did not coincide. Therefore they used an assembly of tubes (three or five) instead of one tube. Measurements of gas pressure and temperature at different distances from the oven wall showed that peaks coincide with the passage of the plastic layer past the probe. The pressure peaks are always greater than the coking pressure recorded at the same time the difference increasing with increasing distance from the heating wall (Fig. 11). They also made measurements of gas pressure and temperature in the neighbourhood of the top of the charge, the oven sole and the doors. They made the following observations: a) two plastic layers are formed at the beginning of the carbonization parallel to the sole and the roof and progress towards the centre of the oven and b) no plastic layers parallel to the doors are formed. For the ratio of gas pressure/wall pressure they found a value around 0.5.

The differences in the ratio of maximum gas pressure and peak pressure reported by various investigators were attributed to differences in the test equipment and procedure. In the movable-wall oven although coking mainly proceeds from the heating walls simultaneously considerable coking proceeds inwards from sole, roof and questionably from the doors and this reduces the area of the plastic layers which meet at the oven centre.

The CPM proposed the following formula for the time of meeting of the plastic layers at the oven centre:

\[
\frac{P_s}{P_i} = \frac{S_i}{S} 
\]

where \(S\)=the lateral surface of the charge, \(S_i\)=the area of the projection of the plastic layer on the central plane at the time of the wall pressure peak, and \(P_i, P_s\) are the internal and wall pressure at the same time. \(S_i\) was evaluated by discharging test ovens at the moment when the two principal plastic layers joined together. The ratio \(k=S_i/S\) by definition is 1 at the moment of charging, during the course of carbonization it decreases due to the end effects and it becomes zero after the coal has resolidified.
In a full-scale oven the end effects are small compared to the height of the wall so that the ratio $S/S$ is approximately 1 and coking wall pressure should be equal to the centre maximum gas pressure.

It was suggested that if a blend carbonized under certain conditions in the test oven produces a wall pressure $P$ then the pressure to be expected in a large oven working under the same conditions must be of the order of $2P$.

Gransden et al.\textsuperscript{49} carbonized 14 coal blends in three different pilot ovens, a gas-fired Koppers (Russell) oven, a 310mm electrically heated and a 460mm also electrically heated. The same blends were carbonized in industrial ovens and a comparison was attempted of industrial and pilot oven coking pressures and coke quality.

From the results of their pilot oven studies, they found that wall pressures were approximately half the gas pressures. They assumed that these results implied that the plastic area over which the centre pressure occurs had been reduced to about one half the wall area and therefore the gas pressure was totally transmitted to the wall and was solely responsible for the wall force. A more detailed analysis for each oven revealed differences between them. Thus the ratio of gas pressure to wall pressure increased from 1.8 for the 460mm oven to 2 for the 310mm and 2.59 for the Koppers oven. The variations were explained by means of differences in the end effects of each oven. They concluded that pilot ovens do not simulate industrial practice perfectly and do not reproduce industrial coke quality or coking pressures, probably because of increased end effects and insufficient static load on the coal.

\subsection*{2.7.3 Setting of safety limits.}

The numerous studies carried out in movable-wall oven and full-scale ovens aimed essentially to control the phenomenon of coking pressure and protect the ovens from damage caused by excessive pressures.

For an assessment of a coal blend, the movable-wall oven test is generally employed and the resulting maximum wall pressure is used to classify the coal blend as safe or dangerous with comparison to previously established limits. The bulk density of the blend in the test oven is considered extremely important. It should be at least equal to the average of the full-scale oven and preferably somewhat higher.
Whether a pressure is excessive or not depends not only on what pressure is exerted but also on what pressure the oven wall can withstand. So various efforts have been made to assess the strength of the coke oven walls.

The wall strength requirement is governed largely by the peak unbalanced coking pressure that is exerted on the walls during the coking process. These unbalanced pressures cause wall bending in the horizontal direction which must be stabilized by the vertical gravity loading, including the weight of the roof and the wall, because the joints in the wall have no consistent tensile strength.

Koppers and Jenkner reported a study of a specially built coke oven wall which was subjected to lateral pressure from a hydraulic press. They showed how low is the resistance of the coke oven wall against lateral pressure. Initial cracks appeared in the wall when the pressure was approximately 9kPa (1.3psi) and the rate of bulging increased rapidly as the pressure rose to 12.8kPa (1.9psi). On the basis of these results from a cold wall they suggested a very low safe limit of 1psi.

A very low limit restricts flexibility in choosing coal sources, coal blends and carbonization conditions. Thus, Russell et al. compared the results of several hundred coals carbonized in the Russell movable-wall oven and, taking into account the behaviour of these coals in commercial ovens, established the following safety limits for coals carbonized in coke ovens:
1) Coals developing a pressure greater than 2psi are dangerous.
2) Coals developing a pressure greater than 1.5psi could be dangerous when carbonized regularly in ovens taller than 3m.
3) Coals that give pressures less than 1.5psi are safe.

On the basis on their work in 1948 and 1952, BCRA concluded that a blend of coals is safe if the pressure that develops in their test oven is <2psi. This limit was confirmed by further work done at BCRA in 1956. In this work they charged several blends to commercial ovens which were at the end of their working life and to a movable-wall oven. They measured the movement of the walls in the full-scale ovens by special apparatus and the walls were examined during the course of the test and after the battery had been cooled down to determine the movement and ascertain the damage.

They suggested that an elastic deflection of commercial oven walls up to 0.5" can take place without the appearance of cracks. Beyond that point further deflection does not occur readily and cracking takes place.
In the 1960's and 1970's, the construction of tall, 6m or more, coke ovens became prevalent. These ovens were operated under the assumption that coking pressures under 2psi were safe. The result was that in some cases these ovens sustained serious, early refractory damage. It was reported that a 6m battery had suffered progressive damage and had to be shut down after less than five years of operation. The investigations to determine the causes of the premature failure included a structural analysis of a 6m wall. McDermott carried out a mathematical study of a 6m oven wall subjected to pressure from one side. From this analysis the unbalanced lateral pressure that could cause collapse was calculated to be just above 1.75psi (12.1kPa). By taking into account the recommended live load factor of 1.7 as well as serviceability relative to cracking, it was recommended that the allowable unbalanced lateral pressure should not exceed \( \approx 1 \) psi (6.9kPa).

After having estimated the pressure on the battery wall for a given coal blend in order to compare it to the above values McDermott suggested that the wall pressure and the internal gas pressure measured in a movable-wall test should be considered as a lower and upper bound respectively.

2.7.4 Laboratory-scale ovens designed to measure internal gas pressures.

The movable-wall oven is widely accepted as the safest and most reliable method of coking blend assessment. With this test it is easy to reproduce plant-scale variables such as width, bulk density and heating. It is however time consuming and requires a large quantity of coal. It is also generally accepted that it gives lower values of coking pressure than those encountered in practice because of the end effects. It is desirable to be able to test quickly coking blends using a small quantity of coal (some kilograms). Therefore interest has been currently focused on the development of a small laboratory test to measure internal gas pressure. These new devices use two sided heating.

At the CPM, they developed a small apparatus for measuring the gas pressure during the coalescence of the plastic layers. The test vessel was a cylinder with 310mm diameter, 200mm long containing 10 to 12kg coal at bulk density 850kg/m\(^3\) and was heated within an electrical furnace. By inserting a pressure probe at the centre of the charge they recorded the gas pressure which is used as an indication of coking pressure. The test time is 4-5 hours and the rate of heating in the plastic zone at the charge centre is 2-3°C/min. Coking pressures measured by this small oven were constantly lower than
those obtained in the 400kg movable-wall oven with some degree of scatter. An unusual feature of their design was that the charge was heated asymmetrically by maintaining the upper part of the furnace at a higher temperature than the lower part to avoid the formation of sealed pockets of gas.

At Coal Research Establishment\textsuperscript{2} (CRE) a 8kg carbonization apparatus (20cm width x 25cm height x 20cm length) was developed. It was heated electrically from silicon carbide elements arranged in three zones for uniform heating distribution. The oven was designed for measuring both wall and gas pressures although finally the gas pressure was adopted as the main parameter for the test since it showed the least variation. The heating rate through the temperature range of 350-550\textdegree C was 4\textdegree C/min. The coking time and the charge density were 5.5h and 800kg/m\textsuperscript{3} respectively.

The gas pressure was measured using a twin gas pressure probe placed side by side at the charge centre, each probe being of 6mm outside diameter. They tried to relate the results obtained in the 8kg test oven with those of the movable-wall oven with a wet charge capacity of 330kg, carbonization time 18h and final temperature 1050\textdegree C. Although some of the tested coals gave wall pressure in the movable-wall oven, they did not give any pressure in the 8kg oven. Because of the small height of the coal charge there exists insufficient headload to prevent free upward expansion of the coal during carbonization and consequently this expansion of the charge acted as a pressure relief mechanism. It was concluded that it was not possible to use the internal gas pressure measured in this oven as general guide for the safety of the coal blends.

A small laboratory oven capable of heating coal from one or both walls for the measurement of internal gas pressure has been developed (Fig. 12).\textsuperscript{1} The oven consisted of a thermally insulated chamber 25cm long, 17cm wide and 22cm high and was heated by elements located behind two vertical walls. The heating of the walls was controlled separately. Approximately 1.4kg of coal was placed in the steel and insulating board charge box sized 19x12x14cm. Its two long steel walls faced the heated walls. For the measurements of internal gas pressure a probe consisting of a 6mm diameter steel tube was inserted horizontally through the centre of the charge, having two slits measuring 10mm long and 1mm wide as gas inlets. A 2mm diameter stainless steel sheathed K-type thermocouple was inserted down the tube so that the tip was in the centre of the charge adjacent to the gas inlets. The open end of the 6mm tube was fitted to a pressure transducer. The outputs of the transducer and the thermocouple were recorded on a twin-pen chart recorder. Seven coals known to give a range of wall pressures in a movable-wall oven were tested using two- and one-sided heating. At high bulk densities,
the recorded curves were multi-peaked for the coals giving high internal pressures. Using lower bulk densities, obtained by the addition of water, the curves were smoother even for the coals giving high pressure. Less difficulty was encountered in obtaining internal gas pressure from charges heated from only one side in which case smooth single peaked pressure curves were observed even at high bulk densities. Figure 13 gives curves of internal gas pressures recorded for the same coal for double- and single-wall heating. Gas pressures in the single plastic layer were approximately half of those observed during double wall heating. The measured gas pressures ranked the coals in the same categories from safe to dangerous as wall pressures determined using a movable-wall oven.

2.7.5 Prediction of coking pressures by determining the plastic properties of coals.

Several investigators have tried to assess the dangerous character of coals by indirect methods by using data obtained from the measurement of the resistance of gas flow shown by softened coal during carbonization or from direct measurements of fluidity of the coal during carbonization and measurements of the rates of volatile matter evolution. Although work of this nature did not provide directly any practical data, some of them were intended as early fundamental studies of the causes of the development of pressure in oven charges.

Soth and Russell\textsuperscript{43} combined the curves obtained by the Gieseler plastometer and the rates of volatile evolution with those of the wall pressure versus time recorded in their movable-wall oven. They attempted to relate the pressure to the fluidity and to the rate of volatile matter evolution (Fig. 14).

The regions in the plastic layers where the fluidity was less than 50div/min (1.5X10\textsuperscript{4} poises) were considered as the primary sources of carbonization pressure.

From their experiments they concluded that the temperature at which the viscosity of the softened coal system becomes 50div/min on the ascending portion of the Gieseler curve is a primary indication of the degree of the peak pressure when the plastic layers meet, while the extent of the temperature interval from 50div/min to resolidification on the descending portion of the Gieseler curve is the primary indication of the degree of
Recent investigation of the plastic layer at CPM\textsuperscript{39} included a permeability study in which the pressure needed to maintain a constant flow of nitrogen through a thin probe inserted in the middle of the charge in a sole heated oven was measured. High VM coals showed a maximum in the pressure drop in the temperature range 420-430°C which corresponds to the plastic temperature range while, for high rank coals they observed a maximum in pressure drop in the temperature range 600-650°C which was much more intense than the drop corresponding to the plastic temperature range. Intermediate rank coals showed a less accentuated maximum in the area 500-600°C.

2.8 PARAMETERS INFLUENCING COKING PRESSURE

From the early 1950's, the movable-wall oven and other similar-sized pilot ovens have been used to evaluate coals for coking. Pilot scale testing is cheaper than full-scale oven testing and generally provides good guidance regarding the behaviour of coals on the larger scale. Some reassurance comes from comparing internal gas pressures generated in the movable-wall and full-scale ovens. Most of the work reported in the literature concerning the factors influencing coking pressure has been obtained using pilot-scale ovens.\textsuperscript{39} Many factors have been found to affect the magnitude of coking pressure. They can be separated into three broad categories specifically: 1) inherent characteristics of the coal, 2) coal preparation and physical properties and, 3) oven operating conditions.

2.8.1 Coal.

Early investigations showed that dangerous pressures were encountered when charging coals with volatile matter content on the dry ash-free basis between 16-30% and never with coals with lower or higher volatile matter content.\textsuperscript{11}
It has been found that the strongly expanding coals principally consist of bright coal while those with a higher proportion of dull coal show less expansive force. From petrographic investigations therefore some conclusions can be drawn as to the degree of expansion of coal.\textsuperscript{38}

A series of experiments was conducted by the Bethlehem Steel Corporation\textsuperscript{54} on the influence of coal composition on coking pressure using a 18" test oven and a large variety of single coals and coal blends. They found the general relationship between coal rank (as shown by vitrinite reflectance) and coking pressure (Fig 15a). From this figure, it can be seen that high coking pressure tends to be generated by some, but not all, low-volatile matter coals with reflectance \(> 1.35\%\). Figure 15b shows that coking pressure not only increases with an increase in coal rank but also increases with decrease in inert content. Coal rank and inert content have a synergistic interaction. At any given level of rank, coking pressure tends to be lower if the coal has a high inert content. When only the effect of the low-volatile matter coal is taken into account the pressure generated by the coal blend increases with an increase in reflectance of the low-volatile matter coal and this increase accelerates when the reflectance of the low-volatile matter coal goes above 1.65\%. A knowledge of the rank does not however permit the assessment of the danger of coking pressure from a coal with any degree of certainty. It can be said that between 18-25\% VM the danger is great and between 25-28\% VM it still remains though to a lesser degree. Low volatile coals with reflectance \(> 1.65\%\) and low inert content produce high pressures whether coked alone or in blends.

\subsection*{2.8.2 Oxidation of coals.}

Oxidation of coals reduces the maximum plasticity and the plastic zone narrows.

It has been found that oxidation of some coals initially increases the coking pressure but thereafter there is a fall in dilatation and an abrupt reduction in coking pressure. At the same time the M10 index increases.\textsuperscript{55}

Fourier transform infrared (FTIR) studies suggest that in the early stages of oxidation the main functional groups formed are carbonyl and carboxyl. At higher degrees of oxidation, evidence indicates a significant increase in ether, ester and phenolic groups. The loss of plastic properties on oxidation is attributed to the formation of ether and ester cross-linkages.\textsuperscript{56}
The effects of air oxidation of three Spanish coals was investigated at INCAR using the Koppers-INCAR test which is a modification of the Koppers test. From their results they concluded that, for coals which were characterized as "dangerous" by their test, the oxidation increased their dangerous character to a maximum at a certain level of oxidation after which it decreased sharply. For a coal characterized as safe by their apparatus, there was no appreciable effect from air oxidation.

At CPM, studies of the influence of oxidation on the low permeability between 500-600°C exhibited by high rank coals showed that the permeability was increased with oxidation. This was attributed to the increased open pore volume in oxidised coals. There is a general agreement that it is difficult to reduce the coking pressure by oxidation without simultaneously impairing coke quality while moderate oxidation may increase the pressure.

2.8.3 Studies of coal blends.

Meltzheim and Buisine made a series of experiments on the behaviour of blends regarding their coking pressure. The blends were charged by gravity at a moisture content of 3.5wt% and simple crushing to 80wt% under 2mm. From their results they concluded the following:

1) Coal giving a medium coking pressure when charged alone affected the coking pressure of a dangerous coal almost linearly as a function of the blend composition.
2) High-volatile matter coals which give no coking pressure, decrease the pressure more rapidly than in proportion to the amount added. So they are more effective in reducing the pressure. The effectiveness of such coals is greater the lower their rank.
3) Semi-anthracite (low VM) behaves differently. If it was crushed with the blend the effect on lowering the pressure was marked but there was a marked deterioration in coke quality. On the other hand if it was crushed separately (95wt% <1mm) an addition of 15wt% was sufficient to decrease the pressure and the coke quality was only slightly reduced. Semi-anthracite which is an inert increased the viscosity of the coal during fusion and this impaired the cohesion of the coal. It also reduced the contraction of the semicoke while with the addition of high volatile coals the contraction was increased.
They also observed blends which gave pressure greater than that generated by individual coals when charged alone. This occurs when a slightly fusible, low-volatile coal is associated with a very fusible coal. Then the fluid conditions allow the dangerous character of the low-volatile coal to be expressed.

At BCRA,\textsuperscript{44,46} they found that, as regards the development of swelling pressures, the behaviour of a binary blend, depends largely on the character of the coal which is in excess in the blend. From their studies on the effects of blending they concluded that:
1) coking pressure occurs only with blends with VM < 24%.
2) 30wt% addition of weakly-coking coal considerably diminishes the dangerous properties of a low-VM coal.
3) in blends of high/low VM coals, a decrease in pressure occurs on increasing the portion of high VM coal.
4) in ternary blends with similar VM content, the addition of 15wt% of an almost non-coking coal prevented the development of any coking pressure.

2.8.4 Effect of pitch addition.

The decrease in availability of coals of high rank led to an increased interest in the use of pitch additives in coal blends for the making of metallurgical coke. Pitch can behave as bridging agent and improve the strength of the resultant coke.\textsuperscript{58}

The pitch: 1) modifies the plastic state and this modification is associated with hydrogen transfer reactions involving movement of hydrogen from the pitch to free radicals thus stabilising the plastic state, 2) widens the plastic layer and 3) increases the evolution of VM.

The addition of pitch to a coal tends to increase the coking pressure but the magnitude of the effect depends on the nature of the coal.

2.8.5 Effect of inerts.

It was found that relatively small proportions of inerts suffice to reduce considerably the pressure of a coal, while the particle size of the inerts has a very large effect.
The inerts may have the following effects: 1) a diluent effect on the coal; since they do not change in volume, the space available for the coal to swell increases.

2) particle size effect; if the size of the inert is finer than the coal it increases the average fineness, thus decreasing the pressure.

3) specific action; they absorb a certain amount of tar and bitumen, reducing the fluidity and swelling of coal, the finer and more porous are the inerts the greater the effect.

4) modify the contraction of the charge after resolidification.

5) inerts may increase the permeability of the plastic layer.

At BCRA, they studied the addition of breeze on coking pressure. Generally the average wall pressure decreased with increasing proportion of breeze. In another series of tests, carried out with a type e coal (see Figure 7) with up to 30wt% coarse breeze, they found that the maximum internal gas pressure decreased with the addition of more than 5wt% breeze while the maximum wall pressure was not appreciably reduced until more than 10wt% was added.46

A U.S.A. patent for reducing the coking pressure suggests the addition of 2-8wt% of flakes formed of sawdust or other inert materials. Their action is considered to be the disruption of the plastic layers in the oven charge, thus providing the necessary passage for the gases.59

2.8.6 Effect of oil addition.

The addition of oil in coal blends changes the bulk density at constant moisture content and decreases the pressure. The added oil acts as a diluent and a reduction in pressure can be achieved without damaging the mechanical properties of the resultant coke. It was observed60 that the addition of anthracene oil decreased the wall pressure of coals considerably while the maximum in the pressure was observed at a very low temperature, <300°C. This was attributed to the "balloon effect" i.e., the volatiles from the oil formed at low temperatures become trapped between the advancing plastic layers and their accumulation leads to the development of pressure.
2.8.7 Effect of moisture.

An increase in the moisture in the charge decreases the pressure by decreasing the bulk density.

The use of wet charges makes the coking process very uneven and highly disturbed. The steam acts on the coal particles affecting their ability to absorb the liquid pyrolysis products. The moisture breaks through the plastic zone at different points and so by travelling along the chamber wall reaches the gas free space. The result is a highly deformed plastic layer.

The joining of the plastic layers is spread chronologically and locally over individual sections. So the pressure on the wall manifests itself only in a reduced form.

On the other hand during carbonization of preheated charges the plastic layers formed converge with parallel faces to the heating walls and at the same time practically join together over the entire length and height of the chamber thus the pressure on the wall attains its maximum value.

During carbonization in slot-type ovens, the moisture content across the charge rises steadily, in comparison with the moisture of the original charge, as moisture is distiled towards the oven centre.

Several investigators measuring internal pressure in the full-scale ovens recorded a peak pressure coinciding with the temperature reaching 100°C at the oven centre. This peak was called the water or steam peak and was attributed to the fact that the steam can no longer condense in this region of the oven and must be expelled. Eventually it becomes trapped within the plastic envelope.

Khan et al. found that the average water peak pressure depended only on the coal moisture and decreased as moisture increased suggesting that the bulk density is the important factor.

2.8.8 Effect of bulk density.

Bulk density is regarded as the most important of the variables affecting coking pressure. By increasing bulk density a safe blend can develop very high pressures.
As long as 1906 it was proved that the danger of damage to the oven increases with greater charge densities.\(^8\)

With the erection of large ovens, the influence of bulk density of coal on the degree of expansion became more important because the coal charge became denser on account of the increased height of the fall during charging.

In a literature review on coking pressure phenomena, Harris et al.,\(^{39}\) describing a series of research studies on the influence of bulk density on coking pressure, gathered that a lack of agreement exists regarding the nature of the functional relationship between test oven wall pressure and bulk density. Thus some researchers claimed that the logarithm of wall pressure with bulk density gives a straight line with slope 0.1, while others suggested that this relationship is better represented by a curve. Benedict et al.,\(^{54}\) by plotting peak wall pressures against bulk density, found a graph consisting of two intersecting lines (Fig. 16). They concluded that at densities above 800kg/m\(^3\) (dry), the rate of increase in pressure with increasing bulk density is enhanced.

Results at BCRA\(^{46}\) showed that gas pressure also shows the same variation with bulk density as wall pressure. They concluded that a given change of bulk density produces a given change in pressure irrespective of the method employed for bulk density control.

More recent work on the influence of bulk density on coking pressure has been done by Meltzheim and Buisine.\(^{55}\)

In their tests a single blend was used with different bulk densities. The variations in bulk density were achieved in different ways such as oil addition, preheating treatment, variations in moisture content. They found that bulk density has a large influence on the coking pressure and it is probably the most important factor affecting the pressure developed by any coal or blend charge.

2.8.9 Effect of particle size.

When coal particles differing in size are heated, the conditions for the transport of the gaseous pyrolysis products from the middle of the particle to the surface will differ.\(^{63}\) The larger the particle the greater will be the pressure developing inside it as a result of the pyrolysis of the organic mass. This promotes condensation which exerts a major
influence on the subsequent thermal changes of the coal substance. It has been found that the initial softening temperature increases and the plastic temperature range becomes smaller as the particle size decreases but the viscosity of the plastic mass increases.

It is difficult in practice to analyse separately the influence of bulk density and particle size on coking pressure. It is known in fact that an increase in the fineness of the blend involves a reduction in charge density and a reduction in coking pressure.

The independent influence of crushing on coking pressure was studied by Meltzheim and Buisine. They examined the influence of the degree of overall fineness of the blend, the degree of fineness of each blend constituent (differential crushing) and finally the effect of the mode of crushing i.e., the shape of the size distribution curve. They found that at practically constant density, the particle size has a very marked effect on coking pressure, fine crushing reducing the pressure.

Crushing the constituents of a blend separately did not seem to present any particular advantage. Their tests showed that systematic crushing can in certain cases have a specific effect i.e., at the same degree of fineness the pressure is lower than with simple crushing. They concluded that the pressure depends much on the proportion of coarse particles (above 2-3mm).

By examining the simultaneous action of bulk density and crushing they found that the effect of one of the factors depends on the level of the other. Thus the effect of density is greater, the coarser the crushing and similarly, the effect of crushing is more pronounced, the higher the density.

2.8.10 Effect of oven width.

The effects of changes in width of the oven chamber, studied using pilot ovens, on the wall pressure is not consistent. In the area of 6-13in, the oven width seems to have a substantial effect; decrease of wall pressure with increasing width. However, for greater widths the effect is small or negligible.

At BCRA by using two different ovens with widths 12 and 16.8in, they found no significant difference between the pressures developed by a given coal when carbonized under similar conditions of bulk density and flue temperature.
Harris et al.\textsuperscript{39} reported a good correlation between wall pressure measured in both 6in and 12in wide ovens. The plastic area/wall area ratio was about the same for both these widths.

The coking pressure value measured in a movable wall oven is associated with the ratio \( K \) given by\textsuperscript{11}:

\[
K = \frac{\text{surface area of plastic zone}}{\text{surface area of heating wall}}
\]

When the width of the chamber is increased so is the carbonization time. So more time is available for carbonization to progress simultaneously from the sole upwards and the roof downwards, the final plastic layer therefore has a smaller area in a wide oven than in a narrow one. This was confirmed by direct measurement of the plastic zone area through premature pushing. Thus widening of the chamber involves a reduction in coking pressure but the magnitude of the variation depends on the blend considered while generally remaining small.\textsuperscript{11}

\section*{2.8.11 Effect of flue temperature.}

An increase in flue temperature: 1) increases the heating rate which in turn a) shifts the softening and resolidification temperatures to higher values widens the plastic temperature range,\textsuperscript{63} b) increases the flow of gas liberated in the plastic layers, c) increases the thickness of the plastic layer,\textsuperscript{64} d) reduces the viscosity and 2) reduces the thickness of the plastic layer due to the increase of the temperature gradient. These effects act on opposite directions so the final effect can be very small or insignificant.

By studying this effect the BCRA\textsuperscript{44} found that with two blends and one coal, higher heating rates resulted in some increase in wall pressure. However with one coal the opposite was observed and with two other coals they found no obvious effect.

Meltzeim and Buisine\textsuperscript{55} tested two blends at three levels of temperature 1020°C, 1120°C, 1200°C. One blend showed an increase in both wall and gas pressure with increasing flue temperature while the effect produced using the other blend was not significant.

Khan \textit{et al.}\textsuperscript{62} studied the influence of coking rate on gas pressure in commercial ovens. They concluded that increased coking rates did not significantly increased the pressure of the charged blends for the range of coking rates used (the centre of the oven reached 900°C in 12.3-18.3h).
Others have found that coking at faster rates increase the pressure in a consistent way (coking rate is based on time required to reach a coke mass centre temperature of 980°C) (Fig. 17).

2.9 COKING PRESSURE DEVELOPMENT

During carbonization coal passes through the plastic stage and volatile matter evolves during and, to a lesser extent, after that phase. It is generally accepted that coking pressures arise in the plastic stage. In a coke oven chamber, two vertical plastic layers parallel to the heating walls are formed from the beginning of carbonization. As the carbonization proceeds these layers move towards the centre of the oven. At the same time similar horizontal layers are formed at the top and bottom of the charge. These are joined with the two vertical layers and the whole forms a continuous region that surrounds the uncarbonized coal and it is referred as the "plastic envelope". The permeability of the plastic layers is low in the case of coking coals. According to Foxwell, with a strongly-plastic coal there is a possibility that a pressure may set up within the cool zone of unconverted coal. The sum of the internal pressure within the plastic layers and between them is transmitted through the coke layers to exert a pressure on the walls. When the plastic layers meet at the oven centre, the central mass of coal receives heat from both sides simultaneously whilst the temperature of the coal is being raised through out the plastic temperature range. The result is an acceleration in the coking rate thus leading to a faster rate of gas evolution with greater resistance to its escape. This results in peak values in both internal and wall pressure.

Russell et al. considered that plastic layers are also formed parallel to the oven doors and thus a complete continuous plastic envelope exists around the unconverted coal as soon as the coal is charged. Thus, the volatile matter evolved from the cold side of the plastic layer is entrapped within the envelope. At the time that the layers are about to meet the rate of heating increases and so the amount of gas evolved increases which results in an increase in pressure. After the resolidification into coke, a rapid decrease in pressure occurs due to the disappearance of the envelope.

A more recent view is that of Meltzeim and Buisine. According to them there is not sufficient heat for the formation of plastic layers parallel to the oven doors. Consequently, a plastic sleeve (tube) is formed from the two principal plastic layers and the two secondary ones, which is roughly rectangular but widens near the doors because of the
heat losses (Fig 18). They suggested that the coking pressure results from the pressure of the gases within the plastic layers and they are transmitted to the walls via the coke and semicoke already formed.

The gases that are evolved on the side nearest the charge centre contain tars which condense and then revaporise as they are captured by the plastic layer. The impregnation of the coal by condensed tars modifies the viscosity of the plastic layer. The internal gas pressure depends very much on the nature of coal and the carbonization conditions. It seems that it is connected to the established equilibrium between the swelling of the plastic layer, the contraction of the semicoke and, to a certain extent, to compression of the uncarbonized coal.

The principal phenomenon is that of the internal gas pressure within the plastic layer while the wall pressure results from the transmitting of the gas pressure through the semicoke and coke to the walls. The magnitude of the internal gas pressure is likely to depend on the rate of evolution of the gaseous matter within the plastic layer and the resistance of the plastic layer to its flow i.e., the permeability of the layer.\textsuperscript{45}

However the rates of devolatilisation in the plastic temperature range are higher for the coals with high VM content and yet these coals do not give high pressures. Thus the permeability could be the most dominant factor in the development of internal gas pressure.

Gryaznov noted that the maximum rate of volatile matter evolution for high rank coals is near the resolidification temperature while at CPM\textsuperscript{53} they found a relationship between the maximum wall pressure in the movable-wall oven and the rate of evolution of the remaining volatile matter near resolidification temperature.

Klose \textit{et al.},\textsuperscript{65} using a single-heated wall oven observed that the permeability is a minimum in the centre of the plastic layer and maximum in the product of resolidification.

In the studies of Hautkappe,\textsuperscript{20} permeability was considered to be due to two contributions. The first is that of the open porosity existing in the plastic zone, ultramicroporosity permitting the molecular flow and macroporosity permitting the viscous flow. The second contribution comes from the flow which follows the bursting of the devolatilisation bubbles.

This phenomenon is described as follows. In the region of the plastic layer adjacent to the semicoke the bursting of the bubbles prevails over their formation while in the centre
of the layer the opposite occurs. Thus, there is a transfer of mass from the centre of the plastic layer to the zone adjacent the semicoke manifested by the maximum in porosity in the centre of the plastic layer.

In the case of coals that give high pressure, Hautkappe observed that this maximum was replaced by a minimum in the coal zone adjacent the plastic layer. The proposed explanation was that for these coals the second contribution in permeability i.e., the bursting of bubbles is low and this assumption was supported from the absence of a maximum in porosity in the centre of the plastic layer. Since the escape of gases is limited, the pressure in the area of the plastic layer increases and brings about a compaction of coal which results in the observed minimum of porosity.
2.10 OUTLINE OF THE RESEARCH

It is apparent from the literature review that, when coals are charged to slot-type ovens, gas pressures generated within the plastic layers are transmitted through the coke and semicoke to exert lateral pressures, sometimes dangerously high, on the oven walls.

The present study forms part of a wider project planned to probe the coking pressure generation and its association with coke structure development. In the first part of the project it was shown that the internal gas pressures could be measured in the centre of a small laboratory oven.

The objectives of the present study were, firstly, to seek links between the magnitude of internal gas pressure observed and the structure of the resultant cokes and, secondly, to study the development of the porous structure during the plastic temperature range in an attempt to identify possible indications which connect the processes occurring to the formation of the internal gas pressure in the plastic layers.

Using the small laboratory oven mentioned earlier coke samples were produced which were examined using:

i) polarized light microscopy to determine the textural composition of the coke
ii) image analysis to characterize the coke pore structure
iii) diametral compression test to determine the tensile strengths

These data provided a characterization of the structural composition and attempts were made to relate the optical anisotropy and the pore structure parameters with the internal gas pressure.

To study the development of the porous structure during the plastic temperature range, coals were carbonized in a small oven heated from one side and polished blocks containing the carbonized products were examined by image analysis techniques.
3 EXPERIMENTAL

3.1 COALS USED

The seven coals used in the present study and their proximate analysis, Gray King coke types, British swelling numbers and U.K. dilatometer results (Table 2) were kindly provided by the British Coal Corporation.

The coals which originated from U.S.A., Canada, U.K. and Australia, ranged in volatile matter content from 17.2 to 28.5wt% (daf).

The wall pressures of these coals recorded in a 300kg movable-wall oven at the Coal Research Establishment of British Coal are given in Table 3. The gas pressures for double- and single-wall heating, measured using the small laboratory-scale oven described previously, are also listed in the same table.

The coals were crushed to normal industrial specification, i.e., approximately 80wt% less than 3mm. They were stored under water in buckets and prior to their utilisation they were air-dried overnight.

3.2 CARBONIZATION OF COALS TO PRODUCE COKE SAMPLES

Coke samples for textural analysis using polarized-light microscopy, for measurement of pore structural parameters using an image analysis system and for tensile strength measurements were obtained as follows.

First the coals were carbonized in the small double-wall-heated oven until the temperature at the centre of the charge reached 600°C. Then the charge box was withdrawn from the oven and quenched with cold water. After drying, the coke was recovered and reheated in a tubular furnace at 5°C/min in flowing nitrogen to 1000°C, before finally being allowed to cool down under nitrogen.

The seven coals were charged after being air-dried overnight and packed at a charge density of 720kg/m³ which was achieved by adding 8wt% water.
It has been found that the pore structure development occurs during the plastic temperature range. Thus, heat treatment up to 1000°C of the double-wall oven cokes outside the oven should not have any significant effect on the coke porosity.

3.2.1 Textural composition measurements.

The textural composition of metallurgical coke is studied microscopically, by viewing polished surfaces under polarized light. The various anisotropic components visible, vary in size with coal rank. Mosaics are usually present in medium-volatile matter coals while flow type components prevail in the texture of low-volatile matter content coals.

In order to obtain satisfactory samples for coke textural analysis, the following sample preparation procedure was adopted. Samples from the prepared cokes were crushed to give grains between 120-600μm in size for analysis. After having been ultrasonically cleaned, the coke was dried and a small quantity (0.5g) was mixed with a few drops of freshly made epoxy resin (Araldite MY 753) and formed into a 15mm diameter pellet. This was further embedded into resin and cured to form a 30mm diameter and 10mm thick block. The upper surface of this block having the coke exposed was ground with silicon carbide papers and polished using progressively finer grades of alumina paste. During this process the sample was smeared with resin if necessary to ensure a void-free surface.

The classification system described in the literature review was first used in this study. According to this scheme the textural components are divided into five classes namely, inerts, isotropic, mosaic, flow and anthracitic, these being further subdivided where necessary (Table 1).

Preliminary examination of the polished samples showed the presence of an anisotropic component which could not be easily classified in the categories according to the above mentioned classification scheme. Therefore, the addition of a new sub-class in the class of flow type components was considered necessary. This sub-class was called disturbed flow and includes the elongated isochromatic components with sizes 3-20μm by 2-10μm. Photographs illustrating each of the textural components are shown in Figures 19-22. These were taken with a Kodacolor 100 colour film, using a Reichert MEF3 polarizing microscope with crossed polars and a full-wave retarder plate. Although the allocation
of structures typical of each class can be made easily, the differentiation between structures at the interface between classes is highly subjective and therefore liable to some error calculated to be ±4% at the 50% level if 500 counts are made.

The polished samples were examined using a Leitz Ortholux microscope under crossed polars fitted with a full wave retarder plate, a x100 air objective and a x10 eyepiece to give an overall magnification of x1000.

The anisotropic components under the cross wire were allocated to one of the textural classes listed in Table 4. Measurements were made at 500 points spread over the sample while a Swift automatic point counter was used for the movement of the sample and the recording of the measurements.

3.2.2 Pore structure measurements.

Image analysis systems have been used in several cases in the past for the measurement of coke pore structure parameters. It was noted that to obtain reproducible results highly polished samples with minimum relief should be used and that the setting of the detection level was very critical.

The image analysis apparatus and its operating principles will be briefly described first followed by the procedures adopted for the present measurements.

The image created by a reflected light microscope is scanned by a closed circuit television camera before being passed through a detector (containing an analogue-to-digital convertor) and finally analyzed by a computer. The image is usually divided into a square or rectangular grid of picture elements known as pixels each of which is allocated to one of 64 grey levels according to its brightness.

Geometric measurements within the field of view are made after conversion of the multi-tonal grey image into a binary image. Therefore instead of the grey tones (represented by the 64 grey levels) only two levels (0 and 1) are used. Binary images are black and white (black for binary level 0 and white for level 1) although some systems allow for a colour to be used instead of white. The process of defining a binary image from a multi-tonal one is absolutely critical in all geometric measurements and is called thresholding. Measurements can be made either on the whole image or on a rectangular region (measuring frame), chosen by the user, within the image. Both field and object mode measurements can be made by image analysis systems. In field measurements the
contribution of each object is not individually known or recorded, but measured information is at pixel level and merely summed to provide a single measurement for the entire field. In contrast, object measurements are measurements of each individual object. Data produced by image analysis programmes are stored in the form of a data file and are analyzed statistically in various ways by other programmes of the system.

In the present study, the pore structural analysis was carried out using a Joyce-Loebl mini-Magiscan image analyser fitted with a reflected light research microscope. Under the reflected light the pores appear dark while the highly reflective carbon appears bright. It is important to use the correct setting of the detection level to convert the image captured by the system into a binary one in which the pores will be black and the pore walls will be white. This was done by setting the detection level at grey level 32 and manually adjusting the light intensity so that pores in the binary image correspond precisely to those in the microscope image. The correct classification of the large pores was ensured by using the lowest available magnification (x4 objective). For the TV camera and the lens used the pixels were rectangular in shape having a size of 3.3 by 2.9μm. If higher magnifications were used, many large pores would be incorrectly classified because they would extend beyond the image area from which measurements are taken.

The coke samples were prepared as follows. From the cokes obtained, cylindrical samples of approximately 10mm diameter by 10mm tall were cut. These samples were ultrasonically cleaned, dried and fifteen to eighteen cylinders for each coke were embedded in epoxy resin (Araldite MY 753) coloured with white pigment to prevent back reflections. The resultant block was 60mm in diameter and 10mm thick and its upper surface (having the coke samples exposed) was smoothed using successively finer silicon carbide papers and finally polished using fine grades of alumina paste. During this procedure, further impregnation with resin was carried out whenever necessary to ensure a void free surface.

The measurements were made using a field of view of 1.11x1.05 mm leaving a guard region necessary so that the detected features extending outside the frame could be measured correctly.

Mini-Magiscan can measure numerous parameters from each field of view. A measurement task list was written so that the system would automatically make the following measurements from each field of view:
1) Total field area  \( TA \)
2) Total pore area  \( PA \)
3) Number of pores  \( N \)
4) Mean pore height  \( H \)
5) Mean pore width  \( W \)
6) Mean pore length  \( L \)
7) Mean pore breadth  \( B \)

Total field area is the area of the measuring frame which in this case was : 1.1704mm\(^2\). Total pore area is the area based on the number of white pixels within the measuring frame. The pore length is the maximum dimension of the pore while the breadth is the dimension at right angles to the maximum dimension. These two are referred as the maximum and minimum Feret diameters. Pore height and width are the maximum dimensions of the pore parallel to the horizontal and vertical edges of the field of view.

The above measurements were used to calculate the following values:

\[ p = \frac{PA}{TA} \]
\[ P = \frac{PA}{N \times (H+W)/2} \]
\[ W = \frac{(TA-PA)}{N \times (H+W)/2} \]

The mean pore size represents the average length of all the horizontal and vertical scan lines which traverse the pores in a field of view. The value obtained for the circular cross section of a single pore would be less than the diameter. It is used since a corresponding value for wall size can be obtained.

Since coke is a very heterogeneous material, the pore structural measurements were made on 50 fields of view randomly spread over the prepared polished blocks in order to obtain representative values.

3.2.3 Tensile strength measurements.

The tensile strengths of the cokes were determined using the diametral compression method. The test is based on fracture of material due to stresses developed when a cylindrical specimen is loaded along a diameter.\(^6^7\)
The maximum tensile stresses acting normal to the loaded diameter have the constant magnitude:

\[ S = \frac{2W}{\pi Dt} \]

where \( S \) is the tensile strength (N.m\(^{-2}\)), \( W \) is the applied load (N) and \( D, t \) are the specimen diameter and thickness (m) respectively.

The cylindrical test pieces (approximately 10mm diameter by 10mm tall) used in the test were drilled from each coke, cleaned ultrasonically, weighed and their length and diameter were measured.

The load was applied using an Instron universal testing machine operating at a cross-head speed of 0.5mm/min. Values of the load at failure were recorded in terms of the deflection of the pen on a chart recorder. Tensile strength values were calculated from the applied load at breakage and the specimen dimensions using the above equation. The values quoted here are the mean values obtained from thirty to fifty individual test pieces for each coke.

### 3.3 INTERRUPTED CARBONIZATIONS USING A SMALL SINGLE WALL HEATED OVEN

Previous attempts to prepare blocks for these studies using the small double-wall oven operating in a single-wall heating mode were confronted with various problems.\(^1\) After interrupting the carbonization and removing the charge box from the oven, the coolest thermocouple gained around 180°C while the hottest started to cool. Also the plastic temperature layer lay at an angle to the heated wall. In the original studies\(^{17,18}\) the plastic layer in the resultant blocks was almost linear, parallel to the heating wall and so there was no temperature gradient along the length of the charge. This is a prerequisite for obtaining meaningful data for the coal-to-coke transformation.

In this work, for the preparation of coal-to-coke blocks, a small single-wall heated oven similar to that used previously\(^{17,18}\) was constructed for the study of porous structure development during carbonization.
The oven chamber measured 10x23x13cm and it was insulated with fire bricks to give external dimensions of 26x44x37cm (Fig. 23). The charge was contained in an asbestos paper box, held in an insulating-board box. Six thermocouples were inserted into the coal charge and lay parallel to the heated wall. The thermocouples were made by melting together two 0.325mm diameter wires of K-type thermocouples end to end and were held inside the charge box by glass tubes (1mm outside diameter, 10cm long, standard melting point determination tube) to protect them from the charge. The box was made from asbestos-substitute board (TAC) (1.2cm thick) and had external dimensions 8.5x12.2x11cm. In its two vertical sides, two rows of holes were drilled for the insertion of the thermocouples. During initial studies thin sheets were used for the construction of the charge box but the sides of the box (especially that attached to the heated wall) suffered serious damage. Consequently thicker (1.2cm) asbestos board had to be used.

The asbestos-paper box was made by wrapping strips of asbestos paper, coated with a paste made from fireclay cement, around a brick cut to the appropriate size for insertion into the TAC box. The brick was held in a plastic bag so that the paper box could easily slide off the mould when it was dried. The asbestos-paper box was placed in the charge box and then the glass tubes and thermocouples were inserted through the box sides. A detailed description of the procedure followed is given below.

First each thermocouple was threaded through a glass tube which was then passed through the first row of the holes in the charge box and the wire that came out from the other side of the box was threaded back through a second glass tube held in the second row of holes (10mm below the first row). Care was taken to ensure that the thermocouple tips lay in the centre of the charge. This procedure was adopted so that both the thermocouple leads were on one side of the charge box. The two bare wires of each thermocouple were then sheathed with ceramic beads along the rest of their length.

The air-dried coals were charged at a packing density of 860kg/m³. The charge was added in three equally-sized increments each of which was tamped down to the appropriate volume. The coal, sized 80wt% less than 3mm, completely filled the box and a TAC lid was wired in position to limit any tendency for upward expansion by the charge.

The charge box was then placed into a cold oven chamber and an insulating brick bearing a hole for the thermocouple wires, was placed in front of it. The thermocouples were then plugged to a computer interface. The wall of the oven was heated to 1000°C at 5°C/min, the temperature of the six thermocouples being monitored by the computer. The rate of temperature rise of the six thermocouples in a typical charge is shown in
Figure 24. Heating continued until the hottest thermocouple reached 650°C. At that time the coolest one was at approximately 200°C. The box was then removed from the oven and quenched by immersion in cold water, while the temperatures indicated by the thermocouples were still monitored. When the temperatures of the thermocouples were approximately 100°C the box was taken out of the water and allowed to dry. Then the thermocouples were cut and the asbestos-paper box was recovered, wrapped with aluminium foil and left overnight in an oven (80-100°C) to dry. The relative positions of the carbonized products were fixed by pouring a low-viscosity epoxy resin (Araldite MY 778) into the paper box. After hardening the resin, the vertical sides of the box were trimmed and refilled with epoxy resin. Then the box was cut horizontally 1.5 cm above the surface of the thermocouples and the lower part was filled again with epoxy resin to ensure the complete filling with resin of any unfilled part of the box. The surface was smoothed in the polishing machine using a course pad (80 mesh) ultrasonically cleaned and further filled with resin if necessary. Finally it was cut 5mm above the surface of the thermocouples and the edges were trimmed to expose a surface of approximately 50mm square.

The surfaces containing the products of the carbonization were smoothed using progressively finer silicon carbide papers and finally polished using successively finer grades of alumina paste and/or diamond paste. The polishing of the surfaces of coal-to-coke blocks was not easy due to variations in hardness of the materials present across the blocks.

At least over the central 40mm, the plastic layer, apparent by the white-resin filled large pores, lay parallel to the alignment of the remains of the thermocouples evident in the edges of the block (Fig. 25). It was therefore assumed that, in general, no significant temperature gradient existed in the direction parallel to the heated wall. Before the examination of the polished sections the positions of the thermocouples visible at the sides of the block, were measured and plots of final temperature against distance from the hot wall were drawn. A smooth curve was drawn through the points and this was used as a reference for relating the measured pore sizes at different points on the surface to the heat treatment temperature (Fig. 26).
3.3.1 Procedure adopted for the study of porous structure development.

A different approach, from that used to measure pore structural parameters of cokes, was adopted in order to follow the pore structure development with temperature. The measurements had to be made along lines parallel to the remains of the thermocouples assuming that these were isothermal traverses. The nature of the measurements made necessary the use of a narrow field of view in order to be able to assume that the materials measured were heated to the same temperature. The field of view chosen was 1x0.256mm.

Using the binary operations provided by the image analysis system, the binary image of the structure to be measured was combined with a random pattern of lines parallel to the directions of the thermocouple wires, the result being an image with equally spaced lines on the pores aligned parallel to the thermocouples as indicated in Figure 27. For each field of view examined, the lines on the pores were measured by the system and the average length of lines in each field of view was taken as a measure of the pore size. Twenty fields of view were examined across each traverse of the block. The total length of the lines on pores from the twenty fields of view was used as an indicator of the volume porosity.

As previously mentioned, the polishing of the block samples proved to be difficult, thus, it was not possible to attain a completely scratch- and relief-free surface. Therefore considerable image editing was necessary for certain fields of view to eliminate the various defects.

It was not possible to measure the pore-wall sizes by applying the technique described above. To do so involved using the binary operations of the system twice and so much of the computer memory was used for the storage of the images to be processed, that, with the available equipment there was insufficient memory for use by the measurement programme.
4 RESULTS

The textural compositions of the seven cokes obtained by heating the coals in the double-wall oven are given in Table 5. The textural components are identified by their initial letters as shown in Table 4. The textural compositions calculated on an inert-free basis are given in Table 6.

Considering the data in Table 6 the textural compositions of the seven cokes clearly varied with the volatile matter content. The two cokes from coals with the lowest volatile matter content, Pinnacle and Buchanan, had a small proportion of anthracitic texture but contained broad flow as the major component. As the rank of the parent coal decreased the cokes contained increasing proportions of disturbed-flow components (Fig. 28), Line Creek the Canadian coal, disturbing the otherwise clear trend. All cokes contained large and small inert components the percentages of which varied from 9-38.4 and 4-10.6 vol% respectively.

The "as measured" pore structural data for the seven cokes measured by the image analysis system are listed in Table 7. The structural data measured for the fifty fields of view examined for each coke were processed by the "Results" package of the image analysis system to give the mean values of porosity, pore and pore-wall sizes quoted in Table 8, where the coals are given in order of decreasing internal gas pressure as measured in a single plastic layer. The coke porosities varied from 50 to 67vol%. The cokes from highest rank coals had the highest porosity and number of pores per field while the dimensions of the pores were the smallest.

The coke sample of Line Creek was very heterogeneous. For this coal more than 100 fields were examined, and the variation of the measured values from field to field was significant (the porosities varied more than 15% percent between different fields). It gave the largest mean number of pores per field. This can be attributed to the high content of porous inert particles with small pores present in this coke (Table 5).

Table 8 also presents the tensile strengths of the seven cokes. The tensile strengths ranged from 1.76 to 3.27MPa, the highest values being obtained for cokes from coals in the middle of the range of volatile matter content.

Temperature data resulting from the carbonization of one of the coals during the preparation of the coal-to-coke blocks are illustrated in Figures 29 and 30. The data is typical of that from all coals examined.
Figure 29 illustrates the variation of the temperature at different points of the charge with time as measured by the six thermocouples inserted along the charge parallel to the heated wall. The quenching of the charge with cold water is visualised in terms of a sharp decrease in temperature. Although the wall temperature was raised linearly, heat transfer to the coal only became effective when the wall started to radiate heat.

Figure 30 shows the temperature gradient through the charge at regular intervals and at the point that the charge was removed from the oven. The upper line shows the maximum temperatures measured at each thermocouple. The heating rates through the plastic temperature range achieved in each test were comparable with the rates achieved in an industrial oven.

The mean pore sizes measured using image analysis along isothermal traverses of the coal-to-coke transformation blocks were referred to the corresponding temperatures by using plots of final temperature against distance from the heated wall (Fig. 26). The variations of mean pore size with temperature gradient attained during single-wall oven heating are illustrated in Figures 31a-37a.

In general, the development of the porous structure in these experiments followed the pattern previously observed. The mean pore size increased to a peak value before falling to a size which was largely unaltered at higher temperatures. The maximum pore size, which was generally observed within the plastic zone, given by the seven coals differed markedly while there was a considerable variation in the compaction pore ratios, that is the ratio of the maximum pore size to the average pore size observed in the semicoke (Table 9).

The shape of the pore size versus temperature curves (Figs. 31a-37a) and the maximum pore size varied widely amongst the seven coals studied. However, neither parameter appeared to vary systematically with internal gas pressures measured for the seven coals in single-wall oven experiments.

In the blocks of two coals i.e., Virginia Crews and Line Creek, the highly porous areas were readily visible in the superficial appearance of the blocks (Fig. 25). These areas appeared white because the embedding resin contained a white dye. These areas are the regions of maximum pore size. However, these large pores were reduced afterwards, giving a more compact structure. These two coals gave the highest compaction ratios. However, for Line Creek the average pore size in the semicoke remained quite high due to the high maximum pore size in the plastic zone.
Volume porosity is the ratio of pore volume $V_p$ to the total volume $V_p + V_s$, where $V_s$ is the volume of solid. The reconstruction of three dimensional information about the pore structure from observations in lower dimensions is conducted by the methods of stereology. If a plane section through a porous material is scanned by a series of lines and $L_p$ and $L_s$ are the total lengths of lines lying in pores and solid respectively, then the definition of porosity can be extended:

$$p = \frac{V_p}{(V_p + V_s)} = \frac{L_p}{(L_p + L_s)} = \frac{L_p}{L_T}$$

Since the same number of fields, scanned by the same number of lines, were examined along isothermal traverses in each block the $L_T$ is the same for all coals. Thus the total length of lines in pores in the 20 fields examined could be taken as an indication of porosity.

The variations of this measure with temperature are illustrated in Figures 31b-37b. The shapes of these curves were similar to those of mean pore size-temperature curves (Figs. 31a-37a).

The graphs of the total number of lines laid on the pores in the twenty fields examined along each traverse are given in Figures 31c-37c. For some coals there was a minimum in the number of these lines at the temperature where there was a maximum in the mean pore size and total length of lines while, for others there was a continuous rise in the number of lines during the whole range of the heat treatment temperature.
5 DISCUSSION

The carbonization process in the slot type oven is a very heterogeneous process in the sense that the developed thermal gradient creates essentially three zones in the chamber consisting of, the coke, the plastic layer and the coal. Almost all the important phenomena related to the commercial carbonization process are concentrated within the plastic layer which advances from the heating walls to the centre of the charge during coking. Among the effects produced by phenomena occurring in the plastic layer is the coking pressure while among the properties of the produced coke, determined at this stage of the carbonization are its optical anisotropy and porosity.

The seven coals studied in this work gave internal gas pressures, as measured in the middle of the charge in the small double-wall oven, which arranged them in the same categories from safe to dangerous as the corresponding wall pressures measured in a 300kg movable wall oven (Figs. 38-39). Thus, small ovens can justifiably be used as tools for investigating the internal gas pressure phenomena by studying the behaviour of coals giving different pressures.

Previous studies of the pore structure development and of the optical anisotropy of coals indicated that the principal effects took place during the plastic temperature range. Thus, the secondary heat treatment of the double-heated wall cokes to 1000°C outside the oven should not have any significant effect on the coke porosity and the textural composition.

The textural composition of the seven cokes obtained seemed to vary closely with the volatile matter content of the parent coals (Fig. 28). In this Figure the coals are arranged in order of increasing volatile matter content and it can be seen that, with the exception of Line Creek, the percentage of broad flow falls regularly with volatile matter content while the percentage of disturbed flow increases. In contrast no clear trend was found between broad flow content and internal gas pressures previously measured in single-wall oven mode (Fig. 40).

Line Creek gave a textural composition that suggested a lower rank coal. It has a high inert content which could explain the very low internal gas pressure measured for this coal in the small laboratory oven.

Generally the inert content was higher for cokes resulting from coals giving the lower values of internal gas pressure. For the analytically-similar coals Woodside and Virginia Crews, the textural composition of the cokes differed markedly. The most obvious
difference is the higher percentage of disturbed flow and higher inert content, present in Woodside coke. Woodside gives a wall pressure only 25% of that generated by Virginia Crews.

For the different coals that give similar values of wall pressure that is, Oakgrove, German Creek and Virginia Crews, the only obvious similarity in their textural compositions is the percentage of disturbed flow.

There was no direct association of the tensile strengths of the resultant cokes either with the volatile matter content or with the internal gas pressures. The greater values of tensile strengths were found in cokes from coals being in the middle of the volatile matter range.

The coke porosities did not vary linearly with volatile matter content of the coals, low porosities occurred in the middle of the volatile matter range. However, the porosities of the cokes increased linearly with the internal gas pressure measured during single-wall heating (Fig. 41).

Figures 42 and 43, show the variation of internal gas pressures (single-wall heating) with mean pore and mean pore-wall sizes for six of the seven coals. It is obvious that high internal pressures are associated with higher number of small pores and larger pore-wall sizes. In these figures the corresponding values for the Line Creek were not included. This coal gave the greatest number of pores with the lowest dimensions but this was attributed to the presence of a high percentage of porous inerts bearing small pores.

The coke porosities appeared to vary with the size of the highly porous "black-ends" visible to the naked eye at the centre of the charges after test. Photographs of the polished blocks prepared after charges had been carbonized from two sides in the small double-wall oven are shown in Figure 44. The two high coking pressure coals, Pinnacle and Buchanan, gave quite a dense semi-coke containing obvious rings of increased porosity. These rings surrounded a more porous central region consisting of small, relatively uniform, sized pores.

For the other coals, central voids varying in size were observed. Therefore, for Pinnacle and Buchanan, the coke substance was spread over a larger volume, hence the high porosity.

It is generally accepted that the evolution of volatile matter within the plastic layer and the resistance offered by the plastic layer to the escape of the volatile matter produced within it are the sources of pressures developed during the coking process. The gas pressure within an individual plastic layer can only reflect that of vapours trapped therein.
Wall pressures are secondary effects resulting from the transmission of plastic layer gas pressures through the semicoke and coke to the oven walls. Thus it is acceptable to probe the mechanism of coking pressure generation by concentrating on gas pressures.

Furthermore, the association of the coke porosity with the peak gas pressure within a single plastic layer must reflect differences in behaviour of coals with different coking pressures within the plastic layer. Hence, it was decided to study the coal-to-coke transformation of the seven coals using the single-wall oven and to attempt to identify differences in the pore structure development which would cast light on the generation of internal gas pressures.

Considering previous studies of pore structure development in more detail, without question the most interesting implications of the pore evolution experiments are related to the volatile matter transport. The initial pore formation is a size dependent intraparticulate property. For the large particles of diameter >1mm the formation of volatiles is governed by the heat transport through the particle towards the centre. The devolatilization which starts at the surface progresses towards the centre in the form of a front. The temperature increases continually until the coal substance in the centre starts to release its own volatiles. This evolution of the volatiles from the particle is limited by the larger path of the diffusion. The accumulation of volatiles in the centre of the particle leads to bubble (spherical pore) formation. For the particles of diameter less than 1mm only the chemical kinetics control the departure of the volatiles. The evacuation of the volatiles by migration at a molecular scale, or by transport via the system which constitutes the intragranular porosity, should be facilitated near the surface of the particle. In non-plastic coals the unchanged open porous structure allows volatiles transport to the particle surface via diffusion and hydrodynamic flow through the pores.

In the case of softened coals, radical changes occur in the structure. The initial solid coal gives a solid-liquid-gaseous mixture which is further converted to resolidified phase. The solid-liquid-gaseous mixture is a mixture of unsoftened coal constituents -minerals, inertinite- in an organic continuum through out which pyrolysis-derived volatiles form bubbles.

In a coke oven charge initial pore formation starts just below the softening point (Ruhr dilatometer) as deformation and flow of the molten coal transform the interconnected pores into tiny sealed cavities of trapped gas. Bubbles in the molten coal can be produced from the pores in the solid coal and can also be generated via nucleation in the molten coal when the concentration of gases and vapours exceed the saturation limit. The
volatiles diffuse either to the particle surface or to bubbles, dispersed through out the molten coal. Once bubbles are available they grow due to influx of volatiles from the plastic coal.\cite{70}

Oh et al.\cite{70} in their model of coal softening pyrolysis suggested 4 mechanisms of bubble growth:

1) addition of gas molecules by diffusion from the molten coal phase.

2) chemical reactions inside or at the surface of bubbles including secondary reactions of tar vapour.

3) changes in gross physical forces such as internal or external pressure.

4) coalescence with other bubbles.

Bubble coalescence is assumed to occur via expansion and spatial contact of two adjacent bubbles. Because of the high viscosity of the molten coal, bubble movement is considered negligible.

High molecular weight species (>1000 amu) of metaplast in bubbles are limited because of their high vapour pressure. Molecular diffusion through the plastic coal and transport outside the particle may therefore be important for these species.

The driving force of swelling according to Melia and Bowman\cite{71} is the pressure differential between the inside and the outside of the particle due to volatile matter evolution. They suggested the following equation for describing the deformation of the pores (bubbles):

\[
\frac{\Delta l}{l} = \frac{3}{8} \frac{\Delta P}{\mu_{coal}} \Delta t
\]

where:  
- \( l \) is the pore length.
- \( \Delta P \) is the centre to surface pressure differential.
- \( \mu_{coal} \) is the viscosity of coal.
- \( \Delta t \) is the time interval.

If the secondary reactions in bubbles occur rather rapidly during the plastic stage, the enhanced growth due to the resulting gas formation causes more bubbles to be released from the particle, thus lowering both the number density of bubbles and the amount of gas hold-up.\cite{70}
The growth of bubbles with increasing temperature leads to the swelling of the particles which cause closure of the intergranular pores in places.\textsuperscript{11} The pyrolysis gases can no longer freely escape and the pressure increases in the interparticular voids giving rise to swelling of the whole mass of coal and this, in its turn, leads to the closure of new intergranular pores. The result is a renewed increase in pressure and the phenomenon becomes self-exciting until the large bubbles of trapped gas burst. The swelling of the larger particles results in the smaller ones being swept into and concentrated in the diminishing void spaces. With continued swelling, all the small particles become engulfed within the expanding cell walls of the larger particles.

Thus the next step following softening and swelling of particles is the transition between the particles of coal in contact at several points and the development of a continuum precursor of the coherent semicoke.

This process is associated generally with the swelling of the particles although, it has been observed that for some coals this development occurs more by flow than by volume expansion.\textsuperscript{19} In this study, as in previous ones,\textsuperscript{17,18,72} this particular behaviour was never observed that is, the examined coals did not fuse completely before pore formation.

In a study conducted by Klose \textit{et al.},\textsuperscript{73} of the agglomeration kinetics between hard coal particles in a mono-layer, the free thermal agglomeration of two softening hard coal particles was described by assuming viscous flow under the effect of surface tension forces.

A simpler model suggested the effect of external pressure on the fusion. It was suggested that the pressure acts in the same way as fluidity and intensifies agglomeration. A pressure like this is actually present in the coke ovens in the form of hydrostatic pressure which assures greater agglomeration between the particles at the bottom of the oven.\textsuperscript{53}

Surface-tension effects may be especially important criteria for influencing the growth of pores. However surface tension properties are quite difficult to define and more difficult to measure. It has been suggested that these properties have lower values for high rank than low rank coals and this results in a greater growth of the bubbles before bursting and that they re-form more easily after bursting.\textsuperscript{11}

The surface tension of molten coal is not adequately understood, but probably varies with temperature, pressure and viscosity. For example, experimental data on coal liquids show that the surface tension in general, decreases with increasing temperature and pressure, but the magnitude of the decrease is small compared to that of the viscosity or the diffusivity.
Within the plastic range the approximately spherical nature of the pores suggests that they are closed trapping released volatiles. From experiments of Miura and Silveston\textsuperscript{74} using adsorption techniques to study the pore structure development during coal carbonization, a maximum was observed in macro-pore volume in a temperature $>600^\circ$C which was greater than expected. This was explained by accepting that at temperatures below $600^\circ$C, the pores are closed. Thus, if the volume available to the swelling coal is restricted, trapped volatile matter could be expected to exist at higher pressures within smaller pores.

With increasing temperature the metaplast is progressively transformed by pyrolysis into coke and volatile matter so it is natural that the plastic state will end. The modification of the existing thermochemical equilibrium between metaplast and bubbles is brought about by resolidification which could result in a diffusion of inverse direction of the bubbles towards the metaplast and, in particular, a reduction of the size of those bubbles. Later when the bubbles break, the opposite effect which could be described in terms of an acceleration of the diffusion from the metaplast to the currently created porosity,\textsuperscript{53} can be conceived. The process of liberation of volatiles is considered as one of the most important stages.

Several researchers claim the occurrence of a rupture in the continuity of the plastic layer which is presumably caused by a sudden advance of the fissures formed in the coke. Others consider the process of resolidification as occurring progressively and that the fissures formed in the coke do not reach the plastic zone.

The question of bubble bursting is debatable. Solomon\textsuperscript{75} calculated the necessary pressure for the breaking of the bubbles by assuming that the behaviour of the molten coal is similar to that of a molten polymer. He obtained a value of 1 MPa. Gray\textsuperscript{76} suggested that such a pressure could be obtained at high heating rates which create a strong thermal gradient within the coal particle thus causing a resolidification of the surface and retention of the majority of the volatiles within the heart of the particle.

The mechanism of the decrease in mean pore size is not obviously related to volatile matter generation since thermogravimetric analysis shows continued significant weight losses at relevant temperatures. The compaction process is supposed to be associated with the interconnection of previously closed pores with the open structure of the semicoke. Expansion of the slightly cooler layer should compress the compaction layer against the rigid semicoke and, by expelling previously trapped volatile matter, partially deflate the pores.\textsuperscript{17,72}
Local heterogeneities are expected to influence the process of liberation of the volatiles. Large inert and porous particles reduce the internal pressure by reducing the homogeneity of the plastic layer and giving outlets to the volatiles. 53

High internal gas pressure must arise from one or more of the following factors:

1) more volatile material in pores of similar size, this not being observable under the microscope;
2) a thicker plastic layer which would make more difficult the escape of the volatiles;
3) the absence of the compaction process in which case the evacuation of gases is limited; the increased pressure in the plastic layer compresses the layer of unconverted coal adjacent to the plastic layer thus reducing the permeability of that layer as well;
4) the maximum of the devolatilisation rates being near the resolidification zone, whereby it is difficult for the bubbles to break the semi-solid forming semicoke. The late maximum in the devolatilisation rate means also that the majority of the volatiles is evolved after complete fusion in which case the escape through the interparticular voids towards the unconverted coal will not be possible.

In the present studies pores were first seen in larger coal particles. Their growth caused the swelling of the particle into the interparticulate voids. Continued swelling eliminated all the voids forming a fully-fused structure for six of the seven coals studied. Woodside gave a partially-fused structure.

Thereafter, the bubbles grew to a maximum after which there was a compaction in the structure. For the cases of Virginia Crews and Line Creek the bubbles grew to a very large size before their size dropped to that of the corresponding semicoke. The compaction process was clearly observed in four of the coals studied. In three cases the maximum in the size of the bubbles was accompanied by a minimum in the number of lines on the pores, which can be taken as a measure of the number of bubbles present. This minimum could be due either to bubble coalescence or to the rupture of some thin walls during the post-fusion expansion process. In the other four coals, during the maximum of the bubble size no minimum in the number of lines was observed but this number continued to rise. This could be attributed either to limited coalescence between the bubbles or to a continuous nucleation of bubbles.

Initially it was expected according to the literature review and to the implications of Figure 44 that the maximum in the porosity (proportional to the total length of lines on the pores) would be absent in the coals that give high coking pressures and so would the compaction process. In contrast with these views Pinnacle, a high pressure coal, gave a curve with a maximum in the porosity during the plastic stage and with an obvious
compaction stage. The shape of that curve was similar to that given by Virginia Crews and Line Creek coals which give intermediate and low coking pressures, respectively. No obvious maximum was observed for Buchanan, coal which gives high coking pressure, but the block of coal-to-coke transformation for this coal had two cracks in the middle of the plastic layer which made impossible the accurate measurements of pore sizes for this coal in the corresponding area.

Present results do not allow conclusions to be drawn about the mechanism of internal gas pressure generation. However, it is believed that the technique used is quite interesting and worthy of further use in studies of the pore structure development. The poor polishing of the blocks made necessary extended editing of the images before measurements could be carried out. That could have affected the final results. If more work is done to overcome the difficulties encountered during polishing then the results would be more precise and the technique could be used with more success for studying the pore structure development of coals in an attempt to elucidate the mechanism of internal gas pressure generation.
6 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

1. During carbonization of coking coals, important phenomena which determine the properties of the resultant cookes, occur within the plastic layer formed over the temperature range when the coal is plastic. Among these properties are the optical anisotropy and the porosity of coke.

2. The high gas pressures, and corresponding wall pressures, developed by some high rank coals result from the equilibria characterising the plastic layer of these coals.

3. The textural composition of the seven cookes produced by carbonising the corresponding coals in a small laboratory oven showed a more close relation with the volatile matter content of the coals than with the internal gas pressure generated in the plastic layer.

4. For six of the coals studied, the porosity of the coke and number of pores per mm² of surface fell with increasing internal gas pressure while the mean pore and mean pore-wall size increased. The anomalous behaviour of the seventh coal appeared to be associated with its high content of inert components which contained many small pores. The high inert content may also explain the very small internal gas pressures generated by this coal.

5. Image analysis can be used to study the pore structure development using coal-to-coke transformation blocks produced from quenched charges carbonized from one side. Initial formation of pores occurs at temperatures near the softening point. The number and size of pores increases with increasing temperature. Then the pore size attains a maximum value in the middle of the plastic temperature range before falling to that in the semicoke.

6. Differences are observed between the behaviour of coals in terms of the variation of pore size as carbonization proceeds. The ratio of the maximum pore size to semicoke pore size varied widely as did the width of the plastic temperature range and the temperature at which the maximum pore size was observed. However in no case did the variation reflect variation in coking pressure exhibited by the coals.

7. Pore growth can occur only if pores are closed and thus trap volatiles within them. Thus pore growth and gas pressure generation are both dependent on restrictions on the
escape from the plastic layer of volatiles released from coal. It is clear however, that no obvious relationship exists and this implies that one effect is strongly influenced by another factor as yet unidentified.

8. The small size of the computer memory limited the image analysis measurements to pore sizes. Increased computer memory would allow a more complete investigation of the pore structure development during carbonization to be carried out.

9. In the present study only two high rank coals, giving high internal pressures were used. A worthwhile future study would be to use the techniques now developed to examine a wider range of high rank coals giving high coking pressures.

10. The polishing of the coal-to-coke blocks for image analysis is not easy due to the differences in hardness across the blocks and this may have introduced some inaccuracies in the measurements obtained. It is recommended that in any future study efforts should be made to develop polishing methods to give scratch- and relief-free surfaces for analysis.
7 REFERENCES

4. Dartnell, J., Ironmaking and Steelmaking, 1978, 1, 18
13. BSI, 1016: Section 107.3 : 1990
14. ASTM Standard, D. 2639-90
15. Waters, P.L., Fuel, 1962, 41, 1
22. Cornford, C., Marsh, H., Northern Coke Research Committee, Progress Report 100, University of Newcastle upon Tyne, April 1976, Section D, p.83
37. Baum, K. and Heuser, P., Fuel, 1931, 10(2), 51
38. Koppers, H. and Jenkner, A., Fuel 1931, 10(5), 232
41. Mott, R.A. and Spooner, C.E., Fuel in Science and Practice 1939, 18, 329
42. ASTM Standard, D.2014-90
43. Soth, G.C. and Russel C.C., Trans Am. Inst. of Min. & Met Eng., 1939, 157, p.281
45. Russel, C.C., Perch, M. and Smith, H.B., Blast Furn., Coke Oven and Raw Mat. Proc. AIME, 1953, 9, 197
51. Centre de Pyrolyse de Marienau, Final Rept. on ECSC Project 7220-EB/308, 1979
52. British Coal Corp., Coal Research Estab., Final Rept. on ECSC Project 7220-EB/833, 1990
53. Centre de Pyrolyse de Marienau, Final Rept. on ECSC Project 7220-EB/328, 1990
63. Gavrikov, V.V., Mozgovaya, E.D. and Belan, Z.G., Coke and Chemistry, USSR, 1967, 1, 7
64. Gryasnov, N.S., Coke and Chemistry, USSR, 1962, 1, 5
65. Klose, W., Heckmann, H., Coal Science Conf., Tokyo, 1989, p.1063
66. Image Analysis Principles & Practice, Published by Joyce Loebl, Short Run Press, Exeter, 1985
73. Klose, W. and Lent, M. Fuel, 1985, 64(2), 193
75. Solomon, P.R. "Chemistry of Coal Conversion", 1985, Plenum Press, NY and London, 121
76. Gray, V.R. Fuel, 1988, 67, 1298
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<table>
<thead>
<tr>
<th>Component type</th>
<th>Symbol</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracitic</td>
<td></td>
<td>A non porous anisotropic material which does not fuse to softening components.</td>
</tr>
<tr>
<td>plain</td>
<td>A</td>
<td>Single coloured particles.</td>
</tr>
<tr>
<td>patterned</td>
<td>Ap</td>
<td>Particles with layered structure of contrasting colour.</td>
</tr>
<tr>
<td>Flow</td>
<td></td>
<td>Composed of elongated isochromatic areas often curved around pores.</td>
</tr>
<tr>
<td>broad</td>
<td>Fb</td>
<td>size $&gt;20 \times 10 \mu m$</td>
</tr>
<tr>
<td>striated</td>
<td>Fs</td>
<td>size $&gt;20 \times 2 \mu m$</td>
</tr>
<tr>
<td>granular</td>
<td>Fg</td>
<td>size $&gt;2 \times 1 \mu m$</td>
</tr>
<tr>
<td>Mosaic</td>
<td></td>
<td>Composed of small rounded isochromatic areas.</td>
</tr>
<tr>
<td>coarse</td>
<td>Mc</td>
<td>mean size 0.91 $\mu m$</td>
</tr>
<tr>
<td>medium</td>
<td>Mm</td>
<td>mean size 0.63 $\mu m$</td>
</tr>
<tr>
<td>fine</td>
<td>Mf</td>
<td>mean size 0.50 $\mu m$</td>
</tr>
<tr>
<td>Isotropic</td>
<td>I</td>
<td>An optically isotropic component of low rank coals, often pored, which fuses to mosaic components.</td>
</tr>
<tr>
<td>Inerts</td>
<td></td>
<td>Carbonaceous inerts are isotropic components identifiable by their woody structure, or if small by their unfused sharp edges. Mineral matter is included in this class.</td>
</tr>
<tr>
<td>large</td>
<td>II</td>
<td>$&gt;50 \mu m$</td>
</tr>
<tr>
<td>small</td>
<td>Is</td>
<td>$&lt;50 \mu m$</td>
</tr>
</tbody>
</table>
Table 2. Analytical data for coals used.

<table>
<thead>
<tr>
<th>Test Parameter</th>
<th>PINNACLE</th>
<th>BUCHANAN</th>
<th>OAKGROVE</th>
<th>LINE CREEK</th>
<th>GERMAN CREEK</th>
<th>VIRGINIA CREWS</th>
<th>WOODSIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (wt %)</td>
<td>0.9</td>
<td>0.8</td>
<td>1.2</td>
<td>1.3</td>
<td>1.3</td>
<td>--</td>
<td>0.7</td>
</tr>
<tr>
<td>Ash (wt %)</td>
<td>5.2</td>
<td>4.9</td>
<td>9.8</td>
<td>10.2</td>
<td>11.4</td>
<td>7.4</td>
<td>8.1</td>
</tr>
<tr>
<td>Volatile matter (db%)</td>
<td>16.3</td>
<td>19.2</td>
<td>19.5</td>
<td>20.9</td>
<td>22.2</td>
<td>25.8</td>
<td>26.2</td>
</tr>
<tr>
<td>Volatile matter (daf%)</td>
<td>17.2</td>
<td>20.1</td>
<td>21.7</td>
<td>23.3</td>
<td>25.1</td>
<td>27.8</td>
<td>28.5</td>
</tr>
<tr>
<td>B.S. swelling No.</td>
<td>7.0</td>
<td>7.5</td>
<td>8.0</td>
<td>3.5</td>
<td>9.0</td>
<td>--</td>
<td>8.0</td>
</tr>
<tr>
<td>Gray King coke type</td>
<td>G3</td>
<td>G6</td>
<td>G7</td>
<td>F</td>
<td>G6</td>
<td>--</td>
<td>G8</td>
</tr>
</tbody>
</table>

**Ruhr Dilatometry**

<table>
<thead>
<tr>
<th></th>
<th>PINNACLE</th>
<th>BUCHANAN</th>
<th>OAKGROVE</th>
<th>LINE CREEK</th>
<th>GERMAN CREEK</th>
<th>VIRGINIA CREWS</th>
<th>WOODSIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softening Temp. °C.</td>
<td>419</td>
<td>399</td>
<td>404</td>
<td>392</td>
<td>381</td>
<td>369</td>
<td>354</td>
</tr>
<tr>
<td>Temp. of max contraction, °C</td>
<td>450</td>
<td>411</td>
<td>441</td>
<td>456</td>
<td>427</td>
<td>--</td>
<td>402</td>
</tr>
<tr>
<td>Resolidification T., °C</td>
<td>479</td>
<td>477</td>
<td>476</td>
<td>483</td>
<td>462</td>
<td>470</td>
<td>453</td>
</tr>
<tr>
<td>Max. contraction (C)</td>
<td>25</td>
<td>27</td>
<td>23</td>
<td>22</td>
<td>26</td>
<td>22</td>
<td>25</td>
</tr>
<tr>
<td>Max. dilatation (D)</td>
<td>30</td>
<td>53</td>
<td>68</td>
<td>-22</td>
<td>72</td>
<td>229</td>
<td>247</td>
</tr>
<tr>
<td>Total dilatation(C+D)</td>
<td>55</td>
<td>80</td>
<td>91</td>
<td>0</td>
<td>98</td>
<td>251</td>
<td>272</td>
</tr>
</tbody>
</table>
Table 3. Wall pressures from the movable-wall oven and internal gas pressures for double- and single-wall heating mode in a small laboratory oven.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Wall pressure, double-wall heating, kPa</th>
<th>Internal gas pressure, double-wall heating, kPa</th>
<th>Internal gas pressure, single-wall heating, kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry coal equivalent bulk densities</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>800kg/m³</td>
<td>720kg/m³</td>
<td>860kg/m³</td>
</tr>
<tr>
<td>Pinnacle</td>
<td>46.2</td>
<td>88</td>
<td>36</td>
</tr>
<tr>
<td>Buchanan</td>
<td>33.1</td>
<td>74</td>
<td>40</td>
</tr>
<tr>
<td>Virginia Crews</td>
<td>17.2</td>
<td>46</td>
<td>15</td>
</tr>
<tr>
<td>Oakgrove</td>
<td>15.9</td>
<td>39</td>
<td>10</td>
</tr>
<tr>
<td>German Creek</td>
<td>9.6</td>
<td>52</td>
<td>9.7</td>
</tr>
<tr>
<td>Woodside</td>
<td>4.8</td>
<td>6.9</td>
<td>4.8</td>
</tr>
<tr>
<td>Line Creek</td>
<td>4.1</td>
<td>0.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Table 4. Classification system of textural components used in the present study.

<table>
<thead>
<tr>
<th>Component type</th>
<th>Symbol</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracitic</td>
<td>A</td>
<td>A non porous anisotropic material which does not fuse to softening components.</td>
</tr>
<tr>
<td>plain</td>
<td>A</td>
<td>Single coloured particles.</td>
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<tr>
<td>patterned</td>
<td>Ap</td>
<td>Particles with layered structure of contrasting colour.</td>
</tr>
<tr>
<td>Flow</td>
<td></td>
<td>Composed of elongated isochromatic areas often curved around pores.</td>
</tr>
<tr>
<td>broad</td>
<td>Fb</td>
<td>size &gt;20 x &gt;10 μm</td>
</tr>
<tr>
<td>striated</td>
<td>Fs</td>
<td>size &gt;20 x 2 μm</td>
</tr>
<tr>
<td>disturbed</td>
<td>Fd</td>
<td>size 3-20 x 2-10 μm</td>
</tr>
<tr>
<td>granular</td>
<td>Fg</td>
<td>size &gt;2 x 1 μm</td>
</tr>
<tr>
<td>Mosaic</td>
<td></td>
<td>Composed of small rounded isochromatic areas.</td>
</tr>
<tr>
<td>coarse</td>
<td>Mc</td>
<td>mean size 0.91 μm</td>
</tr>
<tr>
<td>medium</td>
<td>Mm</td>
<td>mean size 0.63 μm</td>
</tr>
<tr>
<td>fine</td>
<td>Mf</td>
<td>mean size 0.50 μm</td>
</tr>
<tr>
<td>Isotropic</td>
<td>I</td>
<td>An optically isotropic component of low rank coals, often pored, which fuses to mosaic components.</td>
</tr>
<tr>
<td>Inerts</td>
<td></td>
<td>Carbonaceous inerts are isotropic components identifiable by their woody structure, or if small by their unfused sharp edges. Mineral matter is included in this class.</td>
</tr>
<tr>
<td>large</td>
<td>Il</td>
<td>&gt;50 μm</td>
</tr>
<tr>
<td>small</td>
<td>Is</td>
<td>&lt;50 μm</td>
</tr>
</tbody>
</table>
Table 5. Textural composition of double heated-wall oven cokes.

<table>
<thead>
<tr>
<th>Coal</th>
<th>VM daf,wt%</th>
<th>Textural composition, vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Pinnacle</td>
<td>17.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Buchanan</td>
<td>20.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Oakgrove</td>
<td>21.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Line Creek</td>
<td>23.3</td>
<td>0.0</td>
</tr>
<tr>
<td>German Creek</td>
<td>25.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Virginia Crews</td>
<td>27.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Woodside</td>
<td>28.5</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Table 6. Textural composition of double heated-wall oven cokes on an inert free basis.

<table>
<thead>
<tr>
<th>Coal</th>
<th>VM (daf wt%)</th>
<th>Textural composition, vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Pinnacle</td>
<td>17.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Buchanan</td>
<td>20.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Oakgrove</td>
<td>21.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Line Creek</td>
<td>23.3</td>
<td>0.0</td>
</tr>
<tr>
<td>German Creek</td>
<td>25.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Virginia Crews</td>
<td>27.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Woodside</td>
<td>28.5</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Table 7. Measured pore structural data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TA mm²</th>
<th>PA mm²</th>
<th>Pores per mm²</th>
<th>H, μm</th>
<th>W, μm</th>
<th>L, μm</th>
<th>B, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinnacle</td>
<td>58.5</td>
<td>39.7</td>
<td>83.2</td>
<td>88.5</td>
<td>84.2</td>
<td>105.7</td>
<td>65.9</td>
</tr>
<tr>
<td>Buchanan</td>
<td>58.5</td>
<td>39.1</td>
<td>71.9</td>
<td>89.5</td>
<td>87.9</td>
<td>107.8</td>
<td>68.0</td>
</tr>
<tr>
<td>Virginia C.</td>
<td>58.5</td>
<td>32.6</td>
<td>49.2</td>
<td>95.9</td>
<td>100.5</td>
<td>119.1</td>
<td>76.3</td>
</tr>
<tr>
<td>Oakgrove</td>
<td>58.5</td>
<td>31.7</td>
<td>47.0</td>
<td>101.7</td>
<td>101.7</td>
<td>123.2</td>
<td>79.0</td>
</tr>
<tr>
<td>German C.</td>
<td>58.5</td>
<td>31.9</td>
<td>41.4</td>
<td>101.7</td>
<td>103.8</td>
<td>124.4</td>
<td>80.0</td>
</tr>
<tr>
<td>Woodside</td>
<td>58.5</td>
<td>29.2</td>
<td>42.1</td>
<td>87.5</td>
<td>92.8</td>
<td>109.1</td>
<td>70.0</td>
</tr>
<tr>
<td>Line C.</td>
<td>58.5</td>
<td>31.1</td>
<td>104.2</td>
<td>65.1</td>
<td>65.3</td>
<td>79.2</td>
<td>49.4</td>
</tr>
</tbody>
</table>
Table 8. Derived pore structural data and tensile strength values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity vol%</th>
<th>Pore Size μm</th>
<th>Wall Size μm</th>
<th>Tensile strength MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinnacle</td>
<td>66.8</td>
<td>93</td>
<td>46</td>
<td>1.76</td>
</tr>
<tr>
<td>Buchanan</td>
<td>64.2</td>
<td>101</td>
<td>56</td>
<td>2.17</td>
</tr>
<tr>
<td>Virginia Crews</td>
<td>55.8</td>
<td>115</td>
<td>92</td>
<td>3.27</td>
</tr>
<tr>
<td>Oakgrove</td>
<td>54.1</td>
<td>113</td>
<td>96</td>
<td>2.80</td>
</tr>
<tr>
<td>German Creek</td>
<td>54.4</td>
<td>128</td>
<td>107</td>
<td>3.06</td>
</tr>
<tr>
<td>Woodside</td>
<td>50.0</td>
<td>132</td>
<td>132</td>
<td>2.07</td>
</tr>
<tr>
<td>Line Creek</td>
<td>53.2</td>
<td>78</td>
<td>69</td>
<td>2.61</td>
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</tbody>
</table>
Table 9. Change of pore sizes during carbonization.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Average pore size μm maximum</th>
<th>semicoke</th>
<th>Compaction pore ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinnacle</td>
<td>266.8</td>
<td>138.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Buchanan</td>
<td>174.2</td>
<td>136.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Virginia Crews</td>
<td>500.0</td>
<td>157.4</td>
<td>3.2</td>
</tr>
<tr>
<td>Oakgrove</td>
<td>202.6</td>
<td>114.4</td>
<td>1.8</td>
</tr>
<tr>
<td>German Creek</td>
<td>194.4</td>
<td>157.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Woodside</td>
<td>195.1</td>
<td>136.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Line Creek</td>
<td>441.1</td>
<td>208.3</td>
<td>2.1</td>
</tr>
</tbody>
</table>
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   b. at the instant when the plastic layers meet at the central plane\textsuperscript{11}

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Figure 33. Variation in a) mean pore size, b) total length of lines on pores and c) total number of lines with carbonization temperature: Virginia Crews.

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Figure 36. Variation in a) mean pore size, b) total length of lines on pores and c) total number of lines with carbonization temperature: Woodside.

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