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The effect of finishing temperature and soaking of the coke in the oven upon the microstructure and strength of metallurgical coke

W. R. Gadsden

University of Wollongong
THE EFFECT OF FINISHING TEMPERATURE AND SOAKING OF THE COKE IN THE OVEN UPON THE MICROSTRUCTURE AND STRENGTH OF METALLURGICAL COKE

A THESIS PRESENTED IN FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE FROM

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BY

W. R. GADSDEN B.Sc.

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The research work for this thesis was carried out at the University of Wollongong, under the supervision of Professor A.C. Cook. Where the work of others whether published or unpublished, has been referred to, acknowledgement is given.
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Colleagues within my past employer, B.H.P. Steel International Pty. Co. Limited have been most helpful, and include C.D. Coin, W.W. Gill and J.V. Dubrawski of B.H.P. Central Research Laboratories, and K.G. Horrocks and R.J. Nightingale of the Port Kembla plant. The management of that plant facilitated experimental work by making available several items of equipment and data from recent operations, as well as samples of coals and coke. Coal samples also were supplied by operators at Huntley Colliery (N.S.W.) and Norwich Park Mine (Queensland).
ABSTRACT

Large modern blast furnaces, such as No. 5 unit at Port Kembla which produces 7,000 tonnes per day of iron, demand high quality feed materials. The blending of coals to yield coke of the required cold strength was resolved by the mid seventies and in the last decade infurnace properties have been studied critically. Japanese technologists have claimed improvement by the practice of soaking the coke in the ovens at the finishing carbonization temperature.

Researchers have shown that the microstructure and degree of ordering of the coke substance may be altered by heat treatment over a temperature range exceeding that practical in industrial ovens. The finishing temperature in such ovens is poorly defined and often variable within and between ovens. There is scope to improve thermal regimes and this investigation examines the relationship of finishing temperature to microstrength of the coke, the ordering of the microstructure as indicated by bireflectance and changes in crystallite dimension over the temperature range that may exist, (900°C - 1070°C).

Three series of tests with different coals, carbonized in a laboratory furnace, showed common trends to higher values, without evidence of a plateau level. Limited attempts to correlate microstrength from laboratory coke with commercial product raise doubts as to whether changes of the magnitude reported exist in practice, and it is doubted that the benefit from soaking would compensate for the sacrifice in coke size that would result from the faster coking rate required to maintain tonnage output.
It is evident that fundamental coke properties are still being influenced by variations in the finishing temperature within the range occurring in industrial operations. These should be considered in the defining of the finishing carbonization temperature.
PURPOSE OF THE INVESTIGATION

Ironmaking in modern large blast furnaces demands high standards of physical quality of the coke. The purpose of this work was:

i) to establish whether this quality as measured by a selected practical industrial test was improved by

(a) a higher finishing temperature than practiced, or

(b) soaking of the coke in the oven at normal finishing temperature;

ii) relate this to changes in the coke structure; and

iii) to formulate a view of the practice preferable in the situation at Port Kembla Steelplant.
The key to economic steel making is the production in the blast furnace of large volumes of molten iron, rigidly specified in terms of chemical composition and temperature, supplied consistently to oxygen steelmaking plants the output of which feeds continuous casters. Understanding of the science of blast furnace operation has advanced to a stage where highly sophisticated control is practicable and output of 10,000 tonnes per day has been achieved in single large furnaces in Japan. A productivity target of 2.0 tonnes per cubic metre of inner volume is common and the Port Kembla No. 5 blast furnace of B.H.P. Steel International Pty. Co. Limited, with inner volume 3,000 m$^3$ has achieved 7,000 tonnes per day. Such outputs set exacting requirements for the raw materials fed to the furnaces, both in the absolute levels of chemical and physical parameters and in the consistency of these properties.

Ironmakers world wide were realising three decades ago that their definitions of coke quality were elementary. Accepted levels of ash content, strength and size met readily by the cokemaker were becoming inadequate for large furnaces and the range of parameters needed to be extended. This extension was readily realised where chemical composition was concerned, the inclusion of alkali content in routine analyses being an example, but parameters relating to physical quality were less well defined.
Scientific study of the fundamental coking properties of coals has been progressing for half a century and a substantial contribution has been made in Australia by the Commonwealth Scientific and Industrial Research Organisation (CSIRO), some of whose officers had a profound influence on the Australian coking industry at a time preceding the development of coal research in most commercial institutions.

Further impetus to industrial research was given by the boom conditions of the coal industry in the two decades to 1980. Massive increases in coal output were required. That for local consumption came largely from existing or new mines on well developed coal fields. Overseas demand was met by the development of new sources, often in previously untouched coal fields. Along with the upsurge in new collieries went the establishment of transportation and handling facilities that made Australian coal a world commodity. Coal preparation and cleaning became a basic requirement. Few large ironmaking operations were in a position to obtain all their coal tonnage requirements from any one source, nor was it likely that the quality requirement would be met by one source. Blending of a number of coals had long been practiced, developed often on a pragmatic basis; it then became essential to understand and utilise the science of coal blending.

Recognition by operators at the Port Kembla plant of the then Australian Iron and Steel Pty. Ltd. of the "carrying capacity" of Wongawilli seam coal had been applied to cokemaking for many years. As the coking characteristics of the coals from the Bulli seam were defined by petrographic, rheological and other basic properties and
seen to vary among the various colliery sources (as well as generally becoming less favourable for coking as mining advanced south westward) a substantial industrial research effort was mounted in the sixties. That this was effective was due substantially to the direct significance of the CSIRO work to Illawarra coals and the appointment of A.C. Cook, ultimately as Professor of Geology at the University of Wollongong, with whom a very effective liaison was established.

Worldwide, cokemakers were endeavouring to optimise coke quality and costs by obtaining coals from a range of sources, the leaders in this advance being the rapidly expanding Japanese Steelmills. These were largely new plants based on imported coals and ores of high quality, but with a shrewd eye for a price advantage by inclusion of some cheaper, lower quality coals, indigenous and imported. Along with this went a willingness to invest in development, both of knowledge and of equipment replacement and escalation. Their blending studies cover a wide range of world coals because of their import policies and have been better known in Australia than are those of other countries. The pressure upon Australian coal producers to build up markets in Europe and other Eastern countries had required a broadening of the knowledge.

The science of blending coals and its application to meet local circumstances were well elucidated a decade ago, at least in terms of the cold strength and size of the coke at the furnace bins. Well before this, however, there was disquiet that these measures were not adequate for control of what was happening within the blast furnace.
A blast furnace is basically a counterflow unit operation in which complex physical, chemical and thermal reactions occur as the result of hot gases flowing up through the descending mass of solids and liquids. It is the function of the coke to provide a source of heat, to supply the chemical reductants (gaseous and solid) and to maintain the permeability of the mass to the upward flowing gasses and the downward draining molten liquids.

The coke being charged to the top of the furnace must be of sufficient size and strength to reach the tuyere and hearth area still of a size distribution suitable to maintain this permeability. This requirement will be met only if properties such as hot strength or resistance to degradation by gas attack are adequate. Holowaty and Squarcy (1957) reported studies of coke physical properties at high temperature and Echterhof was measuring "hot strength" in Germany by enclosing a cold strength test drum in a furnace. This author visited him at the laboratories of Bergbau-Forschung GMBH in Essen in 1961, specifically because of concern about this issue, and subsequently initiated high temperature compressive testing of coke cubes at Port Kembla. The results were unsatisfactory and were not published, but the fractures which developed in the cubes tested appeared to relate to the presence of relatively large "inert particles".

The increase in size of blast furnaces has been achieved mainly by increase in diameter, and the manipulation of gas flows has become the overriding tool of the operators, given that high grade feed is axiomatic for a unit producing over two million tonnes of iron per year. Penetration and distribution of gases from the tuyeres, wall
working and top gas profiles are matters for the ironmaking technologist, but what seem minor changes in coke can precipitate shortfalls in control from which it may take several weeks to recover. These can have major repercussions in productivity, costs and refractory life. Japanese ironmakers have quenched, painstakingly excavated and examined the contents of at least five blast furnaces (Kanbara et. al., 1977; Kanbara and Shigemi, 1983) and have profoundly altered the understanding of in-furnace conditions. Others, including Australian workers, have extracted residual coke material from the tuyere area of working furnaces (Coin, Gill and Hart, 1982). The hot strength of coke as measured by a cold strength test device in hot conditions has not proved useful and much significance is attached now to the residual strength after attack by $\text{CO}_2$ gas at elevated temperature (the Bouduard or solution loss reaction) during which constituents of the coke (maceral-derived components) are weakened preferentially by this reaction. A body of literature has built up, with broad but not unanimous agreement about the behaviour of coke inside the blast furnace.

The interpretation of results from such tests require statistical evidence that improved furnace results from, or at least appears to correlate with, a particular practice. Such correlations often precede the elucidation of the science, which then must be established to maximise advantage. Such a case is the claim advanced in Japan that a period of "soaking" the coke mass at elevated temperature in the oven after completion of the normal cycle improved the quality. This implies that some basic change in coke structure has been achieved by thermal means at a late stage in coke formation and in circumstances where the critical variables of coal feed (blend, grind, bulk density) and coking rate have been constant.
Australian coking practice could benefit by a soaking time that ensured all coke reached a specified temperature before discharge from the ovens; that is, that the operating malpractice of discharging "green ovens" was eliminated. Such malpractice does not apply in major Japanese plants and in fact has been eliminated largely in Australia as coking times have been extended to produce the larger coke demanded for the larger blast furnaces. This has been facilitated by the economic recession of recent years.

The size of coke is a crucial factor in permeability control, and is determined by the rate at which the coal mass is coked. The maximum time available for coking an oven is fixed in industry by production demand and the plant available. Often there is a clash of interest between the demand for coke and the desire to maximise coke size by slower coking, installation of additional ovens being a very costly and long term solution. This has been the case at the Port Kembla plant where mean coke size 48mm had been achieved by 1983 at the cost of coke output, but this was lower than the mean size 50mm required for the 3,000 cu.m. blast furnace. Subsequently coke size above 50mm has been produced but furnace operators still seek larger coke and opt therefore for the full use of time available for coking, rather than a faster coking rate, then a soaking period. The need to construct new ovens as replacement for aging plant is inevitable and the number of ovens required will be determined by the coking regime that is most satisfactory for blast furnace performance, to a greater extent than applied when smaller furnaces consumed the product.
CHAPTER 2

COKE STRENGTH

Coke is an agglomerate material and the strength of the coke lumps as "seen" by the blast furnace is determined by a combination of macrostructural factors (fissures, pore size) and microtexture that defy quantifying by values having physical dimension. Hence strength is indicated in practice by indices obtained by empirical methods on a collection of lumps.

2.1 Conventional Cold Strength

These empirical tests vary among countries and standards organisations, but generally take the form of assessment by size criteria after degradation in a tumbler at room temperature. Typically a specified mass of sample of the order of 20 kg is placed in a tumbling drum which is rotated for a set number of revolutions, after which the mass is sized. Two indices are used conventionally to characterise the strength, the fraction retained on a relatively large aperture screen is related to volume breakage (along incipient fissures or through the mass) whereas the fine fraction passing an aperture of 6-15mm is considered a measure of abrasion, and relates to the basic structure of the matrix. This view is reiterated in a review of stresses in coke by Miara (1982).

Despite efforts by the various standards organisations a common test has not been agreed and the use of a variety of measures can be found
within Australian cokemaking and coal marketing circles (Laver and Gadsden, 1976 p. 107).

There is a wide variation in duration of the tests, some of which favour severe stressing. Longer testing brings more abrasion factors into play and some investigators have found that measurement of the progressive generation of fines with increasing time of revolution is useful in research works. Others favour shorter times as more realistic and more practical where repeated testing is advantageous for control purposes.

A significant difference occurs among the tests in the size and size distribution of the mass charged to the drum. The various national standard tests used commonly in Australia are the American (ASTM), Japanese (JIS) and the European Micum and Irsid. Some are dictated by overseas market requirements; the following preferences by the author are advanced from his experience with blast furnace feed materials.

The cokemaker is required to meet specific levels of coke strength with high consistency. The difficulties of coal supply and quality, its preparation and rate of coke production are problems for him to solve, for which he needs an assessment of coke quality. His preference is to measure the size of the product and its strength as independent data. A narrow, specific lump size for drum testing is required to eliminate the size factor and is met by the ASTM feed sample. On the other hand, the blast furnace receives and reacts to a feed of size range 20-80mm, with which its behaviour must be correlated. Operators seem to obtain better correlations with those
tests which utilise a wider range of sizes than does the ASTM, despite the provision of separate data about size distribution. Different tests serve different purposes.

Correlations of the various test results have been attempted but have been unsatisfactory in detail, operators being concerned about changes of one or two units within the data (BHP/ACIRL, 1981). The solution adopted at Port Kembla plant was to evaluate coke (by isolated tests) by most of the common tests and to exercise routine quality control by alternating ASTM and JIS tests on 8 hour samples together with sizing. This seemingly obvious solution not infrequently introduces the difficulty that the indices move in contradiction to each other for no assignable cause, but those who inherited the data remain convinced of its value (Nightingale 1986, unpublished comment).

The indices discussed provide no basic data and their value is for quality control purposes, with targets set from practical experience. They have provided a yardstick whereby coke makers have developed coal preparation and blending practices to cope with the higher strength demands for larger blast furnaces and, in the Australian situation, with increasing proportions of less strongly coking coals available to local plants. The ASTM stability index for Port Kembla coke was raised into the low fifties in about 1960 by increasing the fineness of the coal grind and controlling bulk density in the ovens with oiling (Gadsden, 1958). This was adequate for No. 4 blast furnace to hold briefly in 1961 a world record monthly output rate, but it soon proved inadequate for the larger No. 5 furnace commissioned a decade later. The target was raised to 60. This was achieved by 1982.
Coal supply over the two decades, from captive mines largely, but including some purchased in the area, had been marked by the replacement of worked out areas by others with higher proportions of poorly coking or noncoking maceral constituents. The situation required that improvement in coke physical quality be obtained in the face of this lowering of coal quality, a requirement met by a combination of pragmatic pilot oven assessments with an increasing understanding of coal petrology. The stimulus provided by CSIRO has been acknowledged. The acceptance of coal petrography as a tool in coal blending was influenced by the work of Ammosov et al. (1957) and Schapiro, Gray and Busner (1961).

There exists difference of opinion about the behavior of transitional macerals between vitrinite and inerts during carbonization. Cook and Wilson (1969) present succinctly the view that prevailed in Port Kembla's technology, stating that "it has been discussed by Taylor (1957); Brown, Taylor and Cook (1964); Taylor, Mackowsky and Alpern (1967) and Bennett (1968). This would show that the inertinite group of macerals does indeed remain inert during carbonization except for a minor amount of transitional material having a reflectance very close to that of vitrinite".

The view that a portion of the semifusinite should be considered as reactive has been taken by others. Schapiro and Gray (1964) adopted one third in the calculation of their factors for U.S. coals. Others, (Benedict, Thompson and Wanger, 1968; Steyn and Smith, 1977) have been concerned with more clearly separating the "effective inertness" of the transitional macerals, usually in relation to rank. Diessel
(1982) concluded that in some Australian coals the proportion of reactive inertinite is higher than allowed in calculations.

The coals from the Southern coalfield, used in the Port Kembla steelplant blend, are low in exinite but abundant in inertinite, particularly Bulli seam coal, which comprises about 70% of the feed. They have been characterised for blending purposes by their vitrinite content. A relationship of coke strength to vitrinite content has been established (Wilson and Cook 1968) and a pragmatic formula for the guidance of operators was developed (Laver and Gadsden, 1976 p. 108).

\[
\text{Sum} \% \text{ coal} \times \% \text{ vitrinite} \times (\text{reflectance})^P = 53
\]

\[
( \quad 1.30 \quad )
\]

where \( P = 1/2 \) for reflectance > 1.1  
\( P = 1 \) for reflectance 1.1 - 0.8  
\( P = 2 \) for reflectance < 0.8  

This formula was devised to quantify the proportions of available coals, of known composition, needed to achieve a target strength, the latter being characterised by a petrographic factor derived from coal blends found by experience to meet the requirements. The issue of "relative inertness" was not ignored, although believed to be resolved in the negative for the coals involved. As the blend changes are not substantial, (unless catastrophic conditions of coal supply, such as a critical shortage brought about by industrial strife, overrides the importance of quality), the inertinite content is in effect a constant on both sides of the equation.
It is observed that the target figure of 53 is some 5 units higher than indicated as necessary by the research work. This is simply a safety factor, to take account of the vagaries of blending in practice and of the mistrust of the precision of prediction from models forecasting coke strength. This latter fear is confirmed by Gill (1982). The provision of efficient blending plant at Port Kembla in 1983 permits, in the author's opinion, a lowering of the target to 50.

The processes commonly accepted by coke makers for achieving the desired mean size and strength of coke, namely coal quality and blending, grind and bulk density control, and coking time have been established, but the performance of the blast furnaces, or at least that of the 3000 m$^3$ No. 5 unit was not as hoped. It has become evident that assessments concerned with the coke substance, previously limited to the researcher's laboratory, must be brought into the operating field.

Coke is a composite material made up of pores and pore walls; its physical characteristics will be determined by the pore characteristics (porosity, pore size, size distribution and shape) and pore wall characteristics (chemical composition, microstructure, anisotropic texture and degree of crystallisation) (Miura, 1982).

The body of literature about mechanical properties of coke built up over several decades and dealing with tensile strength, compressive strength, Young's modules and analyses of stress patterns has been condensed and elaborated in recent reviews (Jeulen et. al., 1982; Miura, 1982; Waters et. al., 1986).
2.2 Microstrength

An early attempt to measure the strength of the coke substance was made by Blayden, Noble and Riley in 1937, using a 2 gm sample of particles sized about one millimetre in a tumbling tube together with 12 x 5/16" steel balls. This, known now as the microstrength test, aimed to avoid the effects of fissuring and large scale porosity in the sample. The test was little used until Japanese workers adopted it (Kojama 1977) but it stimulated the author in the sixties to add grinding balls to the ASTM drum, to demonstrate that under such conditions the "hardness" of Newcastle coke was lower than that of Illawarra coke, and that the apparent high result reported for Newcastle coke from the conventional test arose probably from lack of autogenous grinding because of weaker lumps, rather than inherently better abrasion resistance. Waters, Vince and Litster (1986) established that when seven cokes were stabilised by preliminary stressing, then subjected to progressive abrasion testing, all seven showed first order plots of mass reaction (minus 1mm) against revolutions. For the purpose of this investigation, the work by Waters et. al. shows that prolonged tumbling after elimination of volume breakage along fissures by severe stressing (such as crushing) results in surface breakage or abrasion of the coke substance.

It is reasonable to conclude that the microstrength test, when applied to cokes made from a given blend or single coal, under similar thermal histories through the plastic zone and transformation from semicoke to coke (thus having similar pore size, pore distribution and shrinkage stressing) will be a measure of the strength of the coke substance.
The microstrength test is used in the investigations reported here of the effects of different finishing temperatures or soaking.

2.3 In-furnace Strength

Jeulin et. al. (1982) summarise the many investigations over four decades of the in-furnace behaviour of coke. They state that the usual mechanical tests on cokes are not suitable to predict coke strength in the lower part of the furnace, where temperature is very high, and coke has been altered by solution loss reaction.

Although 25 to 30% of the coke may be consumed by carbon solution loss, the importance lies not in the extent or rate of reaction but in its contribution to the weakening of coke by mechanical degradation.

Japanese ironmakers have made use of forms of a high temperature solution loss test followed by a cold strength test of the residual coke (Fukuyama et. al., 1973; Sunami, 1977; Ishihara et. al., 1977; Fujita et. al., 1981). The test adopted in Australia follows that of Nippon Steel Corporation (N.S.C.), using CO₂ gas only, reacting at 1100°C and testing the strength of the cooled residue in a revolving I tube. Weight loss is recorded as C.R.I. and strength after reaction as C.S.R. A linear relationship between these two has been established by Ishihara et. al. (1977) and in Port Kembla work (unpublished).

The purpose of such tests is to assess the likelihood of problems arising in furnace operations due to impeding the gas flow or liquids
drainage, or both of these processes, through the interstices of the burden (which by this stage is mainly coke) by small particles or fines arising from degradation of the coke. Experience has shown that in large furnaces a minimum CSR of 50 is required, usually above, and the higher the better.

Reports emanating from Japan that coke quality was improved by soaking were quantified by Hara et al. (1980). They established variability of CSR within commercial ovens and under different soaking conditions, stating that strength, particularly CSR, varies greatly between coke near the wall and in the centre. The expandability and fluidity of coal during coking is affected by rapid rise in temperature and this is fastest at the wall. Here the coke is subject to higher temperature, and for longer duration, causing the anisotropic texture of the coke formed to grow more than at the centre. This difference is lessened by lengthening the soaking time. They further stated that CSR improved linearly as holding time lengthend (from 50 at nil soaking to 58 after 8 hours soaking). Even if the length of time up to completion of coking is the same between ovens, the coke produced will differ if there is a difference in soaking time. CSR increased also with finishing temperature, linearly from about 50 at 900°C to 70 at 1100°C.

The data from various oven positions is informative. At three positions from wall to centre, CSR decreased, at 1.5 hours soaking from 43 to 18 and at 4.5 hours soaking from 50 to 30. In the vertical plane, where temperatures differed by from 30°C to 100°C, there was also a decrease in CSR in the upper parts of the coke mass. This
decrease became less as the finishing temperature was raised. Results obtained in the Japanese work were:

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<td>Number of samples</td>
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<td>62</td>
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<td>Average CSR</td>
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<tr>
<td>Standard Deviation</td>
<td>3.93</td>
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Most of these data show levels of CSR well below that accepted for operations. Some of this may be due to the selection of samples before the coke was subjected to "conditioning" by the severe handling practices that exist in any plant. Possibly poor quality coke is more affected by soaking. Regardless of such reservations, the other data show development of CSR in coke of acceptable level +50 by soaking or higher finishing temperature.

Confidence in reactivity-type tests has been shaken by the demonstration that the style of reaction obtained in the laboratory is not the same as that which occurs in the blast furnace (Coin et al., 1982). In the case of Port Kembla coke, in the residue from the N.S.C. test the reactive derived maceral component was unchanged, whereas in coke specimens extracted from the tuyere area of the blast furnaces, the inert maceral-derived component was the one unaltered, with the surrounding reactive maceral-derived component suffering pervasive attack. The significance of this to Port Kembla's blending practice of incorporating coals high in inert maceral content by achieving critical levels of reactives has been recognised.
European workers have not accepted the "CO$_2$ type only" type of test believing the reaction regime to be different from the gaseous environment within the furnace. Jeulen et al. (1982) use a technique subjecting a coke sample to a gas mixture of 10% CO$_2$, 20% CO, 10% H$_2$ and 60% N$_2$ at temperatures rising to 1200°C until a constant weight loss of 25% is reached. A cold strength of the residue is then determined.

Diessel (1986) has evaluated cokes produced and tested by Centre de Pyrolyse de Marineau of Charbonnages de France on behalf of Kembla Coal and Coke Pty. Limited from coal blends containing 100%, 40% and 20% KCC coal in a European blend. Microscopy of the coke from the reaction test with mixed gases, and 25% weight loss up to 1200°C showed a very mild visible effect on the coke texture, lacking the deep penetration of the NSC test (100% CO$_2$). In the latter tests the proportion of fused coke matrix had increased at the expense of inertinite derived material.
3.1 Mechanisms

A voluminous literature has accumulated about the thermal and rheological behaviour of coal. Much of this has concentrated on those temperature zones where the nature of the coals comprising a blend is paramount in determining coal properties. This study is directed to changes that may occur at higher temperatures, about 1000°C, within what the cokemaker considers to be finished coke. A review of the basic reactions of coke formation preceding this stage, and influencing it, is warranted. This is restricted to the presentation from several authorities widely recognised for their own work, who have drawn also upon the contributions of many others.

The basic process of carbonization was described by van Krevelen (1961) as thermal cracking (depolymerisation) with simultaneous disproportionation of hydrogen. Fragments enriched in hydrogen evaporate as tar, the others recondense to yield semicoke. Side chains are cracked at the same time. Aromatic carbon-hydrogen bonds are broken at higher temperatures (secondary carbonization). Functional groups, such as hydroxyls, give rise to a competing reaction (intermolecular condensation) which has a severe influence on the whole process, especially on the plastic properties. van Krevelen postulated that the decomposition may be distinguished into three successive reactions, firstly formation of an unstable intermediate
phase (named metaplast) which is partly responsible for the plastification; transformation of this intermediary to semicoke and, finally, into coke:

1. coking coal \( k_1 \) metaplast  
   $$\rightarrow$$
2. metaplast \( k_2 \) semicoke + primary volatiles  
   $$\rightarrow$$
3. semicoke \( k_3 \) coke + secondary gas  
   $$\rightarrow$$

where \( k_1, k_2, k_3 \) represent the relevant reaction constants.

Gibson (1979), Board Member for Science of the National Coal Board of Great Britain has drawn upon more recent sources for his summary.

"Upon heating, coal undergoes chemical changes giving rise to the evolution of condensible vapours and gases and leaving behind a solid residue consisting of carbon and mineral matter. Moisture is evolved firstly, then in the temperature range 350°C - 500°C, depending on the rank of the coal, coking coals soften, become plastic and coalesce into a coherent mass which swells and then forms a solid porous substance".

The two important temperature zones distinguished are that in which the coal is plastic, and that at higher temperatures in which the resolidified material contracts.
"The plastic stage involves the breaking of cross linkages, comprising either oxygen or non-aromatic bridges between neighbouring groups, leading to mobility of some of the decomposition products. The lower molecular weight compounds can undergo further changes to yield (a) the gaseous volatile matter consisting of hydrogen, methane and other hydrocarbons, and (b) the highly complex mixtures found in coal tar. The higher molecular weight fractions remain and form semi-coke on solidification, during which adjacent aromatic clusters join up through a free radical condensation mechanism".

These free radicals are formed from the initial scissions and side chains broken off through heat treatment.

"The semi-coke has visco-elastic properties up to 700°C and transforms into hard coke, a brittle solid, as the temperature rises to about 1000°C. The process is accompanied by elimination of hydrogen and growth of graphite-like layers arising during the plastic stage and resolidification to semi-coke. The predominating gaseous product is hydrogen, removed from the periphery of the aromatic layers. X-ray diffraction, magnetic susceptibility and electron microscope data confirm layer growth arranged in graphite type crystallites at these relatively low temperatures".

3.2 Plastic Temperature Range

Prime quality coking coals have volatile matter content in the range 20-32% (d.m.m.f.) and become plastic before active decomposition occurs. Viscosity and the rate of devolatilisation of the plastic
mass are such as to minimise intergranular swelling but enable neighbouring coal particles to adhere strongly. Constraint of the intergranular swelling among the particles of the coal mass causes pressure between particles and progressively eliminates the voids between them. The coke thus formed has fairly uniform pores of small diameter surrounded by relatively thick walls giving rise to a high resistance to abrasion. (Gibson, 1979).

Coals with volatile matter content outside the range 20-32% undergo decomposition both before and during the plastic temperature zone. In many cases strong intergranular swelling occurs and the whole mass may foam, giving rise to high porosity and thin walled pores of large diameter within the coke. This product has a relatively low resistance to abrasion.

Gibson continues "It is clearly seen that the inherent strength and abrasion resistance of coke are determined by the behaviour of the parent coal in the plastic zone".

3.3 Post-plastic Temperature Zone

As the temperature is raised after the plastic mass resolidifies, the solid contracts but at a rate which is non-uniform and dependent upon the devolatilisation and reorientation processes in the solid, varying from coal to coal. Coefficients of contraction, measured in a high temperature dilatometer and plotted against temperature (Saule, 1955) show two peaks for coking coals; the first occurs just after
resolidification (500°C) and the second in the region of 750°C. The latter is smaller than the first.

In the coke oven, where heat is supplied from the parallel oven walls, the plastic layer travels through the coal charge from each wall, leaving behind it an apparently solid but visco-elastic semicoke undergoing further resolidification and contraction. The moving plastic layer is expanding, forming the semicoke. The contraction in the latter as it is heated to the completion of carbonization in the oven to temperature about 1000°C is uneven. Thus alternating compressive and tensile forces develop in the semicoke. Miura (1982) presents figures from Saule (1955) and the modelling work by Konyahin et al., (1973) to illustrate this.

The differential strains that are set up result in the formation of fissures which break up the mass. Gibson (1979) states that a primary fissure network results from the rapid contraction associated with resolidification about 500°C and it has been shown that the size of the coke discharged from the oven is related to the height of the first peak in the contraction curve.

A second network of fissures is apparent in these coke pieces when sectioned. On impact these fissures extend and cause the lumps to break into smaller pieces. The impact strength of coke is seen to be related therefore, to the height of the second peak in the contraction curve.
3.4 Microtextural Changes

Stach et al. (1982) attributes the first investigations by microscopic examination of the transition from coal into coke of a coke oven charge which was quenched after half the carbonization time to Echterhoff and Mackowsky (1960). They reported that the texture of the coke which is formed in the plastic zone remains unchanged during the transition from low temperature to high temperature coke and concluded that all essential phases of coke formation take place in the plastic zone. The shrinkage resulting from the loss of volatile matter does not cause any changes of the pores or cell walls of the coke, but it produces tensions which give rise to fissures. The author was aware of similar studies being made at CSIRO Coal Division laboratories at North Ryde, N.S.W. about the same time.

Attention in this study is directed now to the transformation taking place within the substance of the cell walls at temperatures reached in commercial ovens. This is nominally about 1000°C, but frequently some areas of the coke mass may not reach the desired temperature level. It would be a poor practice where the peak temperature for any part of the coke mass did not exceed 900°C, but such does occur. It is necessary therefore to consider the extent of knowledge of temperature distribution within commercial ovens.
Coking rate in slot ovens is defined by operators as the width of the oven divided by the coking time, representing the condition where the two heat fronts moving inward horizontally from the walls have met and the centre has reached a suitable temperature condition. Thus ovens 450mm wide coking in 18 hours have a nominal coking rate of 25mm per hour. This is an artificial rate; a combination of the two rates significant scientifically to coke structure, namely that of heating through the plastic zone and that through the semicoke zone that follows. The latter is faster than that through the plastic zone due to the increased thermal conductivity of the coke, but in practice both are set by the "coking rate" nominated.

The operator can increase or decrease the overall rate, over a period of days, by altering gas input to the battery but variation within the coking cycle is not possible. He can increase the temperature to which the coke mass is taken either by extending the coking time, at the cost of reduced output, or maintain the coking time but increase the coking rate, incurring a reduction in coke size. A trend to longer coking times has been general in the industry, firstly to produce larger coke (with the advantage of better control of emissions as an important side effect) but also as a result of a fall in demand because of the slump in the steel industry. High costs for energy have focussed attention on maximising efficient use of fuel. All of these have encouraged better management of heating, using
sophisticated measuring devices in association with modern data processing systems.

The Dutch plant Hoogovens found (Thijssen and Vander, 1985) that "coke end temperature, i.e. final temperature, is a good and practical criterion for optimising the heat input to improve coke quality, coke cake properties (shrinkage) and energy consumption". To that end a coke end temperature measurement has been incorporated in their heat input control system. Coke strength was shown to increase as finishing temperature rose to 1020°C, beyond which a plateau was reached. It was concluded that to achieve the desired coke quality and shrinkage in the oven, end temperature should be between 1000°C and 1080°C.

Plants in Japan were enabled or forced to extend coking time, in some instances as much as six hours beyond normal coking time and a practice of soaking was developed that is claimed to be beneficial to coke quality, in particular those assessments done routinely for quality control relating to the solution loss reaction (Hara et. al., 1980). CSR has been discussed under coke strength.

It is well established that coke size is determined by coking rate, mean size at Port Kembla increasing from 42mm at coking rate 30mm per hour to 48mm at coking rate 23mm per hour (Gadsden, unpublished) but this falls below that demanded for the 3000m³ furnace. The route which has been preferred at Port Kembla to achieve the required size is the slowest coking rate consistent with achieving the desired end temperature in the time available. An understanding of the effect of
end temperature upon the fundamental properties of the coke substance is necessary.

This relationship of quality to final temperature is distinguished from the quality factors influenced by the rate of heating through the plastic zone and which are better understood.

Control of the temperature within an oven has long been done by indirect means, measuring the temperature at defined positions in the heating flues on each side of the oven and setting levels that will achieve coking in a specified time. A battery of 72 ovens will have 73 walls, each with 32-35 individual flues and measurement by optical pyrometry is no mean task, complicated by half hourly reversals of gas cycles from "burning" flues to "waste gas" flues. The several thousand tonnes of refractory brick making up such a battery represent a massive heat sink, insensitive to small thermal fluctuations, but the shortcomings of thermal standards have been tolerated by technologists largely because of the absence of sophisticated and reliable techniques of assessment and, in the experience of this author, because their extent has not been appreciated.

Technologists and operators accept that coking is complete when the only gas evolved is hydrogen and its rate of evolution is falling. This has been assessed conventionally by visual inspection of the colour and volume of the offtake gases burning when they are vented to atmosphere. This is subjective, at least in terms of tens of minutes, and is being replaced by systems such as opacity meters or thermocouples in a convenient position in the offtakes (Satomi, 1980).
The impulse generated may be used for recording or for control of fuel gas. The relationship of these parameters to temperature within internal areas of the coke mass is noticeably absent from publications.

Techniques for measuring the wall temperature of the emerging coke by pyrometers or thermal cameras mounted on the coke guide, or the use of sensors above the hot car (Horvath et. al., 1985; Thijsen and Vander, 1985) have proved effective for tuning of temperature distribution or for correlation purposes. These do not measure the minimum temperature which is likely to be in the centre of the oven, and which presumably is that critical to coke quality.

Temperature surveys of the research pilot oven at Port Kembla and the industrial oven were done about 1961 in conjunction with the Company's Central Research Laboratories officers, by inserting thermocouples vertically and horizontally into the coal mass in the oven. The technique was cumbersome, impractical for other than single trials and unreliable because of doubt about the ultimate position of the couple. Nevertheless some areas of poor distribution of heat were found with temperatures lower than required, whatever the position of the thermocouple. Improvement in temperature distribution was effected but the real issue of the minimum temperature reached by the centre coke was not resolved. It is observed that a finishing temperature of 975°C in the centre of the oven was adopted (by this author) for pilot oven practice over the succeeding years.
As technical concern has been freed from attention to selection of coal blends, and spurred by economic considerations of fuel gas consumption as well as coke quality factors, considerable work on heating and control has been published, leading to inferences concerning finishing temperature.

Solmar data (Barbier et al., 1983) show that the centre temperature of the lower 5 metres of a 7 metre high coke mass exceeded 1000°C, with maximum 1100°C, but that of the top 1.5 metres fell to below 900°C.

A Stelco plant, with a set aim of 850°C minimum, reported (Stelco 1979) a normal range of from 1130°C to 980°C, narrowed with better control to between 1100°C to 1000°C. A soaking time of 1.4 hours (after temperature of 950°C achieved in 15.7 hours) was practiced to ensure clean pushes.

Hoogovens plant (Thijssen and Vander, 1985) reported finishing temperatures 1050°C to 990°C, improved by better control to a much smaller spread about an average of 1050°C. Nevertheless, their end temperatures ranged from 1005°C to 1075°C.

Bethlehem steelplant report temperatures from sightings on the emerging coke as 1150°C (Horvath et al., 1985).

Japanese technology is in the forefront of heating control but specific correlations of the parameters measured to coke temperature
are absent from published data, possibly as they see them being different for different coal blends.

The improved pyrometry and data processing facilities that have accompanied this work over the past 15 years have shown many established operators that their heating standards are much less satisfactory than had been supposed.

Temperature gradients exist in an oven heating system along the walls from pusher to coke side, to take account of the oven taper (necessary for pushing) and therefore a greater coal mass, and in the vertical plane of the wall because of combustion performance. There is also a gradient from wall to centre, changing as coal becomes coke. In addition, there are substantial differences of bulk density of the coal charge within the oven, arising from gravity charging and levelling. The complex flue systems and gas flows designed into the batteries provide some scope for adjustments to distribution of heat but they are difficult to effect and worse to quantify. It is not surprising that coke emerging from the oven shows variability or that careful and constant attention is necessary to achieve a uniform temperature. A soaking time ranging up to one hour has been incorporated in most plant practices to aid this.

Satomi et. al., (1980) showed that more effective control of thermal conditions, especially where computerised, reduced the variability of coke quality parameters. The D1_{30/15} strength index increased marginally during the computer controlled period, from 94.97 to 95.15 and deviation fell from 0.45 to 0.30. Similar improvement in indices has been reported in association with better, but not computerised heating control at Port Kembla plant (Nightingale, 1986, unpublished).
CHAPTER 5

THE MESOPHASE, LIQUID CRYSTALS AND ANISOTROPY

It is evident that the end temperature of lumps of coke from any oven varies considerably and it follows that, where the parameters used to measure quality are temperature affected, they are an average of a range. It is likely that experience has set targets at levels which ensure the minimums are acceptable, without knowledge of the basic variations or whether they are significant.

The crystallite structure of coke likely affects its physical properties and chemical reactivity. Studies of anisotropic texture by optical microscopy, by X-ray diffraction and by other techniques have a longer history than often is recognised.

Taylor (1961) attributed the view "that changes that occur in the optical properties of vitrinite during heating are indicative of changes in its physical structure" to W. J. Schmidt in 1945. Taylor examined the optical changes taking place up to the resolidified semicoke stage, using initially samples of thermally metamorphosed coal from the Wongawilli seam of the Illawarra coalfield and then artificially carbonized samples.

The phenomena observed included the loss of the initial optical anisotropy as the vitrinite became plastic, followed by the formation and enlargement of fine spherical bodies. These bodies, each of which had a single crystallographic orientation, grew until they began to
interfere with one another's growth as the mosaic type structure started to form. Completion of the mosaic formation coincided with the resolidification point of the coal. Taylor commented that "since these mosaic units are, in a sense and to a degree graphitic, the tendency to marked anisotropic expansion on heating is to be expected".

Further studies (Brooks and Taylor, 1965) on a range of organic substances including vitrinites from bituminous coals led to the conclusion that "the formation of graphitising low temperature carbons by solidification from a liquid phase proceeds via the separation of a mesophase having properties similar to those of liquid-crystals. Initially the mesophase separates in the isotropic liquid as spherical droplets having a considerable degree of molecular order, with the aromatic sheets stacked in parallel arrays. The spheres grow at the expense of the plastic material until a three dimensional mosaic structure is formed".

Spheres and pitch like material were present in the vitrinite from bituminous coals at temperatures in the range 460°C - 470°C. When semicoke was heated, the mosaic texture and lamellar orientation remained, but the perfection of order within each unit increased. (It appears, however, that the heating was to a very high temperature, up to 2500°C).

Marsh (1973) concluded that the ability of prime coking coals to produce metallurgical coke represented an optimum in capability and extent of liquid-crystal formation, the term being preferred by him to that of mesophase because of the imprecision of the latter.
"Liquid-crystal systems have been known since 1888 and possess more structural order than that found in normal isotropic liquids but are not genuinely crystalline. Of the several categories into which liquid-crystals may be placed it is the nematic (threadlike) which has relevance to carbonization. It is now established that liquid-crystal, nematic structures are formed during the carbonization of aromatic hydrocarbons, petroleum and coal tar pitches. During the pyrolysis of the isotropic liquid or plastic stage through which the above materials pass with increasing temperature, the constituent compounds undergo intra and intermolecular rearrangement and condensation reactions, producing new molecules which facilitate the growth of the nematic liquid-crystals from within the plastic phase. These separate as spherical droplets which eventually coalesces to give the mosaic texture. These droplets are anisotropic and the arrangement of the molecules is envisaged as one in which they lie parallel to one another but with no order in the stacking sequence. It is inferred that within the nematic mesophase there is a number of domains which possess this molecular orientation, each domain having a different optical axial direction".

Marsh proposed a model process based on the assumption that liquid-crystal growth processes occur during the carbonization of coal. In this context the most important entity within the coal is the reactive vitrinite, which supplies the necessary controlled fluidity and it is its pyrolysis that forms liquid-crystals. As the liquid-crystals coalesce a mechanism of flow can be established, with a tendency to flow over surfaces, whether of nonfusing solids or the vesicles of gaseous volatiles. The development of anisotropic
structures provides a restriction upon the growth of vesicles and may contribute directly to strength by a reinforcing mechanism.

The long range stacking order within the crystals as evidenced by Brooks and Taylor (1965) is retained as the liquid-crystals are modified by temperature to form the semicoke and ultimately the coke. Marsh (1973, p. 207) makes the statement that from the lamellar molecules there is established a stacked lattice which can be made more perfect during graphitisation.

Patrick et. al. (1983) agreed that the vitrinite-derived components of carbonized coals exhibit anisotropy varying from mosaic to flow type, the latter being consistent with extensively aligned structure but commented that as a result it frequently seemed to be assumed that the behaviour of coal during carbonization conforms closely to the pattern of behaviour exhibited by carbonizing pitches. They stated that, except under special circumstances, spherical mesophase units have not been observed during coal carbonization. They went on to say that the statement does not exclude the possibility that such units are present in size range below the limit of resolution of the optical microscope.

Patrick et. al. (1973) set out to ascertain if the various types of optical anisotropy found in cokes could form a basis for the characterisation of cokes produced from different coals. Vitrains from a range of coals were carbonized at temperatures from 370°C to 1000°C and the types and amounts of optical anisotropy in the resultant semicoke and cokes were determined from microscopic examination, the anisotropic compounds being classified according to
the grain size of the granular mosaics and appearance. The anisotropy developed directly from the isotropic phase, appearing initially as a fine grained mosaic. With increasing carbonization temperature the fine grained mosaic was transformed into progressively coarse grained anisotropy, the extent of this transformation depending on the rank of the coal. The identifiable components were divided into six categories, starting with the basic anisotropy of vitrain (not evidenced in cokes made at temperatures above 460°C); isotropic; mosaic; fine grained; mosaic - medium grained; mosaic - coarse grained and flow. The changes that occurred with increasing temperature of coking demonstrated the temperature dependence of the development of anisotropy, as illustrated for vitrain from a coking coal in Fig. 1. This vitrain was handpicked from a sample from Craghead Busty seam and contained 93% vitrinite, with reflectance 1.13%.

A prime coking coal gives a mosaic size usually of the order of 1mm and with decreasing rank, coking coals have progressively smaller sized mosaics (Patrick et. al., 1973). The coke made from low rank coal appears isotropic but it is not known whether it is truly isotropic or has a mosaic size too small to be resolved by an optical microscope. In a coke made from high rank coal the mosaic effect is replaced by a lamellar texture.

Goodarzi and Murchison (1972) examined the optical properties of three vitrinite-rich coals (of varying rank) carbonized at temperature intervals of 25°C over a range up to 950°C, using a heating rate of 2.45°C per minute. In general, as the temperature rose the variation
FIG 1  ANISOTROPIC CONTENT IN CARBONISED VITRAIN FROM A COKING COAL CARBONISED TO DIFFERING FINISHING TEMPERATURES.

(REPRODUCED FROM PATRICK, REYNOLDS AND SHAW, 1973)
of all the optical properties reflected the growth and development of organised polycondensed aromatic systems, but in detail reflectivity did not prove as sensitive an indicator of structural change as did other optical parameters, particularly refractive index. They concluded that the behaviour of the refractive index curve of the carbonized vitrinite is governed by changes in the heights of the crystallites forming the aromatic system. The shape of these curves closely follows the shape of curves produced in independent X-ray diffraction studies giving the heights of crystallites.

Goodarzi and Murchison (1978) attributed the variations in optical properties observed in their previous work principally to two factors, firstly to the increased aromaticity of the chars and secondly to the reorientation of the aromatic lamellae within the crystallites which produces a higher degree of molecular ordering. The influence of different heating rates upon the optical properties of carbonized vitrinites was then examined by them, using bireflectance as a quantitative measure of variation. Their results for vitrinites of rank of the order of interest at the Port Kembla steelplant are shown in Fig. 2. Among their conclusions was that with vitrinites in the medium bituminous rank range, at temperatures in the region of 950°C, very high bireflectance levels approaching those of graphite can be obtained with fast coking rates.

They stated that individual bireflectance measurements are not highly specific. The range of heating rates employed in the experiments reported was greater than met in the commercial coking process, but the range of heating rates within an industrial oven may still be
FIG. 2. VARIATION WITH TEMPERATURE OF THE CURVES OF OIL BIREFLECTANCE OF SIX VITRINITES CARBONISED TO DIFFERENT TEMPERATURES

(REPRODUCED FROM GOODARZI AND MURCHISON)
sufficiently large to allow bireflectance measurements to be of some value in assessing carbonization conditions and/or the initial characters of the coke components, particularly when combined with measurement of the size of the mosaic units.
Coal is not a crystalline substance, but the concept that forms of crystallites are present in the carbonized product has existed in an unsophisticated form for many years and the application of X-ray diffraction techniques to the study of carbonization was an inevitable research approach. Such studies have shown that there is a marked difference in the crystallite sizes relative to final carbonization temperature for those coals which pass through a plastic stage compared with substances which do not form graphitising carbons.

van Krevelen (1961) reports that the first X-ray examination of coals were carried out in 1929. Blayden et. al. (1943) studied the crystallographic changes which occurred during the carbonization of some pure organic substances, intrinsically simpler than coals, as a preliminary to similar investigations of the crystallite growth which occurred during the carbonization of coals of different rank, their primary aim being to gain a fuller knowledge of some of the important features of coal structure. They covered a substantial range of coals and temperatures of treatment, including in their studies solvent extraction and the removal of inorganic "ash" before the determination of crystallite size in order to avoid interference effects.

While succeeding investigators are critical of quantitative aspects of this early study (van Krevelen, 1961; Goodarzi and Murchison, 1972) qualitatively the results agree well with later observations and the
graphical presentation of the crystallite dimensions on the c axis (Lc) and a axis (La) is reproduced in later publications as representing the situation.

Although a weakly coking Northumberland coal and a strongly coking Durham coal had very different coking properties, they showed very similar growth curves. (Fig. 3). The lateral growth of the hexagon layer-planes up to a carbonizing temperature of 700°C was relatively small; thereafter up to 1400°C it was more pronounced. The c dimension showed a small but steady increase up to a carbonizing temperature of 600°C and thereafter a decrease; at 900°C the values passed through a minimum which was followed by a pronounced increase as the temperature increased.

Blayden et. al. postulated that "the stacking of the lamellae in coal involves the movement of relatively large, cumbersome units and will be affected by the chemical and physical forces between the lamellae and their environment. The decrease in the c dimension between 500°C and 900°C is probably due to the disordering of the structure by the evolution of gas, possibly involving the disruption of some of the layer-planes. The re-establishment of order along the c axis as the carbonization temperature is increased above 900°C is no doubt due to the stacking of the carbon hexagon layer-planes, rendered possible by the greatly increased thermal vibration".

Pitt (1979) states that work by Diamond in 1960 gives evidence that the degree of parallel stacking of the layers follows the pattern reported by Blayden. Although a higher degree of order exists in a
FIG 3. CHANGE OF CRYSTALLITE DIMENSION WITH TEMPERATURE

( AFTER BLAYDEN GIBSON AND RILEY, 1943)
coke prepared at about 1000°C the structure is still far from ordered in a crystalline sense. The stacks of aromatic layers are still relatively small and moreover they are not mutually well oriented or positioned for further growth.

A schematic representation of the structures of cokes made from three coals of different rank (Fig. 4) is reproduced from van Krevelen.

Marsh and Stadler (1967) state that X-ray diffraction methods reveal the increase in ordering (anisotropy) as an increase in the Lc dimension but conclude that the stacking heights and layer diameters of the crystallites thus reflect no more than the dimensions of very much smaller, randomly distributed regions of overlap of lamellar molecules lying sufficiently parallel to permit the development of a diffraction pattern. The X-ray dimensions Lc and La of the crystallites will be a poor measure of actual stack dimensions.

Despite such reservations Marsh (1973) when publishing the work on liquid-crystal nematic structures states that there is a long range stacking order within these crystals which can be made more perfect during graphitisation.

Goodarzi (1984) subjected three vitrinites to heat treatment temperatures of 1000°C to 1400°C, i.e. semigraphitisation. The continuous increase of bireflectance, in his view, indicated progressive improvement in the ordering of the molecular structure.

Sunami (1977), using laboratory coking techniques, examined the relationships among coal types in coking blends, the crystallite size
FIG. 4 SCHEMATIC REPRESENTATION OF THE STRUCTURES OF COKES MADE FROM:

a. A LOW-RANK COAL 

b. A COKING COAL 

c. AN ANTHRACITE 

(REPRODUCED FROM VAN KREVELEN 1961)
and the reactivity of the coke, but all carbonization runs finished at 1000°C. Ishihara et al. (1977) also concluded in similar work that the Lc values of the cokes largely depend upon the properties of the coals. Fujita et al. (1980) made cokes from different coals in a 1/4 ton oven and plotted relationships between vitrinite reflectance and coke reactivity, vitrinite reflectance and coke Lc. The present author is led to conclude that the last relationship derives from dependent variables stemming from coal rank.

Okuyama et al. (1983), continuing the work on the coke extracted in the dissection of the quenched contents of Kawasaki's Nos. 2 and 3 blast furnaces, established relationships between crystallite size Lc and microstrength, heat treatment temperature (in the furnace), the amount of coke gasified and factors of coke ash constituents. Dubrawski and Gill (1982) measured coke crystallite dimensions in samples extracted from the tuyere zone of Australian blast furnaces and observed Lc to be sensitive to temperatures above 1200°C.

The temperature to which the cokes in these studies have been subjected exceed the range of concern to the cokemaker but crystallite size is one of a number of fundamental coke properties of revived interest to technologists in practical operating conditions. Although the changes that occur within the spread of temperature or thermal conditions feasible in coking practice may be small, they may be sufficient to determine the required finishing temperature based on structures which can be measured on the coke substance.
7.1 Introduction

It is shown in the literature reviewed in the previous chapters that changes in the nature of the coke substance continue as the temperature rises into and above the range usually considered to be the end point of coking in commercial operation (900°C - 1050°C). A systematic increase in the ordering of the "liquid-crystals" towards a more parallel stacking of the lamellae is evidenced, although the extent to which this occurs at the end point of coking appears to be small.

The aim was to establish whether such changes could be shown to occur in cokes made from coals similar to those used at Port Kembla steelplant, either by:

1. a small increase in the finishing temperature of the coke, of the order of 50°C - 100°C, or
2. soaking the coke at the nominal finishing temperature,

and whether any such change is reflected in the strength of the coke substance that makes up the cell walls.
The poor state of knowledge of the thermal gradients and final temperature within coke ovens has been discussed. This obviates the use of lumps of coke from ovens, commercial or pilot scale, thus eliminating testing of the cokes by the pragmatic procedures used in practice, all of which require a mass of coke and a number of lumps beyond that obtainable in bench scale ovens.

It was necessary that the coke specimens produced were made in such a way that the temperature gradient within the mass was small and that, within any one series, variables such as bulk density were constant.

The thickness of the coal layer to be coked has to be limited, but of sufficient mass to yield enough coke for test purposes, after discarding portions possibly subject to end effects. A cylindrical retort 50mm diameter and 200mm in height heated in a vertical position in a 75mm tube furnace, met the requirement. The apparatus is shown in Fig. 5 and the assembled retort ready for charging, in Fig. 6. The retort tube and furnace tube were silica. End plugs were cast from refractory mix. Thermo-couples were 3mm diameter including sheath, the minimum consistent with rigidity for penetration.

Coal charges had a maximum top size particle of 5mm, achieved either by scalping or crushing. All coals were air dried to maximise yield of coke, briefly in the case of Norwich Park, which is prone to oxidation and upon which coking tests were performed within seven days of receipt of the coarse sample fresh from the washery.
FIG 5. LABORATORY COKING APPARATUS
( NOT TO SCALE)
FIG. 6  THE ASSEMBLED RETORT READY FOR CHARGING TO THE FURNACE
A specific mass of coal was charged for each series, ranging from 160 to 175 gms depending on the coal. The height of this mass in the retort fell well within the height of the uniform temperature zone within the furnace. The retort was lined on bottom and side with thin cardboard, then charged by repeatedly pouring into it from a fixed height batches of one third of the coal charge. Each addition was tamped lightly with a 25mm wooden rod. The bulk density of the full charge approximated the average within a commercial oven. Thermocouples were inserted through neat holes in the fitted refractory top. The assembled retort, furnace cap and thermocouples was lowered into the cold furnace to a predetermined position and the fume exhaust system installed.

Heating was controlled manually by a variac. Many of the tests used to evaluate coals use a heating rate through the plastic stage of 3°C per minute. Possibly this is now faster than in practice where coking time has become longer, but a compromise target of 5°C per minute was set, partly to reduce the length of the runs but mainly because the results of Goodarzi and Murchison (1978) indicate that changes are more likely to be measurable at the higher rate. In the event, a practice was developed that produced a slightly lower rate and this control rate was used in comparative tests, by frequent, small adjustments to match recorded temperature to a template (Fig. 7).

The cold start was adopted on the ground that the coke maker's reference point is in fact the quality of the coke made in the most suspect position in the oven. Quality control tests use sufficient lumps to average variations, but it is contended that if it was
FIG. 7  TEMPERATURE PROFILES FOR A CHARGE CARBONISED TO 900°C AND THEN SOAKED
practicable, they should measure the level of the poorest material reporting to the blast furnace. The coke least likely to reach the desired end temperature is that in the centre of the oven. Much of the coal remains cold, or at 100°C, for a number of hours before the coal between it and the heating wall becomes semicoke and thermal conductance increases. The conditions of the laboratory cokemaking were intended to simulate those some 75% of the distance from an oven heating wall to the centre of the oven.

Initially four thermocouples were inserted vertically, one between the furnace tube and the retort, one beside the internal wall of the retort, one in the centre of the coal mass and the fourth intermediate between the latter two. The position of the first two could be verified by contact with the walls but that of the others could not. It transpired that the gradient from retort wall to centre once a temperature of 700°C had been reached was consistently about 10°C, and use of the intermediate couple was abandoned.

The coke mass was removed from the furnace when the desired centre temperature was reached, or held at that temperature for the desired soaking time before removal, and water quenched.

The coke was recovered usually from the top of the furnace, sliding the mass from the retort unless a swelling occurred from the base in cases where this was not properly fitted. (The use of a charcoal lining is an old operator's ploy in ovens where a damaged floor causes "stickers" on pushing). The coke came out as a plug, adhering to the thermocouple, and on breaking showed a central cavity, almost
continuous except for occasional and very friable sponge walls. Top and bottom ends, and the periphery of the cylinder were comprised of coke 7 to 10mm thick. This phenomenon is reported as occurring in bench scale briquetting of coking coals (Callcott, private communication).

The coke plugs had to be broken but the ends could be readily identified and discarded, and pieces selected comprising the annulus of coke known to have been carbonized to a finishing temperature varying less than 10°C from wall to centre of the retort.

The making of the cokes was well within the experience of the author, but not so the microscopy. The problems arising are discussed later. Four effective series of coking were done, shown in Table I.

The use of commercial blend from the Port Kembla plant was based on direct practical interest, but led to difficulties in the measurement of reflectance because of:

a) the relatively fine texture of the mosaic; and

b) the mixture of two coals, the rank difference being of the order of \( R_{\text{max}} \) for Bulli seam mix 1.24 and Wongawilli seam mix 1.18.

Huntley filter cake was selected as being a concentration of vitrinite in the fines from Wongawilli seam, the purpose being to maximise vitrinite content in a series from which the cokes were to be subject to XRD analysis, to measure crystallite growth. The penalty accepted
was a lower rank than the Port Kembla Wongawilli seam coal and an even finer mosaic in the coke.

Norwich Park coal was that of highest rank conveniently available \((R^\text{max} 1.64)\) and likely to yield coke with large domains including much flow type mosaic, thus facilitating measurement of bireflectance. It is prone to oxidation and the first sample coked was unsatisfactory due to delay in testing (minor flooding of the laboratory – entirely not the fault of the author). A freshly washed batch, coked immediately on receipt was satisfactory.

Analytical data on the coals are shown in Table II.
### TABLE I

**COKING TESTS SERIES**

1. Commercial coking blend from Port Kembla plant, nominally 70% Bulli seam coal and 30% Wongawilli seam coal, heated to:

   - 800°C
   - 900°C
   - 900°C + soaking time 60 minutes
   - 1000°C
   - 1000°C + soaking time 60 minutes
   - 1070°C

2. Second sample of above blend, heated to:

   - 1000°C
   - 1000°C + soaking time 50 minutes
     - 100 minutes
     - 150 minutes
   - 1000°C at heating rate 4.0°C/minute
     - 5.8°C/minute
     - 7.3°C/minute

3. Wongawilli seam coal-filter cake from Huntley coal preparation plant, heated to:

   - 900°C
   - 1000°C
   - 1000°C + soaking time 100 minutes
   - 1070°C

4. Norwich Park coal, fresh from the preparation plant, heated to:

   - 900°C
   - 900°C + soaking time 150 minutes
   - 1000°C
   - 1000°C + soaking time 150 minutes
   - 1050°C
TABLE II
COAL AND COKE DATA

<table>
<thead>
<tr>
<th>Blend</th>
<th>Huntley</th>
<th>Norwich</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulli/Wongawilli</td>
<td>12.0</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>26.0</td>
</tr>
<tr>
<td>Coal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>15.3</td>
<td>14.4</td>
</tr>
<tr>
<td>V.M.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Petrography</td>
<td></td>
<td></td>
</tr>
<tr>
<td>vitrinite</td>
<td>54</td>
<td>81</td>
</tr>
<tr>
<td>inertinite</td>
<td>41</td>
<td>15</td>
</tr>
<tr>
<td>minerals</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>$\bar{R}_{\text{O, max}}$</td>
<td>1.24/1.18</td>
<td>1.14</td>
</tr>
</tbody>
</table>

Included in the testing of the cokes was a piece sectioned from a lump from a well coked oven in Port Kembla plant. This was produced from a similar Bulli/Wongawilli coal blend to that used in the laboratory work.
7.3 Testing the Cokes

The top and bottom ends of the coke mass, to a distance of 10 mm minimum were rejected.

A piece some 6 mm high was sectioned from about the middle height of the annulus and prepared for microscopy.

The balance of the coke was crushed, by a minimum fines technique, using a hammer and plate, to yield at least 10 gm of material after sizing to 1.0 mm x 0.5 mm, on a sieving machine. The prepared specimens were again oven dried.

7.3.1 Microstrength

The equipment used was basically that used by Blayden et al. in 1937 and is shown in Fig. 8. A pair of tubes, each twelve inches long and one inch diameter, closed at the ends with removable plugs, is mounted to rotate about the short axis at 25 rpm for 800 revolutions. Each tube contains 12 steel balls 5/16" dia and is charged with 2 gm of sized coke grains. The product is sized and a convenient index used. Two pairs of results (i.e. four individual tests) are set as the requirement for one quoted measurement.

It was observed that on damp days there was a tendency to shortfall in the weight of residue recovered from the tubes and after screening, exceeding 2.5%. This was attributed to the retention of the ultra-fines passing 125 micrometre screen on tube or screens and, once detected, such days were avoided.
FIG. 8 THE MICROSTRENGTH TEST RIG
The size of feed particles nominated by Blayden was 1200 x 600 microns. The test, long dormant in popularity, has been revived in Japan and an evaluation of its reproducibility in Australian testwork was made by Gill (1981), using data from 74 tests. The standard deviation of variation between duplicates was for MSI600 = 1.61 and for MSI212 = 2.09.

Cook and Depers (1983) examined by Quantimet the distribution by size of the pores in a coke made from Bulli seam coal, and included among their four categories those 0.1 to 1.0 sq mm and those greater than 1.0 sq mm. The reason for the choice by Blayden of particle size 1.2 x 0.6 mm is not known, but the possibility that a reduction of the top size of the particles would improve reproducibility was pursued. A head sample sized 850 x 500 microns was prepared from a piece of coke sectioned midway between the cauliflower and sponge ends of a lump of coke from a well coked commercial oven and five replicate runs of duplicates made (i.e. twenty single tests). Practical reasons had dictated the use of different aperture screens for strength indices and those finally adopted were 500 and 250 microns. The standard deviations of the duplicates of the ten tests were MSI500 = 0.9 and MSI250 = 2.1. As would be expected, pores were still readily visible under the microscope in the smaller particle size selected.

The 850 micron top size of particles was used for the first series of coking tests, but it was apparent that the MSI500 index was insensitive whatever the top size and the MSI250 figure was adopted. Preparation of the 850 micron size was difficult and required the crushing of more of the limited coke sample than was desired, with no
improvement in reproducibility. A compromise was made, using a size of 1000 x 500 microns. At least these are readily recognised metric. The standard deviation between duplicates in the subsequent testing was, for MSI250 = 2.2.

Results for the various coke runs are shown in Table III and Fig. 9. The trends shown are similar to those reported by Nishioka et. al. (1982) in cokes made in a 250 kg pilot oven 450 mm in width.
### TABLE III

**MICROSTRENGTHS OF THE COKES**

<table>
<thead>
<tr>
<th>Coke Finishing Temperature</th>
<th>MSI250</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulli seam/Wonganillia seam blend - Sample 1</strong></td>
<td></td>
</tr>
<tr>
<td>Note: feed 850 x 500 microns</td>
<td></td>
</tr>
<tr>
<td>800°C</td>
<td>35</td>
</tr>
<tr>
<td>900°C</td>
<td>38.5</td>
</tr>
<tr>
<td>900°C + soak 60 mins.</td>
<td>42</td>
</tr>
<tr>
<td>1000°C</td>
<td>43.5</td>
</tr>
<tr>
<td>1000°C + soak 60 mins.</td>
<td>48</td>
</tr>
<tr>
<td>1070°C</td>
<td>47</td>
</tr>
<tr>
<td><strong>Bulli seam/Wonganillia seam blend - Sample 2</strong></td>
<td></td>
</tr>
<tr>
<td>1000°C</td>
<td>30</td>
</tr>
<tr>
<td>1000°C + soak 50 mins.</td>
<td>30.5</td>
</tr>
<tr>
<td>1000°C + soak 150 mins.</td>
<td>35</td>
</tr>
<tr>
<td>1000°C + soak 250 mins.</td>
<td>37</td>
</tr>
<tr>
<td>1000°C - heating rate 4.0°C/min</td>
<td>29.5</td>
</tr>
<tr>
<td>1000°C - heating rate 5.8°C/min</td>
<td>32</td>
</tr>
<tr>
<td>1000°C - heating rate 7.3°C/min</td>
<td>30</td>
</tr>
<tr>
<td><strong>Huntley Filter Cake</strong></td>
<td></td>
</tr>
<tr>
<td>900°C</td>
<td>19.5</td>
</tr>
<tr>
<td>1000°C</td>
<td>28.5</td>
</tr>
<tr>
<td>1000°C + soak 100 mins.</td>
<td>34</td>
</tr>
<tr>
<td>1070°C</td>
<td>37</td>
</tr>
<tr>
<td><strong>Norwich Park</strong></td>
<td></td>
</tr>
<tr>
<td>900°C</td>
<td>21</td>
</tr>
<tr>
<td>900°C + soak 150 mins.</td>
<td>26</td>
</tr>
<tr>
<td>1000°C</td>
<td>27.5</td>
</tr>
<tr>
<td>1000°C + soak 150 mins.</td>
<td>34.5</td>
</tr>
<tr>
<td>1050°C</td>
<td>33</td>
</tr>
</tbody>
</table>

Variations in heating rates were made in the second series of Bulli/Wonganillia blend tests, ranging from 4°C per minute to 7°C per minute. Changes of this magnitude about a nominal rate far exceed those practicable in industry although they are recognised to be small for comparative research work. As there was no significant difference in the microstrengths of the cokes the matter was not pursued.
FIG. 9 MICROSTRENGTH OF THE COKES MADE AT VARYING CARBONISATION TEMPERATURE AND SHOWING THE EFFECT OF SOAKING
The coke pieces sectioned from the middle (vertically) of the coke mass were mounted in resin and polished in the manner usual for coals, with the exception that after cutting back the surface with 200 grain lap, it was resealed with resin and the full polishing sequence then followed. Reflectances were measured using a Leitz Ortholux I microscope fitted with a Leitz MPV I photometer, output of which was passed to a Kipp and Zonen Light spot galvanometer AL3. Monochromatic light of wavelength 546nm and oil immersion were used, with reference standards of synthetic spinel and garnets of reflectances 0.413, 0.917 and 1.726.

The author was almost devoid of experience on modern geological microscopes, previous information used in his industrial research being provided on request. Measurement of the petrographic composition and reflectance of coals (by measurements of maxima at 180°) was mastered readily, but the measurement of bireflectance of the cokes by dual maxima and minima was less satisfactory.

Goodarzi and Murchison (1972) discuss the accuracy of such measurements, referring to the considerations of Cook and Murchison (unpublished) of the errors arising for materials whose reflectivity lies within the limits of cokes. Even with reflectance photometers and their restricted field size, measurements on individual units of the coke mosaic are rarely possible because of their small areal dimensions. Whatever restriction is placed upon the field size, a number of units will usually be involved and, while the units
gradually become more oriented with rise of temperature through the
effect of strain and solidification, cokes cannot be considered in the
same light as vitrinites, i.e. as particulate preparations of
optically negative uniaxial materials.

Their behaviour resembles more that of optically biaxial materials,
although often less so as the mosaic increases its degree of
orientation. There are consequently fluctuations in the maximum
reflectance values recorded from a number of particles, as well as the
customary variation in the minimum reflectivity. In their earlier
studies, Goodarzi and Murchison calculated bireflectance from the
highest 20% of the maximum readings and the lowest 20% of the minimum
readings of 50 individual measurements. This was varied slightly by
them in 1978, to take the 10 measurements of the 50 that showed the
highest bireflectance.

The textures of the mosaics in the cokes produced in this work are
shown in micrographs (Figs. 13 to 26), including that of the
commercial Port Kembla coke. The microscope was set mostly to measure
a field of reflectance of area 2.5 sq microns, but a reduced area,
requiring a further adjustment of approximately x 3 to galvanometer
readings was used in some cases, mainly for Huntley samples but also
as a check on the Bulli/Wongawilli blends.

A single maximum reflectance for a given position could be located and
then readily reproduced by revolution through 360°, but the selected
area was often lost from the field of measurement during revolution to
find the second maximum. The mechanical condition of the stage and
the finesse of centering varied over time and among the series. Thus with some samples it was possible to obtain maxima at 180°, differing by less than 10%, but not consistently throughout the studies. As experience was gained in identifying the fields, it became common to select sites which showed high degree of extinction upon revolving with crossed nicols and to establish a reproducible single maximum (and minimum) and it is this that is reported.

It must be admitted that these difficulties were no less with Norwich Park cokes, despite the larger domains, which must reflect adversely upon the reliability of the absolute values recorded. To offset this, repeat readings were made on each series, over a period of up to two years. The results were more variable than desired, but in all cases the trends were similar. Occasional checks by a competent petrographer gave similar maxima and minima to those being obtained by the investigator at that time.

The considerable extrapolation involved by the use of the garnets as reference standards makes the absolute values less accurate but probably not less precise.

Statistical analysis of the results for the Series 1 with Bulli/Wongawillli blend is shown in Table IV using the single, reproducible maximum reflectance value to which reference has been made, and taking the ten highest values from batches of readings obtained over several weeks. Testing the significance of the differences between means by the Student-t method (Freund and Williams, 1965), the appropriate formula where the number of data points is small is:
\[ t = \frac{x_1 - x_2}{\sqrt{\frac{(n_1-1)s_1^2 + (n_2-1)s_2^2}{n_1 + n_2 - 2} + \frac{1}{n_1} + \frac{1}{n_2}}} \]

where
\[ x = \text{mean of results} \]
\[ s = \text{standard deviation of results} \]
\[ n = \text{number of data points} \]

It is ascertained from statistical tables that \( t \) must exceed 2.101 at 18 degrees of freedom for a difference between means to be established at 95% confidence level. The standard deviation is reasonably consistent among the samples.

It is concluded that while the absolute values quoted in the various series may be less certain than those of more competent petrographers, the trends within series have been established and inferences may be drawn therefrom.

The results obtained by the technique recorded are shown in Table V and Fig. 10.
TABLE IV

STATISTICAL ANALYSIS OF REFLECTANCE RESULTS

Series 1: Bulli Seam/Wongawilli Seam Blend

Single maximum reflectance. 10 highest in each case

Coke Finishing Temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>800°C</th>
<th>900°C</th>
<th>900°C + soak</th>
<th>1000°C</th>
<th>1000°C + soak</th>
<th>1070°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.8</td>
<td>10.1</td>
<td>12.2</td>
<td>13.3</td>
<td>13.5</td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td>8.3</td>
<td>9.9</td>
<td>12.1</td>
<td>13.3</td>
<td>13.3</td>
<td>13.5</td>
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<tr>
<td></td>
<td>8.1</td>
<td>9.5</td>
<td>12.1</td>
<td>13.0</td>
<td>12.8</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>7.9</td>
<td>9.5</td>
<td>11.9</td>
<td>13.0</td>
<td>12.8</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>7.7</td>
<td>9.5</td>
<td>11.5</td>
<td>13.0</td>
<td>12.8</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td>7.6</td>
<td>9.5</td>
<td>11.5</td>
<td>13.0</td>
<td>12.8</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>9.2</td>
<td>11.3</td>
<td>12.2</td>
<td>12.8</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>9.0</td>
<td>11.2</td>
<td>12.2</td>
<td>12.2</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>8.8</td>
<td>11.2</td>
<td>12.1</td>
<td>12.2</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>8.6</td>
<td>11.0</td>
<td>12.1</td>
<td>12.1</td>
<td>12.6</td>
</tr>
<tr>
<td>Av</td>
<td>7.8</td>
<td>9.4</td>
<td>11.6</td>
<td>12.7</td>
<td>12.7</td>
<td>13.1</td>
</tr>
<tr>
<td>S.D</td>
<td>0.47</td>
<td>0.47</td>
<td>0.43</td>
<td>0.50</td>
<td>0.46</td>
<td>0.35</td>
</tr>
<tr>
<td>t</td>
<td>7.6</td>
<td>11.0</td>
<td>5.2</td>
<td>-</td>
<td>2.16</td>
<td></td>
</tr>
</tbody>
</table>

(Where t evaluates the difference between the means of pairs of results. For example t = 7.6 for results at 800°C and 900°C finishing temperature).

From statistical tables, at 95% confidence level and 18 degrees of freedom,

\[ t_{0.025} (18) = 2.101 \]
## TABLE V

**Reflectance of Cokes**

### Bulli Seam/Wongawilli Seam Blend - Sample 1

<table>
<thead>
<tr>
<th>Coke Finishing Temperature</th>
<th>Max.</th>
<th>Min.</th>
<th>Bireflectance (Single Results)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C</td>
<td>7.8</td>
<td>1.6</td>
<td>6.2</td>
</tr>
<tr>
<td>900°C</td>
<td>9.4</td>
<td>2.2</td>
<td>7.2</td>
</tr>
<tr>
<td>900°C + soak</td>
<td>11.6</td>
<td>2.2</td>
<td>9.4</td>
</tr>
<tr>
<td>1000°C</td>
<td>12.7</td>
<td>2.0</td>
<td>10.7</td>
</tr>
<tr>
<td>1000°C + soak</td>
<td>12.7</td>
<td>2.2</td>
<td>10.5</td>
</tr>
<tr>
<td>1070°C</td>
<td>13.1</td>
<td>2.2</td>
<td>11.9</td>
</tr>
</tbody>
</table>

### Bulli Seam/Wongawilli Seam Blend - Sample 2

<table>
<thead>
<tr>
<th>Coke Finishing Temperature</th>
<th>Max.</th>
<th>Min.</th>
<th>Bireflectance (Single Results)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000°C</td>
<td>11.6</td>
<td>2.5</td>
<td>9.1</td>
</tr>
<tr>
<td>1000°C - 50 minutes soak</td>
<td>13.2</td>
<td>2.5</td>
<td>10.7</td>
</tr>
<tr>
<td>1000°C - 150 minutes soak</td>
<td>13.5</td>
<td>2.7</td>
<td>10.8</td>
</tr>
<tr>
<td>1000°C - 250 minutes soak</td>
<td>13.8</td>
<td>2.5</td>
<td>11.3</td>
</tr>
</tbody>
</table>

### Huntley Filter Cake

<table>
<thead>
<tr>
<th>Coke Finishing Temperature</th>
<th>Max.</th>
<th>Min.</th>
<th>Bireflectance (Single Results)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900°C</td>
<td>9.6</td>
<td>2.2</td>
<td>7.4</td>
</tr>
<tr>
<td>900°C + soak</td>
<td>11.8</td>
<td>2.2</td>
<td>9.6</td>
</tr>
<tr>
<td>1000°C</td>
<td>12.1</td>
<td>2.1</td>
<td>10.0</td>
</tr>
<tr>
<td>1000°C + soak</td>
<td>13.1</td>
<td>2.3</td>
<td>10.8</td>
</tr>
<tr>
<td>1070°C</td>
<td>13.8</td>
<td>2.2</td>
<td>11.6</td>
</tr>
</tbody>
</table>

### Norwich Park

<table>
<thead>
<tr>
<th>Coke Finishing Temperature</th>
<th>Max.</th>
<th>Min.</th>
<th>Bireflectance (Single Results)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900°C</td>
<td>7.7</td>
<td>1.2</td>
<td>6.5</td>
</tr>
<tr>
<td>900°C + soak</td>
<td>11.5</td>
<td>1.1</td>
<td>10.4</td>
</tr>
<tr>
<td>1000°C</td>
<td>11.5</td>
<td>1.1</td>
<td>10.4</td>
</tr>
<tr>
<td>1000°C + soak</td>
<td>12.8</td>
<td>1.1</td>
<td>11.7</td>
</tr>
<tr>
<td>1050°C</td>
<td>14.1</td>
<td>1.2</td>
<td>12.9</td>
</tr>
</tbody>
</table>
FIG. 10  BIREFLECTANCE OF THE COKES MADE AT VARYING CARBONISATION TEMPERATURES AND SHOWING THE EFFECT OF SOAKING
7.3.3 Crystallite Size Measurement

The crystallites composing a powdered coke sample cause line broadening of the X-ray diffraction profile as compared with the lines resulting from single crystals of graphite. For crystallites suffering no lattice strain or distortion, the mean apparent crystallite dimension $L_{hkl}$, in a direction perpendicular to the reflecting plane $hkl$, can be expressed by the Scherrer equation (Blayden et al., 1943).

$$L_{hkl} = \frac{K \lambda}{B \cos \theta}$$

where $K$ is a constant dependent on crystallite shape, $\lambda$ is the wavelength, $B$ is the line breadth at half height, and $\theta$ the peak position of the $hkl$ reflection.

Detailed descriptions of procedures used to examine a number of Russian cokes, heat treated at temperatures up to 1700°C were given by Bogayavlenski (1962) and of work on coke samples, extracted from Australian blast furnaces by Dubrawski and Gill (1984). The latter reported that for cokes the dimension along the structural c axis ($L_c$) is determined almost solely by the value of $B$.

Measurement of coke $L_c$ has traditionally involved prior demineralisation in order to remove mineral phases such as quartz, which can interfere with the coke reflections. Results from demineralisation studies by Dubrowski and Gill (1984) indicate that
removal of the mineral constituents from coke does not, in general, significantly affect the measured level of Lc compared with the untreated sample. Demineralisation is labour intensive and time consuming and where 5% precision is adequate, Lc can be calculated satisfactorily without recourse to it. It was not done in this study, but Dubrawski has commented privately that doing it may have increased the sensitivity of the comparisons.

Wongawilli seam coal fines, obtainable as a floated product (filter cake) from Huntley coal preparation plant, were selected as the feed for the series for X-ray diffraction studies. This coal has high vitrinite content (81%) and was chosen to minimise the quantity of inertinite macerals present. The extent to which these macerals participate along with vitrinite in the bonding mechanism has been discussed in the section on coke strength. Many of the models in use for the prediction of coke strength from petrographic data assume that 1/3 of the semifusinite reacts as vitrinite. Diessel (1981) concluded from studies using bireflectance techniques that a substantial portion of coal composites belonging to the inertinite group of macerals are quite reactive during carbonization and proposed a number of steps to determine the threshold between reactive and nonreactive inertinite.

Sunami (1977) and Nishioka et al. (1980) have shown that for cokes made from coals of the same rank, Lc decreases with increasing inert and semi-inert content. For the purpose of assessing changes in crystallite dimension it was considered that these maceral derived components would be diluents.
Diffraction traces by X-ray powder diffraction method were done by University of Wollongong Geology Department officer J. Patterson, using a Phillips PW 1130/90 generator and a PW 1965/60 proportional detector. Scans from 2°2θ to 70°2θ were performed using a copper target. Evaluation of the crystallite dimension $L_c(A)$ for each coke was made by J.V. Dubrawski of B.H.P. Central Research Laboratories, Shortland (private communication). He states that (for copper radiation) the general expression can be simplified to:

$$L_c = \frac{78.5}{B \cos \theta}$$

In practice the coke diffraction pattern reveals only the (002) reflection of the carbon structure at approximately 25°2θ which is of use for the determination of $L_c$. A baseline is drawn beneath the peak (as shown in Fig. 11). The peak width at half-height ($B$ measured in cm) and the peak position ($\theta$) are measured and inserted into the equation.

Dubrawski's results are shown in Table VI.
FIG. 11 - X-RAY DIFFRACTION TRACE FOR COKE WITH FINISHING TEMPERATURE 1000°C
TABLE VI

CRYSTALLITE DIMENSION $L_c$ OF COKES MADE FROM HUNTLLEY FILTER CAKE

Determined by X-ray Diffraction Technique

<table>
<thead>
<tr>
<th>Coke Finishing Temperature</th>
<th>$L_c$ (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900°C</td>
<td>12.9</td>
</tr>
<tr>
<td>1000°C</td>
<td>13.7</td>
</tr>
<tr>
<td>1000°C + soak 100 mins.</td>
<td>14.9</td>
</tr>
<tr>
<td>1070°C</td>
<td>14.8</td>
</tr>
</tbody>
</table>

The diffraction trace obtained from the coke sample finished at 1000°C is shown in Fig. 11. Note that the physical dimensions have been reduced disproportionately in reproduction and that all measurements refer to those made on the original patterns.
7.4 Discussion

7.4.1 Trends for the experimental cokes

Similar trends to higher values with increasing finishing temperature or with soaking are shown for microstrength MSI250 and bireflectance in each of the three series of tests.

The standard deviation among duplicates of MSI250 has been shown to be 2.2. As each result finally quoted is an average of two duplicates, an improvement by the factor 1/2 is introduced, to 1.55. The standard deviation in Gill's evaluation on commercial cokes was 1.3.

The "Student t" test applied to the maximum reflectance measurements of the Bulli/Wongawilli series 1 (Table IV) shows the trend to be significant statistically, although there are instances in which the incremental increase from one temperature to the next cannot be shown to be so.

A similar relationship with final temperatures was shown for the Lc dimension of crystallite size for the Huntley series. Four data points only were available and statistical evaluation is not feasible, but the extent of the increase from 900°C to 1070°C was from 12.9A to 14.8A, namely 15%. This is well in excess of the 5% variation in routine Lc measurement quoted by Dubrawski and Gill (1984).

The effect of soaking was to give a stepwise increase to all indices, although the extent was variable.
The effect of extending the soaking time was considered in the second series with Bulli/Wongawilli blend. (Tables III and V). The increases in MSI250 and bireflectance are more consistent at the longer times and an aim of 150 minutes soaking time was adopted after series 1.

7.4.2 Correlation with commercial coke

Several lumps of coke from well coked commercial ovens were sectioned and portions crushed for microstrength testing. MSI250 ranged from 56 to 59, higher than the 37-47 obtained on Bulli/Wongawilli blend of series 1 and considerably more than those of series 2, a similar blend. The bulk density of the charge in the retort was made similar to that taken as average in commercial ovens, but it was evident from the void in the core of the coke mass that the pressure exerted upon the particles during the stages of gas evolution and swelling must have differed greatly from the pressures that occur in the coal mass constrained in an oven. The rejection of even a small proportion of the mix, possibly higher in inerts content, by sizing the charge at 5mm topsize may be a contributing factor.

Reflectance measurements on the commercial coke were:

<table>
<thead>
<tr>
<th></th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>maximum</td>
<td>8.7</td>
</tr>
<tr>
<td>minimum</td>
<td>2.0</td>
</tr>
<tr>
<td>bireflectance</td>
<td>6.7</td>
</tr>
</tbody>
</table>
Of significance to this study, the results obtained from the two lumps sectioned from wall to centre showed little change in MSI250 across the lump.

Slices 20mm thick were tested (Fig. 12).

<table>
<thead>
<tr>
<th>Distance from wall</th>
<th>MSI250</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
</tr>
<tr>
<td>10 mm</td>
<td>56.5</td>
</tr>
<tr>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>80</td>
<td>56.5</td>
</tr>
<tr>
<td>170</td>
<td>56.5</td>
</tr>
</tbody>
</table>

These results do not exhibit the trend shown in the 450mm pilot oven used by Nishioka and Yoshida (1983) in which MSI65 (mesh) decreased smoothly from 62 at the wall to 50 near the centre, and they suggest that, in well coked ovens the thermal gradient across the coke may be less than suspected or that more of the coke has reached a higher temperature than realised. A substantial investigation, requiring sufficient data for statistical evaluation, is required to explain these discrepancies.
FIG. 12  MICROSTRENGTH OF COKE SECTIONS
FROM LUMPS FROM WELL COKED COMMERCIAL Ovens
It has been established that cokes made by laboratory techniques exhibit changes in their microstrength and microstructure over the variations in finishing temperature common in commercial ovens, the indices measured increasing with increased finishing temperature and soaking. In some cases the rate of increase slackened above 1000°C, but no plateau was shown in the temperature range considered practical.

It has not been shown that the effects produced in laboratory coking occur in commercial ovens and the few checks done on microstrength of coke sectioned from lumps extending from wall to centre cast doubt upon this vital point.

The advantage of maximum microstrength probably is axiomatic, and it is shown that microstrength increased with a more ordered structure.

During the two decades in which the petrography of coals and microstructure of cokes were impacting upon coking technologists, interest was shown in similar properties in the sintering of iron ores, by this author among others. Much improved strength was obtained by replacing a slag or glass bonding with a highly disordered, needlelike ferrite structure. The dichotomy of approaches is apparent, and prompts the question as to whether a more ordered structure might not facilitate the penetration of furnace gases,
leading to chemical disintegration of the bond between reactive derived maceral components and inert derived maceral components.

Pitt (1979) discusses the effects of direction difference of properties in the parallel and perpendicular direction in the anisotropic units responsible for coke texture and the difference in strength resulting from a random mosaic compared with one with a preferential orientation, the latter being weak in one direction.

Diessel (1986) observed in microscopic examination of the residue from solution loss tests on cokes made in pilot ovens (including a Bulli seam coal component) that there was evidence that the parallel orientation of the elongated anisotropic domains provided relatively easy gas diffusion parallel to the graphitic crystallites.

Coke oven batteries are complex structures of costly refractory brickshapes. Limitations to the maximum temperature achievable at the centre of the oven are set by the maximum temperature acceptable in the heating flue system. An operator would see advantage in achieving a coked oven by setting a lower finishing temperature and then soaking, rather than pushing to high flue temperatures. The longer coking times generally practiced these days largely vitiate this argument. Until more effective measurement of temperature within the coke mass and throughout the oven is available, some time for homogenising the heating is desirable as a precautionary measure. This soaking is of short duration in Australia, more likely 15-30 minutes than the Japanese practice which may exceed four hours.
Most plants have a production requirement that necessitates a compromise on coking time; thus the desired endpoint must be reached at Port Kembla plant in 18 to 20 hours, depending on demand. A significant soaking time of two hours would require that coking rate through the plastic zone be increased by some 12.5% with overriding deleterious effects upon coke size.

The evidence by Hara et. al. (1980) that soaking time improves CSR has been discussed, and the point made that much of it applies to low levels of CSR. Monthly average figures for CSR at Port Kembla plant during 1986 fell within the range 68.5 to 69.7. These are more consistent and somewhat higher than previously, associated with improved heating practices (private communication). Whether there would be any advantage to furnace operation gained by increasing beyond this relatively high level of CSR has to be questioned.

It is apparent that measurable changes in some coke quality parameters occur as temperature rises to 1000°C and beyond. There is also strong possibility of considerable variation of finishing temperature within ovens. As the quality parameters measured for routine control are averages from a sample varying within itself, the indices would improve if all particles included have reached a specified minimum.
CONCLUSIONS

The microstrengths and the ordering of the microstructures of a series of cokes produced in the laboratory increased as the finishing temperature increased from 900°C to 1070°C. The rate of increase appeared to slacken above 1000°C but a plateau was not reached. A soaking time at a given temperature is equivalent to a higher finishing temperature, but the relationship was variable and correlation with plant practice inadequate.

Commercial coke is assessed by empirical tests measuring size, cold strength and infurnace strength, but the measurable changes in coke texture provide a basic parameter by which the minimum finishing temperature may be defined and to which other properties may be correlated.

While coking time in the ovens at Port Kembla is constrained by demand for coke, and coke size is below that desired at the blast furnace, it would appear that quality is best served by utilising coking time fully to reach finishing temperature, other than for a brief precautionary holding time. This finishing temperature should be the minimum achieved in the coke mass and a critical level should be established. The opinion advanced is that it should be at least 970°C.
Resolution of three issues is required:

a) a technique is needed to provide reliable measurement of the end temperature within the coke,

b) correlation of the laboratory coking results with properties of oven coke, stepwise from wall to centre and in the vertical plane, and

c) verification that changes of temperature to the extent considered have significance to in-furnace properties that have reached the level already maintained at Port Kembla.
REFERENCES

Ammosov, I.I., et. al., 1957. The calculation of coking charges on the basis of the petrographic characteristics of coals, Coke and Chemistry USSR 12: 9-12 (not sighted).


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Figure 13 Coke from Huntley Filter Cake $R_{\text{max}} = 1.14$. Finishing temperature 1000°C. Field width 0.23mm.

Figure 14 Coke from Bulli/Wongawilli Blend $R_{\text{max}} = 1.24/1.18$. Finishing temperature 1000°C. Field width 0.23mm.
Figure 15 Coke from Norwich Park Coal $R_{\text{max}}$ 1.64. Finishing temperature 1000°C. Field width 0.23mm.

Figure 16 Coke from Port Kembla Steelplant Ovens Bulli/Wongawilli Blend $R_{\text{max}}$ 1.24/1.18. Field width 0.23mm.
Figure 17 Coke from Bulli/Wongawilli Blend. Finishing temperature 800°C. Field width 0.23mm.

Figure 18 Coke from Bulli/Wongawilli Blend. Finishing temperature 900°C. Field width 0.23mm.
Figure 19 Coke from Bulli/Wongawillii Blend. Finishing temperature 900°C + soak. Field width 0.23mm.

Figure 20 Coke from Bulli/Wongawillii Blend. Finishing temperature 1000°C. Field width 0.23mm.
Figure 21 Coke from Bulli/Wongawilli Blend. Finishing temperature 1000°C + soak. Field width 0.23mm.

Figure 22 Coke from Bulli/Wongawilli Blend. Finishing temperature 1070°C. Field width 0.23mm.
Figure 23 Coke from Norwich Park Coal. Finishing temperature 900°C. Field width 0.23mm.

Figure 24 Coke from Norwich Park Coal. Finishing temperature 1000°C. Field width 0.23mm.
Figure 25 Coke from Norwich Park Coal. Finishing temperature 1000°C + soak. Field width 0.23mm.

Figure 26 Coke from Norwich Park Coal. Finishing temperature 1050°C. Field width 0.23mm.