FACTORS AFFECTING THE MECHANICAL PROPERTIES OF BLAST FURNACE COKE

by

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Metals and Materials Engineering

We accept this thesis as conforming to the required standard

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Date Feb 20, 1987
Abstract

The influence of coking conditions, with respect to position in a commercial coke-oven, on the mechanical behaviour of blast furnace coke has been studied. This involved the determination of density, porosity, the characterization of microstructure and assessing the influence of all three on the compressive strength of coke. The plastic flow properties were also investigated at temperatures greater than 1000°C.

Three coke batches, originating in a 5m commercial coke-oven at three different positions with respect to height (0.8m, 3.3m and 5m below the coal line), along with three coke batches produced in a 460mm test-oven, were supplied by Energy, Mines and Resources (CANMET) in Ottawa. A warf coke batch was also provided as a control sample. Several hundred core-drilled specimens (≈1.3cm diameter and 1.3cm length) were produced from the seven coke batches. The bulk density of each cylindrical coke specimen was determined. Also, a detailed microstructural analysis, using a Leitz Image Analyzer, of the flat faces of the coke cylinders was performed to quantitatively characterize the pore and cell wall size, and the pore geometry. The compressive strength of each coke cylinder was determined both at ambient temperature and at 1400°C. In addition, the plastic flow behaviour of the commercially produced coke batches was studied.
Results indicate that the coke product bulk density was affected by the coke-oven pressure (static load). Studies of the test-oven coke batches revealed that coke bulk density increased with higher oven pressure. Furthermore, the pore size was found to be larger for cokes produced at lower oven pressures. The cell wall size did not appear to be affected by coke-oven pressure. The bulk density of the commercially produced samples increased with depth below the coal line. This was attributed to a higher temperature and static load that existed at the bottom of the battery. The pore size was larger in cokes extracted from higher regions. No correlation of cell wall size with depth below the coal line was found. However, an oven size effect on the pore and wall size was noticed. Both the pore and wall size was smaller in the test-oven coke batches.

The compressive strength of coke was higher in batches subjected to higher coke-oven pressures. Similarly, the compressive strength of commercial coke batches was higher for coke batches extracted from regions near the sole of the coke-oven, than that for coke batches extracted from higher regions. It was concluded that high oven pressures resulted in cokes exhibiting a lower porosity and small pores which had the combined effect of producing stronger coke. Coke strength was generally shown to be higher at 1400°C than at room temperature. The test-oven cokes were always stronger than cokes produced in the 5m commercial coke-oven.
Constant load tests revealed that coke exhibited plastic flow behaviour at temperatures above 1000°C. The time dependent strain data was described using an interactive-double-Kelvin element visco-elastic model.
Acknowledgements

The author wishes to express his gratitude to his research supervisor, Dr. A.C.D. Chaklader for his advice and encouragement during this project. Thanks are also extended to the faculty, staff and fellow graduate students. The assistance of J. Arblaster and A. Darnbrough are especially appreciated. Financial assistance from the Energy, Mines and Resources (CANMET) in Ottawa, is gratefully acknowledged.
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\[ \sigma = -n \varepsilon + b \]

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\[ \sigma = \sigma_0 \exp(-b\varepsilon) \]

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Single-Kelvin Unit

Interactive-double-Kelvin Unit

Three-non-interactive-Kelvin Units

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<td>A</td>
<td>Fraction of the total creep attributed to the first exponent of the experimental creep equation</td>
</tr>
<tr>
<td>a</td>
<td>Crack half-length</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Standard for Testing Materials</td>
</tr>
<tr>
<td>A.T.</td>
<td>Ambient Temperature</td>
</tr>
<tr>
<td>B</td>
<td>Fraction of the total creep attributed to the second exponent of the experimental creep equation</td>
</tr>
<tr>
<td>BCRA</td>
<td>British Carbonization Research Association</td>
</tr>
<tr>
<td>CSR</td>
<td>Coke Strength after Reaction in 100% CO₂</td>
</tr>
<tr>
<td>CSR*</td>
<td>Coke Strength after Reaction in 10% CO₂</td>
</tr>
<tr>
<td>ECE</td>
<td>European Commission for Europe</td>
</tr>
<tr>
<td>Fmax</td>
<td>Maximum Feret's diameter</td>
</tr>
<tr>
<td>Fmin</td>
<td>Minimum Feret's diameter</td>
</tr>
<tr>
<td>H.V.</td>
<td>High volatile bituminous coal</td>
</tr>
<tr>
<td>ISO</td>
<td>International Standards Organization</td>
</tr>
<tr>
<td>JIS</td>
<td>Japanese Industrial Standards</td>
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<tr>
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<tr>
<td>KIC</td>
<td>Calculated critical stress intensity factors</td>
</tr>
<tr>
<td>L.V.</td>
<td>Low volatile bituminous coal</td>
</tr>
<tr>
<td>L.V.D.T.</td>
<td>Linear Voltage Differential Transformer</td>
</tr>
<tr>
<td>m</td>
<td>Weibull modulus</td>
</tr>
<tr>
<td>Mᵢ</td>
<td>Spring constant in the i-th spring of the visco-elastic model</td>
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</table>
M.V.  Medium Volatile Bituminous Coal

P  Oven-pressure

P(σ)  Probability of failure

s  Laplace operator

t  Time

Uc(t)  Step function of input stress

Vf  Volume fraction of porosity

a, β  Exponention constants of the first and second terms of creep equation

ε  Strain

εp  Percent porosity determined using pynometric and bulk density values

εI  Percent porosity determined using the image analyzer

ηi  Viscosity of the i-th dashpot in the visco-elastic model

ρb  Bulk Density

μρb  Mean bulk density

σρb  Standard deviation of bulk density values

σ  Applied Stress

σo  Nominal applied stress
1. **INTRODUCTION**

The strength properties of coke from ambient temperature to \( \approx 1800^\circ \text{C} \) is very important for efficient blast furnace operations. This research program was designed to determine the strength properties of coke both at ambient and high temperatures and then to correlate the strength properties with other coke parameters. The coke samples used in this study were supplied by CANMET, Ottawa, but were prepared both in a conventional coke-oven at the Algoma Steel Corporation at Sault Ste. Marie, Ontario and in a test-oven at the Energy Research Laboratories in Ottawa. However, before going into details of the research project, it will be worthwhile to outline some background on:

1. the importance and functions of coke,
2. how it is produced,
3. significant properties normally determined for evaluating coke characteristics, and
4. performance.

It is important to know some of these aspects as the relevance of this research project will be apparent with this background.

Coke is a carbonaceous product made from a special type of coal known as metallurgical coal. Table I shows the nominal coke-making capacity of the Western World in 1981 \( (1) \). At least ninety-two percent of coke produced in the Western World in 1981 was from carbonizing coal and seventy-eight percent of that was used for the steel
<table>
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<th>COUNTRY</th>
<th>Steel Industry</th>
<th>Coal Industry</th>
<th>Independent</th>
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<tr>
<td></td>
<td>mmt(1)</td>
<td>%</td>
<td>mmt(1)</td>
<td>%</td>
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<td>1.20</td>
<td>100.0</td>
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<td>-</td>
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<td>97.2</td>
<td>-</td>
<td>-</td>
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<td>4.18</td>
<td>96.3</td>
<td>-</td>
<td>-</td>
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<td>98.2</td>
<td>0.11</td>
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<td>India</td>
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<tr>
<td>Pakistan</td>
<td>0.75</td>
<td>100.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Peru</td>
<td>0.65</td>
<td>100.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Portugal</td>
<td>0.51</td>
<td>100.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>South Africa</td>
<td>5.60</td>
<td>92.7</td>
<td>0.44</td>
<td>7.3</td>
</tr>
<tr>
<td>Spain</td>
<td>4.88</td>
<td>100.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sweden</td>
<td>1.20</td>
<td>100.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Taiwan</td>
<td>0.91</td>
<td>82.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Turkey</td>
<td>4.76</td>
<td>100.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>7.23(2)</td>
<td>65.7</td>
<td>3.32(3)</td>
<td>30.2</td>
</tr>
<tr>
<td>United States</td>
<td>92.40</td>
<td>86.9</td>
<td>0.70(3)</td>
<td>1.2</td>
</tr>
<tr>
<td>Yugoslavia</td>
<td>3.58</td>
<td>100.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zimbabwe</td>
<td>0.40</td>
<td>100.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>204.14</td>
<td>78.0</td>
<td>36.78</td>
<td>14.0</td>
</tr>
</tbody>
</table>

(1) Millions of metric tons
(2) Blast Furnace coke producers
(3) Plant using Beehive Ovens
(4) Foundry coke producers

Table I. Nominal Cokemaking Capacity of the Western World in 1981 (ref. 1).
As indicated in Table I, the vast majority of coke was produced for the steel industry where it was used to make pig iron in the blast furnace. In pig iron production, coke, ore and fluxes are the ingredients charged into a blast furnace. Coke consumption in the blast furnace is more than 500 kg per ton of pig iron (2). A smaller type of blast furnace is also normally used in producing lead from the roasted lead oxide. However, lower temperatures ($\approx 1200^\circ$C in the hearth) and a higher CO$_2$/CO ratio in the gas in the lead blast furnace, mean that coke consumption is considerably less in these furnaces, than in the iron blast furnace.

The coke used in blast furnaces is derived from blends of low, medium and high volatile bituminous coals. Such coals which are used to produce blast furnace coke are often termed "metallurgical coals" and only metallurgical coals are suitable for blast furnace coke production.

1.1 ROLE OF COKE IN THE BLAST FURNACE

Coke has three important functions:

1. provides fuel for combustion and supplies heat to the charge,
2. supplies reductant gases for smelting the iron ore, and
3. physically supports the burden while it descends down the blast furnace shaft.
1.1.1 COKE AS A FUEL

Figure 1 is a schematic representation of the ironmaking blast furnace (2). Shown are the temperatures varying with height in the shaft and the principle reactions that occur at each level. At the tuyere level, hot blast air between 900 and 1000°C is injected and this reacts with the coke to produce mainly carbon dioxide. The temperature in this region is between 1800 and 2000°C at which point, the only solid phase present is the coke. The carbon dioxide penetrates to the center of the furnace forming carbon monoxide via the Boudouard reaction. The heat involved from burning coke at the tuyeres is needed to achieve the minimum temperature required in this region (≈1800°C). This temperature at the tuyere is necessary to ensure that the burden higher up in the furnace is heated sufficiently.

1.1.2 COKE AS A REDUCING AGENT

Both carbon dioxide and carbon monoxide are produced above the tuyere region of the blast furnace. The carbon monoxide is the reducing agent needed to reduce the iron ore. The blast furnace can be divided into two separate reduction zones represented by the dotted line in Figure 1: the direct reduction zone (the lower half of the furnace) and the indirect reduction zone (the upper half). In the direct reduction zone, metal oxides are reduced by carbon monoxide to form carbon dioxide, however, the Boudouard reaction is also occurring to produce carbon monoxide and
Figure 1. Schematic Representation of the Ironmaking Blast Furnace (ref. 2).
consuming coke at the same time. For example:

\[
\begin{align*}
\text{FeO} + \text{CO} & = \text{Fe} + \text{CO}_2 \\
\text{CO}_2 + \text{C} & = 2\text{CO} \\
\hline \\
\text{FeO} + \text{C} & = \text{Fe} + \text{CO}
\end{align*}
\]

(A)

The Boudouard reaction in [A] controls the \(\text{CO}_2/\text{CO}\) ratio so the net reaction results in the consumption of coke.

The indirect reduction zone is characterized by the consumption of carbon monoxide to produce carbon dioxide. This zone exists above the 900°C isotherm (dotted line in Figure 1). Below 900°C, the Boudouard reaction is sluggish and therefore provides no significant contribution to the reduction mechanisms. In the upper regions of the stack \(\text{Fe}_2\text{O}_3\) and \(\text{Fe}_3\text{O}_4\) are reduced to \(\text{FeO}\). It is interesting to note that a "sooting" reaction also occurs in the upper regions of the furnace forming carbon dioxide and carbon from carbon monoxide. This is undesirable because it consumes carbon monoxide needed for the reduction of the ore, thereby increasing the need for a higher coke consumption rate.

1.1.3 COKE AS A PHYSICAL SUPPORT FOR THE BURDEN

Perhaps the most important function of coke in the iron blast furnace is its ability to physically support the burden as it descends down the shaft. The blast furnace is a counter current reactor where, as mentioned before, hot reducing gases formed at the tuyere region must find their
way to the top of the shaft while the burden progresses downward. An evenly distributed upward gas flow is necessary for stable blast furnace operation. This ensures an evenly reduced burden as well as even heat exchange between the hot gas and the descending burden.

Figure 2 demonstrates how gas flow is impeded by a decrease in the harmonic mean size of coke lumps (3). It is, therefore, desirable to use a coke which degrades as little as possible during its descent. This is particularly important in the lower half of the furnace where, between 1100°C and 1400°C, the burden fuses and melts leaving coke as the only solid phase present. Figure 3 shows in some detail how the burden behaves in the blast furnace. The burden in the melting zone fuses into stratified layers of coke, ore, and flux (4). The gases moving upward rely on the coke layers (coke slits) to allow these to escape into the lumpy zone at the top half of the furnace.

Closer to the raceway, the phases present are liquid metal, slag, and coke. In this region, the coke lumps are supporting the entire burden while allowing hot metal to percolate to the hearth and the combustion gases to penetrate to the center of the furnace. Coke fines near the raceway will prevent adequate penetration of gases to the center of the furnace, therefore forcing the gases upward near the wall and trapping molten metal and slag from flowing downward resulting, in insufficient tapping volume and increasing tapping frequency. Coke fines suspended in
FLOW RESISTANCE COEFFICIENT \( K_r = \frac{\Delta (P/h)}{\Delta (\rho u^2)} \)
WHERE \( P = \) PRESSURE DROP OVER BED HEIGHT, \( h \).
\( \rho = \) GAS DENSITY \( u = \) GAS VELOCITY
(MKS UNITS)
TEST AIR VELOCITY RANGE \( u = 0.3 - 1.5 \text{ ms}^{-1} \)
COEFFICIENT OF SIZE VARIATION, \( K_v \)
\( K_v = 100 \times \frac{\sigma}{S_m} \%
\)
\( \sigma \equiv K_v < 20\% \)
\( x \equiv K_v > 20\% \)

**Figure 2.** EFFECT OF COKE SIZE AND UNIFORMITY ON BULK RESISTANCE TO AIR FLOW
Figure 3. Schematic Representation of Layers of Coke, Ore, and Flux as They Occur in The Blast Furnace (ref. 4).
the slag and liquid metal can result in uneven tapping.

It is apparent that the blast furnace will operate more efficiently if the coke lumps maintain their integrity as much as possible while physically supporting the burden and being attacked by carbon dioxide and alkali vapours. For this reason, coke must be physically strong without losing its strength while being subjected to the harsh conditions in the lower part of the furnace.

1.2 COKE CHARACTERISTICS NECESSARY FOR THE BLAST FURNACE
The carbon content of coke is the primary agent, in addition to the small concentrations of hydrogen, for the reduction of iron ore. Therefore, it is desirable to reduce the impurity components in the coke such as moisture, ash, and sulfur as much as possible. A good coke should be reactive enough to supply the reducing gas required for a particular ore (5). It is generally better, however, to have an ore which is very reactive and a coke which has low reactivity. This lowers the coke consumption by reducing the effect of the Boudouard reaction. A coke with low reactivity is more likely to maintain its mechanical strength in the direct reduction zone of the blast furnace.

The impurities in the coke have detrimental effects other than lowering the coke-carbon content. A low sulfur content is preferred since this impurity generally ends up in the pig iron which makes refining to steel more difficult. Moisture escaping from the coke in the upper regions of the
furnace will disturb the reducing gases as they pass upward through the burden.

Perhaps the most detrimental impurity in coke is ash which has two negative effects on the performance of coke: catalyzing the Boudouard reaction and reacting internally with the carbon in the matrix. The presence of minerals is known to affect the reactivity of coke to CO₂ (6). In these investigations various ash components commonly found in coal were separately added to a very low ash coal (less than 1.0%) to determine their effect on reactivity with CO₂. The results show that reactivity increased with the following order of effect:

K & Na > Ca > Fe > Mg > (Si, Al, Ti)

The alkali oxides greatly increased the reactivity of coke with Si, Al, and Ti having a much lower effect. Ash-carbon reactions were found to occur at temperatures between 1600 and 1800°C. It was shown that all the oxides in the minerals (ash) contained in the coke were reduced producing carbon monoxide as a product (6). Silicon was found to react most readily with the carbon producing silicon carbide and carbon monoxide. These reactions all contributed to carbon loss thereby weakening the coke matrix.

Typical blast furnace coke characteristics are given in Table II (5). The first two columns are strength indices from drum tests. These indices will be explained later. Coke characteristics must be closely controlled for optimum blast furnace operation.
### Table II. Typical Properties of Blast Furnace Coke (ref. 5)

<table>
<thead>
<tr>
<th>Property</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tumbler strength (%)</td>
<td>85</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Abradability, M₁₀ (%)</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Moisture (% of raw product)</td>
<td>1.5±0.5</td>
<td>2.5±0.5</td>
<td>3.5±0.5</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>8.5±0.3</td>
<td>8.5±0.3</td>
<td>8.5±0.3</td>
</tr>
<tr>
<td>Sulfur (% of dry product)</td>
<td>0.9±0.03</td>
<td>0.9±0.03</td>
<td>0.9±0.03</td>
</tr>
<tr>
<td>Volatile matter (% of dry product)</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Alkali (% of dry product)</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>Bulk density (kg/m³)</td>
<td>438</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*¹ Content of Na₂O and K₂O determined in different plants.
1.3 PRODUCTION OF BLAST FURNACE COKE

Since the major fraction of coke produced in the world is made from metallurgical coal, it is important to know the coal characteristics suitable for coke-making.

1.3.1 COAL CHARACTERISTICS

1.3.1.1 Coal Chemistry

Coal is composed of organic minerals containing carbon, hydrogen, oxygen, and small amounts of sulfur and nitrogen. Studies have shown that coal is made up of both aromatic and aliphatic molecules (7). Aromatic molecules consist of rings of six carbon atoms joined to form a hexagonal shape - the simplest type being benzene. Aliphatic molecules are chains of hydro-carbons - the simplest form is methane. There is a definite relationship between carbon content of the coal and the relative amounts of aliphatic and aromatic molecules. The carbon content of the coal increases with the aromatic/aliphatic ratio.

1.3.1.2 Coal Rank

There are several classifications of coal depending on their origins. Figure 4 shows the stages of metamorphosis to form various types of coal (5). The metamorphosis of coal increases with increasing time and pressure inside the earth. The term most often used to represent the degree of metamorphosis is rank, which
Figure 4. Schematic Representation of the Coalification Process (ref. 5).
increases with increasing metamorphic change. In other words, anthracite has a high rank, whereas lignite is a low rank coal. In general, rank increases with increasing carbon content, decreasing volatile matter content, decreasing moisture content, and increasing calorific value. To form a high rank coal (low volatile matter content), extreme depths and times of the order of 150 million years are needed. The best coals for making metallurgical coke are generally a combination of high volatile coal for low bulk density, and a medium or low volatile coke for high strength (5).

1.3.1.3 Coal Minerals

Coal is not a homogeneous substance, but is comprised of metamorphized organic minerals (from different sources) called macerals. The origins of different macerals are listed in Figure 5 (5). During metamorphosis, the chemical composition and the percent aromatic structures changes but the proportion of each maceral in the coal change very little. The most common maceral shown in Figure 5 is vitrinite (5). This along with resinite and exinite are termed "reactive" due to their ability to become plastic and release volatiles during pyrolysis. Vitrinite makes up 75 to 80 percent of coals in the bituminous range. Reactive macerals are noted for their high H/C ratio.

The other important macerals are called "inerts" - which are high carbon macerals that release small
Figure 5. Origins of Different Coal Macerals (ref. 5).
amounts of volatile compounds and do not become plastic during pyrolysis. Macerals such as fusinite and micrinite are classified under the name inertinite. These originate from charred or decomposed plant matters.

1.3.1.4 Reflectance

Coal scientists have found that all macerals exhibit distinguishing optical properties when viewed under an optical microscope. Each maceral reflects and absorbs light differently. A special microscope is used in which the light reflected off the specimens can go either to the eye-piece or to a photomultiplier tube (8,9). The incident light is polarized at an angle of 45° and a filter with a peak transmittance of 546 nm (monochromatic green) is used at any position along the path of light. A drop of immersion oil is added on the sample to provide more contrast between the various phases. The percent reflectance (in oil) of each phase is measured by the photomultiplier and is based on glass standards.

Since 75-80% of the coal is vitrinite, it is possible to represent the rank of the coal by its vitrinite reflectance as described above. In general, the higher rank materials have higher reflectance values. The best coking coal blends have reflectance between 1.3 and 1.5 (percent) in oil.
1.3.2 COAL PYROLYSIS

Coal pyrolysis (or carbonization) is the term used to describe the transformation of coal to coke. As coal is heated in the absence of oxygen, many reactions occur up to 1000°C. Between 110°C and 150°C, absorbed moisture is released. Gases, such as H₂S, are released between 150°C and 350°C. The coal itself begins to decompose between 300°C and 350°C. Above 350°C, thermal decomposition becomes rapid with the release of primary volatile gases and the solid mass begins to liquefy (mesophase). Between 500°C and 1000°C the solid mass undergoes a polymerization reaction which causes the liquefied coal to solidify, when densification and shrinkage occur simultaneously with the release of secondary volatile components such as methane and carbon monoxide. At 1000°C, the coking process is virtually complete with the product being coke containing mineral matter (ash).

1.3.2.1 Pyrolysis Reaction

The pyrolysis reaction has been represented by three simplified consecutive reactions (10):

\[ K_1 \]

\[ P \rightarrow M \]  \hspace{1cm} (B) \]

\[ K_2 \]

\[ M \rightarrow R + G_1 \]  \hspace{1cm} (C) \]

\[ K_3 \]

\[ R \rightarrow S + G_2 \]  \hspace{1cm} (D) \]

where P denotes the original coal, M denotes the
mesophase (or liquid phase), R is the semi-coke, S is the final coke product, G₁ and G₂ are the primary and secondary volatile gases, respectively. These reactions have been treated as being first order, but in reality they are probably more complex since each reaction [B-D] represents a large number of separate reaction steps (7).

It has been shown that the relative magnitude of each of these reaction rates determines whether or not a coal is suitable to make metallurgical coke (10). A good coal should be fusible (good bonding characteristics) and this is determined by the amount of mesophase produced and by its fluidity. If there is an accumulation of mesophase, the coal is said to be caking and will produce coke. This will occur if K₁ is much larger than K₂. If K₂ is larger than K₁, a char (non-fusible product) will be formed. It is important to realize that all metallurgical coals are caking coals but not all caking coals will produce metallurgical coke.

1.3.2.2 Fluidity during Pyrolysis

Fluidity is commonly measured using a Gieseler plastometer (11). It essentially consists of a stirrer, which has an electric motor, and a hysteresis brake controlling the torque. Each rotation is counted photo-electrically and the fluidity is measured by the dial divisions per minute (100 dial divisions per
Another method of assessing the mesophase is the Free Swelling Index. The Free Swelling Index is measured by placing one gram of coal in a silica crucible and visually comparing the coke button produced afterward with a set of standards (see Figure 6) (39). Good metallurgical coal has a Free Swelling Index between five and seven.

1.3.3 CONVENTIONAL COKE MAKING PROCESS

Figure 7a is a schematic representation of the charge in a conventional coke-oven at some intermediate stage during the heat. The coke-oven consists of a vertical retort approximately 6m high, 15m long, and 0.5m wide. Coal is charged into the chamber between two externally heated refractory walls. The charge mass closest to the wall experiences a higher temperature than at the center. Near the wall, the mass softens and then solidifies into coke where the temperature is above 600°C. The plastic zone moves toward the center of the coke-oven as the charge heats up and the particulate coal near the center liquefies and decomposes. The large fissures shown in Figure 7a are a result of differential contraction during resolidification of the charge near the oven wall. The final coke product is a highly porous, carbonaceous product containing large fissures throughout. Figure 7b shows the arrangement of coke lumps with respect to their position in a coke-oven.
Figure 6. ASTM Free Swelling Index (ref. 39).
Figure 7a. Schematic Representation of the Charge in a Conventional Coke-oven at some Intermediate Stage During the Heat (ref 52).
Figure 7b. Coke Lumps as They Would Be Positioned in a Coke-oven Battery (ref. 4).
battery (arrangements were suggested by CANMET).

The coking chambers are arranged in batteries as illustrated in Figure 7c. Between two oven walls there is a flue chamber which heats two oven walls simultaneously. The flue is often fueled by the volatile gases from the coking process itself. When the charge has reached the final temperature (1000-1200°C), the mass is "pushed" out of the slot into rail cars and subsequently water quenched (see Figure 7d). The coking process from charging to pushing can take up to twenty one hours.

1.4 TESTING METHODS FOR COKE

Three characteristics of coke are normally used to predict its performance in the blast furnace:
1. porosity and true specific gravity
2. reactivity to carbon dioxide, and
3. tumbler strength tests.

Porosity is studied due to its contribution to the weakening of coke and to coke reactivity. Reactivity assessment is important for minimizing the coke consumption rate. Tumbler tests are used as general information on the ability of coke to resist volumetric breakage and abrasion.

1.4.1 POROSITY AND TRUE SPECIFIC GRAVITY

In North America, coke porosity and true specific gravity are normally assessed in accordance with ASTM designation D167-73 (12). The apparent specific gravity is
Figure 7c. Arrangement of Typical Commercial Coke-oven Batteries (ref. 4).
Figure 7d. Cross-section of a Typical Coke-oven Battery (showing the rail car) (ref. 4).
first measured by a water displacement method. The true specific gravity is determined using pycnometry. The porosity is then calculated using the measured true and apparent specific gravity values.

Some workers have begun to explore ways of measuring porosity using computerized image analyzers. Such methods rely on the subjective way the operator determines the level of greyness (explained later) the pore features appear on the computer monitor. Since this work is still in the development stage, no standard has yet been presented.

1.4.2 TUMBLER TESTS

Tumbler testing of coke is the most common method used in industry for determining coke quality. There are many accepted standards for measuring the drum strength of coke. Leeder, Price, and Gransden have made comparisons of different drum standards as given in Table III (13). From Table III, it is apparent that the four standards shown, vary significantly from one another. Variations include coke lump size, sample weight, drum dimensions, drum rotational speed, duration of the test, moisture content of the coke, and the number and widths of the lifts. Lifts are slats in the drum which lift the coke lumps upward with the revolution of the drum until the angle of the lifts is large enough to cause lumps to fall. These variations have made it difficult to make correlations between the different standard drum tests, and such correlations are unreliable
<table>
<thead>
<tr>
<th>Test</th>
<th>Designation</th>
<th>Coke</th>
<th>Drum Dimensions</th>
<th>Test Method</th>
<th>Strength Indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>D 294-64</td>
<td>3x2 in. 22 lb dry 18 in. 36 in. 2 2 in.</td>
<td>24±1 58 1400</td>
<td>x&gt;1&quot; Stability Factor</td>
<td></td>
</tr>
<tr>
<td>JIS Drum Test</td>
<td>2151-72</td>
<td>+50mm 10 kg dry 1.5 m 1.5 m 6 250mm 15</td>
<td>2 30</td>
<td>x&gt;15mm=DI^{15}</td>
<td></td>
</tr>
<tr>
<td>Micum*</td>
<td>R 556</td>
<td>+60mm 50 kg &lt;5 1.0 m 1.0 m 4 100mm 25±1 4 100</td>
<td>x&gt;40mm, M_{10}</td>
<td>x&lt;10mm</td>
<td></td>
</tr>
<tr>
<td>IRSID*</td>
<td>R 1881</td>
<td>+20mm 50 kg &lt;3 1.0 m 1.0 m 4 100mm 25±1 20 500</td>
<td>x&gt;40,20mm, I_{10}</td>
<td>x&lt;10mm</td>
<td></td>
</tr>
</tbody>
</table>

*Round-hole sieves used - other tests use square-hole sieves

Table III. ASTM, JIS, and ISO Standard Coke Drum Tests (ref. 13).
Two types of breakage mechanisms occur during drum tests: volume breakage and surface abrasion. Peirce and Horton (14,15) and Peirce et al (16) have shown that the volume breakage is associated with the propagation of large fissures and that surface abrasion is due to localized stress at contact points between the lumps. Considering this, as well as observing Table III, it is obvious that the ASTM drum test relies more on abrasion than on impact to degrade coke since it only has two small lifts. In contrast, the JIS, Micum and IRID standards specify six or four wide lifts respectively, which inflict more impact breakage.

1.4.3 REACTIVITY TESTS

There has been no ASTM standard proposed to date for determining the reactivity of coke. Three methods are worth noting: the ECE test (European Commision for Europe) (6), the NSC test (Nippon Steel Corporation) (17), and a test used by Jeulin et al (18).

The ECE test requires 7 grams of -3+1mm particles to be reacted in pure CO$_2$ for thirty minutes. The reactivity is expressed as a reaction rate constant by monitoring the CO$_2$ in the off gas.

The NSC test uses 200 grams of +19-21mm coke reacted in pure CO$_2$ for 120 minutes at 1100°C. The reactivity is calculated as the weight present lost during the test.
Jeulin et al (18) used -30+20mm coke lumps which were gasified in a gas mixture containing 10% CO₂, 20% CO, 10% H₂, and 60% N₂. The sample was heated to 650°C under nitrogen and from 650 to 1200°C at 200°C per hour in the reactive gas. The sample weight was continuously monitored during the experiment. The relevant parameter studied was the gasification threshold temperature. This is defined as the temperature where the rate of weight loss due to gasification becomes significant. The importance of the gasification threshold temperature stems from the fact that the Boudouard reaction consumes heat. Therefore, a low gasification threshold will decrease the length of indirect reduction zone of the blast furnace and a shift in its thermal profile will occur.

The ECE and the NSC tests are similar in principle but the ECE test uses a small coke particle size. The use of larger particle sizes in the NSC test distinguishes mass transfer rates between cokes as well as reactivity of the solid itself. The method used by Jeulin et al (18) helps to predict the effect the coke will have on the thermal profile of the blast furnace.

1.4.4 COKE STRENGTH AFTER GASIFICATION

A test which is gaining increased popularity is the coke strength after reaction test (CSR). This involves measuring the strength of -21+19mm coke after it has been gasified at 1100°C for two hours in 100% carbon dioxide.
Nippon Steel Corporation employs an I-drum for 600 revolutions at 20 revolutions per minute and this has become the most commonly used CSR test.

The CSR test has been employed by Fellows and Wilmers (17), and by BCRA workers (19). Both groups found approximately negative linear relationships between reactivity and post reaction strength. Brown et al (6) found that the CSR test exaggerates the extent of reaction occurring in the blast furnace. So the CSR* test was developed using 10% CO₂ and 90% N₂ which more closely represented the extent of reaction of tuyere coke. It was found that little correlation existed between CSR* and CSR tests. The results show a general weakening of coke after gasification.

1.4.5 SHATTER TESTS

The drop shatter test for coke is perhaps the most primitive of the coke quality assessment techniques. The ASTM standard (20) for measuring the shatter strength of coke requires that fifty pounds of coke be dropped from a height of six feet. The minus half inch is removed from the sample and the procedure is repeated three more times. A sieve analysis is then performed on the coke sample. The shatter test has the disadvantage that it only measures the coke's resistance to impact and not abrasion.
1.5 PREVIOUS STRENGTH TESTS AND ANALYSIS

With the realization that the quality of coke affects the operation of the blast furnace, coke researchers have been turning towards a more fundamental approach to assessing coke quality. High temperature drum tests are being used to see how impact and abrasion resistance are affected by high temperatures. Also, since drum tests induce very complex stress states, more simple states of stress such as uniaxial compressive and tensile stresses are being used to characterize coke strength. Microstructural techniques have recently been employed to determine the effect of microstructural variations on the strength of coke.

1.5.1 HIGH TEMPERATURE TUMBLER TESTS

A comprehensive review made by Reeve, Price, and Gransden (21) produced several conclusions about the tumbler strength of coke at high temperatures: coke strength is lower at high temperatures than at ambient temperature, there is no correlation between cold and hot strength tests, and the higher the cold Micum index value, the lower the reduction in hot Micum values at elevated temperatures. Patrick and Wilkinson (22) and other workers at the BCRA (19) found a general decrease in the drum strength indices as temperature increased. This suggests that resistance to volume and surface breakage is reduced as temperature of testing is increased.
1.5.2 FUNDAMENTAL STRENGTH TESTS

The nature of stresses induced in coke during tumbler tests is difficult to assess. Therefore, more fundamental test methods such as uniaxial compressive and tensile strength tests are being more frequently used. Both these tests on coke specimens have been performed at ambient and elevated temperatures.

1.5.2.1 Ambient Temperature Tests

Perhaps the first group to consider testing coke on a fundamental basis was Holoway and Squarcy (23). They performed compressive strength tests on 1.27cm cubical specimens and obtained strengths ranging from 4.41MPa to 31.83MPa for all cokes tested. However, only three tests were performed on each coke specimen, thereby raising doubt as to the credibility of these values for representing the whole population.

The BCRA researchers (19) performed tensile strength tests on 16 industrial cokes using the diametral compression test. This test is shown schematically in Figure 8a. The tensile stress is calculated using the equation:

\[ \sigma_t = \frac{2w}{\pi Dt} \]  

where \( w \) is the applied load, \( D \) is the specimen diameter, and \( t \) is the thickness of the disk. Fifty specimens were used for each coke where mean tensile strengths ranged
The Schematic Representation of the Diametral Compression Test Showing:

a. The Disc Sample

b. The Typical Fracture Pattern, and

c. The Stress Field Within The Disc (ref. 25).
between 1.62 and 6.0MPa. Similar tests were conducted by Patrick and Wilkinson (22) yielding nearly the same results. Klose and Suginobe (24) measured tensile strengths of industrial cokes also using diametral compression. Strengths ranged between 2.0 and 7.0MPa. There was a definite strength dependence on specimen size with larger samples tending towards being weaker. No statistical evidence showing an effect of cross-head speed (ie. strain rate) was found.

The diametral testing method has two serious drawbacks which affect the practicality of its use for assessing coke quality. The theory from which equation 1 was derived, states that for the method to yield the correct tensile strength, the material being tested must be homogeneous and elastic (24). It is well known that coke is a very heterogeneous material. Samples which do not exhibit the fracture pattern in Figure 8b, can not be included in the test results. The stress field shows that the compressive stress at the points of loading tends toward infinity (Figure 8c), and that an uneven tensile stress field is induced in the specimen. Furthermore, the tensile strength is measured by the fracture stress at the point of loading. In most cases, small tributary cracks occur at the point of loading which raises question as to the mode of fracture (25). Klose and Suginobe (24) found that only 25% of the coke discs tested produced the fracture pattern in Figure 8b.
Therefore, a very large number of tests are needed for statistical reliability of the data. Also, by discarding 75% of the tests made, there will be a bias toward the homogeneous samples which may not be representative of the coke as a whole.

1.5.2.2 High Temperature Tests

High temperature compressive and tensile strengths of coke have been less widely studied than tests at ambient temperature due to the inherent difficulty of performing the large number of tests needed to characterize coke. The earliest work encountered was that of Holoway and Squarcy (23). Compression tests were performed on 0.635cm (edge length) cubes at 1650°C. They found that the compressive strength was higher than that observed at room temperature. However, only three to six samples were tested for each coke on a different testing machine than the Baldwin tensile machine used at room temperature. The test sample size was smaller than those tested at room temperature. This is not a good practice since coke has been shown to exhibit a strength dependence on specimen size (24). Patrick and Wilkinson (22), BCRA workers (19), and Jeulin et al (18), all observed a strength increase as temperature increased. They attributed this behaviour to the possibility that coke continued to graphitize after exceeding the final coking temperature. This is in accordance with dilatometer tests performed by Golezka and Roberts
(26,27), Golezka et al (3), and Fellows and Willmers (17). These workers have shown that coke expands upon heating to the final coking temperature and subsequently contracts as graphitization continues above this temperature.

1.5.3 PORE STRUCTURE AND COKE STRENGTH

With the availability of automated microscopes with attached image analytical facilities, a new technique of coke quality assessment is being developed. This technique can quickly examine the pore structure of a coke sample, and with the aid of computerized image processing, can statistically quantify such features as pore size, shape, area fractioning, and cell wall thickness.

Klose and Suginobe (24) used a Leitz TAS system to determine the porosity and maximum pore size by examining half of each fractured tensile specimen. They found that coke tensile strength correlated well with the porosity and maximum pore size according to the semi-empirical relation:

\[ \sigma = (K/\sqrt{dp})[\exp(-Be)] \]  

(2)

where \( dp \) is the maximum pore size, \( \epsilon \) is the porosity (pore fraction), and \( K \) and \( B \) are empirical constants. This equation is a modified form of porosity dependence on strength equation developed by Knudsen (28) for porous alumina:
\[ \sigma = \sigma_0 \exp \left( -b\epsilon \right) \]  

where \( \sigma_0 \) is the strength of the non-porous body. The term \( K/V_{dp} \) is derived from the Griffith crack theory.

Pitt and Rumsey (30) claimed to have estimated the strength of the non-porous coke by extrapolation of strength-porosity relationships developed by previous workers. These values differed by an order of magnitude depending on the equation used, with values ranging between 16MPa and 524MPa for one type of coke tested. They also attempted to measure the strength of non-porous coke by crushing 0.13mm coke particles between two steel plates. The values obtained were within the range of values calculated by extrapolation, but were determined on the assumption that the coke particles crushed were spherical.

Jeulin et al (18) used a texture analyser to measure pore volume fraction and specific pore surface area. They found that the best correlation between tensile strength and pore volume fraction was obeyed by equation 2. However, their derivation of this equation was more theoretically based than that of Klose and Suginobe (24).

The most detailed studies made to date were those of Patrick et al (31-36). These studies included a very detailed analysis of the porous structure of coke by employing a Quantimet 720 Image Analyzer. The analysis was divided into two sections: field data (values describing each field of view as a whole), and feature data (individual
features were examined separately). In an earlier work (32), pore and wall sizes were assessed by horizontal chord sizing. The analysis also included the number of pores per field. Porosity was determined as the area fraction of the pores. It was found that thirty to forty fields of view were needed to characterize the pore structure of a particular coke type. Most pores were found to occur in the size range 1µm to 120µm and a definite positive skewness was observed in the pore size distribution. Tensile strengths of some cokes were found to fit the Knudsen equation (28), but variations from the relationship were found to occur when a variety of coke types were tested (33).

Patrick (31), and Patrick and Stacey (35), found definite trends between coke structure and coking conditions. They concluded that preheating coal charges produced a greater number of smaller pores and decreased porosity which resulted in a stronger coke. Additions of up to 30% of petroleum coke decreased the porosity, increased the wall thickness, and increased the number of smaller pores which had the combined effect of increasing tensile strength. The strength was found to be related to pore and wall size by equation 4:

\[
\sigma N = 10^5 \left( \frac{W}{P^2} \right) - K
\]

where \( \sigma \) is the tensile strength, \( N \) is the number of pores per field, \( W \) is the wall size, \( P \) is the pore size, and \( K \) is
a constant. It is clear that equation 4 has no theoretical basis, and is therefore not reliable for predicting the strength of cokes outside the range of cokes tested.

Patrick and Stacey (35) and other workers at the BCRA (34) both realized the inadequacy of equation 4 and derived another equation which is more theoretically based. They utilized an equation of the form proposed by Jeulin et al (18), and by Klose and Suginobe (24) which is similar to equation 2. The crack length ($dp$ in equation 2) was assumed to be the mean maximum Feret's diameter of the pores. The Quantimet 720 Image Analyzer used is capable of measuring the maximum and minimum caliper dimensions (Feret's diameter) of a feature (in this case individual pores). The constant $b$ (in equation 2) was assumed (34,35) to be the stress concentration factor:

$$2\left(\frac{F_{\text{max}}}{F_{\text{min}}}\right)^{0.5}$$

of an elliptical crack perpendicular to the applied stress. The resulting equation used was then:

$$\sigma = 450 \left(\frac{F_{\text{max}}}{F_{\text{min}}}\right)^{-0.5} \exp\left[-2\left(\frac{F_{\text{max}}}{F_{\text{min}}}\right)^{0.5} p\right]$$

(5)

where $F_{\text{max}}$ and $F_{\text{min}}$ are the mean maximum and mean minimum Feret's diameters respectively, and $p$ is the porosity. This equation was found to predict the strength of various cokes with a standard error of $\approx 10\%$. It should be noted that the feature analysis was only performed on pores greater than $0.015\text{mm}^2$ in area, and is therefore, biased toward the larger
pores. This is theoretically valid since larger flaws (pores) are considered to be the origin of most failures.

1.5.4 COKE MECHANICAL PROPERTIES IN RELATION TO POSITION IN COKE OVEN

Nishioka and Yoshida (37) performed experiments to evaluate the effect of position with respect to the oven width on coke mechanical properties. The coke was made in a 250kg coke-oven with a width of 0.450m. Temperature measurements were made at ten positions across the oven width. The general trend was a decrease in tensile strength of coke toward the center of the coke-oven. Porosity reached a minimum at the 1/4 width position in the oven, but increased to a maximum at the oven center.

There appears to be no information available on the effect of coke quality as a function of position for commercial coke-ovens. Furthermore, no information on the coke quality as a function of vertical position in the coke-oven has been reported in the literature.

1.6 OBJECTIVES OF THIS RESEARCH PROJECT

It is clear from the discussion above that coke is a very complex material. This complexity and diversity arise for several reasons:

1. Blendings of High Volatile, Medium Volatile and Low Volatile coals are used, which determine the pore volume content and pore size distributions.
2. Cokes at the bottom of the coke-oven batteries are denser (less porous) because of the static load (burden) present during coking on these cokes.

3. Cokes nearer the refractory walls are subjected to higher temperatures than those which are present at the center of the battery.

Thus, a large number of coke samples for commercial cokes have to be tested to get a representative value of any property. The properties of warf coke (aggregated commercial coke) vary widely from sample to sample. On the other hand, most coke quality studies have been performed to date on "test-oven" cokes which generally exhibit relatively uniform properties throughout.

In this research program, experiments have been performed to fulfil the following objectives:

1. The effect of coking conditions on the microstructure of coke was assessed using an image analyzer. The analysis was performed on industrial coke batches extracted from three different heights in an Algoma 5m coke-oven. These microstructural characteristics were compared with those obtained from coke batches produced using the same coal blend, but under various conditions in a 460mm test-oven at CANMET Laboratories in Ottawa.

2. The mean strength values of the aforementioned seven coke batches were determined both at ambient temperature and at 1400°C. These results were treated statistically and were correlated with microstructural parameters and
coking conditions.

3. The plastic behavior of some coke samples have also been qualitatively evaluated as this property may have significant influence on the coke performance in a blast furnace.
2. EXPERIMENTAL

The coke samples used in this study were supplied by the Energy Research Laboratory (CANMET) in Ottawa, Ontario. The samples originated from two sources: CANMET—a 460mm test-oven, and an Algoma 5m industrial oven at Sault Ste. Marie. The test-oven coke was produced from the same coal blend used in the 5m oven at Algoma. The blend consisted of 35% low volatile (LV) coal and 65% high volatile (HV) coal. The conditions of coking are listed in Table IV for the test-oven cokes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CPR-264</th>
<th>CPR-265</th>
<th>CPR-266</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Moisture, %</td>
<td>5.9</td>
<td>4.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Coal Bulk Density, gm/cm³</td>
<td>0.578</td>
<td>0.863</td>
<td>0.976</td>
</tr>
<tr>
<td>Coking Time, h</td>
<td>17.2</td>
<td>17.15</td>
<td>18.1</td>
</tr>
<tr>
<td>Oven Wall Pressure, kPa</td>
<td>3.2</td>
<td>5.9</td>
<td>17.8</td>
</tr>
</tbody>
</table>

Table IV. Coking Conditions For Test-oven Cokes

The as-received test-oven cokes have the standard ASTM characteristics as shown in Table V (values determined at CANMET) (38).

The coke samples produced in the 5m industrial oven were sampled from
<table>
<thead>
<tr>
<th>Sample</th>
<th>CPR-264</th>
<th>CPR-265</th>
<th>CPR-266</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent Specific Gravity</td>
<td>0.781</td>
<td>0.903</td>
<td>0.936</td>
</tr>
<tr>
<td>Stability</td>
<td>59.5</td>
<td>59.2</td>
<td>57.4</td>
</tr>
<tr>
<td>Hardness</td>
<td>69.3</td>
<td>70.2</td>
<td>71.1</td>
</tr>
</tbody>
</table>

Table V. Characteristics of the As-received Test-oven Cokes.

steel mesh cages (28x28x35.6cm) that had been lowered into the oven through the center charging hole as illustrated in Figure 9a(38). On the first day of testing, a basket was lowered to the bottom of the empty coke-oven before charging. On the second day, charging was interrupted after the oven was half full and another basket was placed in the oven. Finally, on the third day, a third basket was placed in the coke-oven after 80% charging. Figures 9(b-d) show the variation in coke properties as a function of height as measured by CANMET. The as-received coke properties are summarized in Table VI. The sample CPR-270 is wharf coke (ie. from the same battery in which cages were positioned). Wharf coke is refered to as the representative
Figure 9. The Origin and Corresponding ASTM Properties of the Algoma Coke Batches.
Table VI. As-received Algoma coke properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CPR-267</th>
<th>CPR-268</th>
<th>CPR-269</th>
<th>CPR-270</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent Specific Gravity</td>
<td>0.947</td>
<td>0.880</td>
<td>0.798</td>
<td>0.888</td>
</tr>
<tr>
<td>ASTM Stability</td>
<td>53.6</td>
<td>48.2</td>
<td>46.4</td>
<td>58.5</td>
</tr>
<tr>
<td>ASTM Hardness</td>
<td>71.2</td>
<td>63.3</td>
<td>57.2</td>
<td>69.8</td>
</tr>
<tr>
<td>Height Below Coal Line, m</td>
<td>5.0</td>
<td>3.3</td>
<td>0.8</td>
<td>-</td>
</tr>
</tbody>
</table>

coke for the whole oven. The parameters listed in Table IV, V, and VI were considered to be independent variables to be used in this study.

The dependent variables (to be determined) in this study are:

1. Bulk density (apparent specific gravity)
2. True density (true specific gravity)
3. Porosity
4. Ambient temperature compressive strength
5. High temperature compressive strength, and
6. Microstructure

Variables (1-3) and (6) were also used as independent variables to assess their influence on ambient and high temperature compressive strength of the cokes used in this study. The procedures used for sample preparation and for determining properties (1-6) are described in the following sections of this chapter. These methods were necessary to
minimize inconsistencies attributed to variations in experiential procedure.

2.1 SAMPLE IDENTIFICATION

A systematic procedure for identifying the seven coke packages received from CANMET has been developed. The method involved four steps:

1. Positioning the coke lumps according to their approximate position along the width of the oven
2. Selection of suitable lumps to be used
3. Sectioning each of the selected test lumps by a diamond saw, and then
4. Core-drilling specimens from each lump section.

2.1.1 POSITIONING OF COKE LUMPS

Each of the seven coke packages were examined and each lump was positioned according to its approximate location across the coke-oven width. Positions were determined by the visual appearance of each lump. For example, lumps with a cauliflower type structure at one end were located at the wall of the coke-oven as shown in Figure 10. This was earlier suggested by Dr. W.R. Leeder of Denison Mines. In contrast, lumps with darker coloring were considered to be "coked" to a lesser degree, and therefore, were assumed to have originated close to the center of the oven. The approximate position of the coke lumps of the seven coke batches are shown in photographs (Figure 10a-g). These lumps
Figure 10. The positions of Coke Lumps as they were Assumed to be in the Coke-oven.
were numbered and photographed for further reference. The lumps considered suitable for further study were selected from each of the seven coke batches.

2.1.2 SELECTION OF TEST LUMPS

The selection of test lumps was based mainly on their size, position, and their as-received condition. Larger lumps which exhibited the cauliflower structure were preferred because the structural variation according to distance from the oven wall can be more readily compared in large lumps. The position in the oven of smaller lumps not exhibiting the cauliflower structure is less certain. Coke lumps which contained a large number of fissures were generally not used due to the difficulty of sectioning them. It was also desirable to, wherever possible, select an equivalent number of each wall and center coke lumps.

The best example of large lump selections are those of CPR-267 as shown in Figure 11. These lumps contain both the cauliflower structure and darker center regions. This enabled classification, according to distance from the wall, to be more easily performed.

2.1.3 SECTIONING OF TEST LUMPS

Each selected coke lump was sectioned into several 2cm thick sections. Attempts were made to cut the coke lumps in such a way that the faces of each section were approximately parallel to the coke-oven wall. Each section was numbered
Figure 11. An Example of Coke Lumps Selected for Further Study.
and the position with respect to the coke-oven wall (or oven center for some lumps) was recorded. Figure 12 is a schematic diagram of the sectioning procedure used for all selected test lumps.

2.1.4 CORE DRILLING OF COKE SPECIMENS

Individual test samples were made by core-drilling specimens from each of the sections described above. This is illustrated in Figure 12. The drill cores were approximately 1.3cm in diameter. The variation in the properties of drill-cored specimens is sufficiently large, so the exact position of the specimen within the slice was not taken into consideration.

2.2 PREPARATION OF TEST SPECIMENS

The core drilled cylindrical specimens were each inserted into a hardened steel die with a 1.3cm diameter hole, then ground and polished down to 1.3cm in length using polishing wheels between 80 and 600 grit. This method ensured that each specimen had smooth parallel faces at both ends of the coke cylinder. The parallel faces are essential for good alignment during compression testing.

2.3 BULK DENSITY MEASUREMENT

Since the polished core-drilled specimens were near perfect cylinders, the volume could easily be determined from the dimensions (measured by a caliper). Each recorded sample
Figure 12. Schematic Representation of the Procedure for Sectioning Coke Lumps (ref. 4).
diameter was the mean of three such measurements and the recorded height was the average of two measurements. The separate measurements rarely differed by more than 0.025mm (0.001 in). The bulk density was easily determined by dividing the sample weight by its measured volume.

2.4 TEST SAMPLE SELECTION

The samples used for compression testing, creep testing, and microstructural analysis were grouped on the basis of their bulk density. The samples selected from each of the seven batches fell inside the range of bulk densities described by:

\[ \mu_{pb} - \sigma_{pb} \leq \mu_{pb} \leq \mu_{pb} + \sigma_{pb} \]  

(6)

where \( \mu_{pb} \) is the mean bulk density and \( \sigma_{pb} \) is the sample standard deviation. This method was used in order to minimize the effect of bulk density variation on coke strength amongst test samples in each of the seven coke batches studied.

2.5 MICROSTRUCTURAL ANALYSIS

The microstructure of the seven coke batches was analyzed using a Leitz TAS PLUS computerized image analyzer. This image analyzer has the capability of quantitatively measuring textural features of optical images and determining their quantity, size distribution, area, form, and other optically distinguishable parameters. Figure 13
Figure 13. Schematic Representation of the Leitz TAS PLUS Image Analyzer.
schematically illustrates the Leitz TAS PLUS image analyzer. The system at U.B.C. has both an optical microscope and a macrostand for analyzing photographs. The macrostand was used in this study to analyze photomicrographs of the coke texture. This method was chosen due to the ease with which the photographs can be used with the image analyzer. Also, specimens can be re-examined without additional polishing and after the specimens have undergone compression testing.

2.5.1 PHOTOMICROGRAPH PREPARATION

Each of the coke specimens selected for further study based on their bulk density, were photographed for quantitative examination using the image analyzer. The samples were prepared by first lightly dry polishing each end using Carborundum 3/0 Flexbac polishing paper. The surface pores were then coated with soot from a luminous candle flame to eliminate any internal reflection (from the shallow pore channels in the coke) which may affect the accuracy of the texture analysis. Each end of the coke cylinder was then photographed at a magnification of 12.8X on polaroid films with an exposure time of two minutes for high contrast between pore walls and pore channels. An example of the excellent contrast achievable using this method is shown in Figure 14 in which the dark regions are pores and the light regions are pore walls.
Figure 14. A Typical Coke Microstructure.

magnification (12.8X)
2.5.2 IMAGE ANALYSIS

The Leitz image analyzer is easily automated using software to analyze the porous structure of coke. This software has been developed indigenously to measure seven parameters of coke structure. The parameters that are considered important for characterizing the porous structures are pore (channel) perimeter, cell wall thickness, pore area, equivalent diameter, mean chord length, form factor, maximum and minimum Feret's diameters.

Mean chord length (also used to determine cell wall thickness) was determined by averaging the chord lengths of the features at three orientations (0°, 60° and 120° to the horizontal). Form factor is used to characterize shape using area and perimeter measurements (i.e. form factor = \(4\pi(aera)/perimeter^2\)). Maximum and minimum Feret's diameters were determined by measuring the caliper dimensions at 12 orientations (15° intervals) and taking the maximum and minimum values of these.

All of these measurements were performed on each individual pore in the photographs. A flow chart of this program is presented in Figure 15. A second software program has been developed to do field-based mean chord measurements for cell walls.

The image analyzer detects features by their grey-levels on a black and white TV monitor. The TAS PLUS image analyzer has a grey level range between 1 (white) and 100 (black). Measurements are performed on objects which
Figure 15. A Flow Chart of the Software Used to Quantify Coke Microstructure.
fall inside the specified grey-levels. This method is called threshold detection. However, another method of detection (edge detection) was found to be more suitable for analyzing coke microstructure. This method utilizes the sharp contrast between pore and wall grey levels and detects pores by these abrupt changes. Edge detection eliminates errors associated with judging grey levels of features by an operator.

The image analyzer makes measurements on features by counting hexagonal pixel points. Very small features are therefore inaccurately measured. For this reason, features with dimensions less than 12\(\mu\)m in diameter were not included in these measurements. This was done by a series of image erosions followed by a series of dilations to reconstruct the remaining larger pores. The seven parameters measured were classified into seven different histograms describing their size distribution. It should be noted that measurements made on individual features of the porous structure, may not be absolute but can be regarded as being relative because image analyzer results are resolution dependent (section 4.2).

2.5.3 TRUE DENSITY

The true density of each of the seven coke types was measured to enable porosity calculations based on bulk density to be made. This was done to verify the porosity measurements made using the image analyzer. The true density was determined using the pycnometric method.
The coke slices, sectioned 2 cm from the cauliflor end, were ground to minus 75 \mu m in a Spex Mixer Mill. Approximately 2 gm of this powder was used for true density determination. The fine powder was needed to eliminate any closed pores that might be present in the coke. The 2 gm sample was placed in a 25 ml pycnometric flask and evacuated or boiled to remove trapped air. Both distilled water and methanol were used as the measuring fluids for all seven coke batches. The true density of the coke powders was calculated using the following equation:

$$\text{Density} = \frac{W_2 - W_1}{\rho_1} - \frac{(W_4 - W_1) - (W_3 - W_2)}{\rho_1}$$  \hspace{1cm} (7)

where $W_1 = \text{Weight of Pycnometer bottle}$,
$W_2 = \text{Weight of Pycnometer bottle + sample}$,
$W_3 = \text{Weight of Pycnometer + sample + fluid}$,
$W_4 = \text{Weight of Pycnometer filled with fluid alone}$, and
$\rho_1 = \text{Density of fluid}$.

The porosity was calculated from the relative density, which was obtained by dividing the average bulk density by the measured true density.

2.6 MECHANICAL TESTS

All mechanical tests on coke cylinders were performed under compression. Compression strengths were determined both at ambient temperatures and at 1400°C. Some tests were also carried out at 1000°C for three of the seven coke batches.
Constant load tests were performed on all four of the Algoma coke samples.

2.6.1 COMPRESSION TEST APPARATUS

These studies were made using the apparatus illustrated schematically in Figure 16. The coke sample was positioned between two graphite plungers which acted as susceptors in the induction coil. The graphite plungers and the specimen were enclosed in a quartz tube with two water cooled copper disks at each of the top and bottom ends of the tube. The system was flushed with argon to prevent oxidation of the coke specimen and the graphite plungers. It is important that the oxidation of the specimens was kept to a minimum so that the pore structure of the coke remained unchanged during the test. The temperature of the specimen was monitored using a Pt-10%RdPt thermocouple inserted through the bottom plunger to an approximate distance of 2mm away from the specimen.

2.6.2 PROCEDURE OF TESTING

The load was applied using a hydraulic system. The loading rate can be controlled using a leak valve which allows a linear build-up of pressure in the piston chamber. The loading rate used on all strength and constant load tests was approximately 1.2MPa/sec. The load was recorded using a load cell made by A.L. Design Inc. of Tonawanda, N.Y. situated at the bottom of the assembly. The load cell
Figure 16. A Schematic Representation of the Compression Testing Apparatus.
was connected to a Kipp and Zonen BD-41 chart recorder set to an 800 pound full scale load. The cell was calibrated using an Instron testing machine with an FR tension-compression cell.

The linear dimensional change was monitored by an LVDT mechanically connected to the top of the plunger. The transducer was connected to a second pen on the same chart recorder.

The heating rate was arbitrarily set at \( \approx 200^\circ C/min \) and used in all experiments. For both high temperature strength and constant load tests, specimens were heated to the desired temperature and maintained at that temperature for ten minutes before the load was applied. The constant load tests were carried out normally between thirty and sixty minutes.

2.6.3 EXPERIMENTAL PARAMETERS

The fixed experimental parameters used for all compression and constant load tests are summarized in Table VII. Room temperature compression strength tests were also performed in accordance with Table VII except without the argon atmosphere which was unnecessary.

2.7 GRAPHITIZATION TESTS

To determine the extent of coke shrinkage during heating, graphitization tests were also performed. These tests involved placing a sample in the strength testing apparatus,
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Diameter</td>
<td>1.3cm</td>
</tr>
<tr>
<td>Sample Length</td>
<td>1.3cm</td>
</tr>
<tr>
<td>Loading Rate</td>
<td>1.2MPa/sec</td>
</tr>
<tr>
<td>Heating Rate</td>
<td>~200°C/min.</td>
</tr>
<tr>
<td>Time at Temperature (before testing)</td>
<td>10 min.</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Argon</td>
</tr>
<tr>
<td>Number of Compression Tests per Condition</td>
<td>12-25</td>
</tr>
</tbody>
</table>

Table VII. Values of Fixed Compression Test Parameters.

and heating to 1400°C for thirty minutes without applying any load to the coke sample. The dimensions of the sample were measured after cooling.
3. RESULTS AND ANALYSIS

3.1 GENERAL COMMENTS

It should be noted that because of the wide variation in microstructure and other properties of coke even within a single lump, all properties (physical and mechanical) should be treated statistically. This wide variation of properties arises from the method of coke production where temperature variations of \( \approx 200^\circ C \) exists from the center of the batteries to the refractory wall, and from the top of the battery to the sole (\( \Delta T \approx 300^\circ C \)). Furthermore, the coke at the top of the batteries is not subjected to as much a static load as the coke at the bottom (i.e. significant differences in oven wall pressure are encountered). In addition to these, the raw material used in coke-making (coal) is extremely heterogeneous. So, it is not surprising that coke has such a complex texture with wide variations in properties. In spite of this fact, very few results reported in the literature are treated statistically. In this project, almost all results (except the creep data) are treated statistically.

3.2 DENSITY

3.2.1 BULK DENSITY

Bulk density was used as an initial criterion for characterizing the seven different coke batches. The bulk densities were classified into histograms for each coke type.
from which their mean bulk densities and standard deviations were obtained. Figure 17 is the distribution of bulk densities for all seven coke batches (CPR-264-CPR-270). The histograms for the individual coke batches are included in the Appendix A. Figure 18a is a summary of the mean bulk density as a function of coke type. The error bars correspond to the standard deviations. The mean bulk densities range between 0.779gm/cm$^3$ (CPR-269) and 0.947gm/cm$^3$ (CPR-266). The variation between oven wall pressure and bulk density for the test-oven cokes is illustrated in Figure 18b. There is a strong correlation between bulk density and oven wall pressure when plotted in a semi-logarithmic scale. Also included are the bulk density values of three industrial cokes on the straight line obtained from the test-oven cokes. The best fit curve which describes the relationship between oven pressure and bulk density of the test-oven coke is:

$$\rho_b (\text{gm/cm}^3) = 0.11 \log_{10} P (\text{KPa}) + 0.808 \quad r=0.997 \quad (8)$$

where $\rho_b$ is the bulk density and $P$ is the oven wall pressure. Table VIII shows the relationship between estimated (from Figure 18b) static load pressure and depth below the coal line for the industrial cokes. As expected, there is an increase of static load with increasing depth below the coal line, resulting in a higher coke bulk density.
### Coke Type: All Coke Samples

<table>
<thead>
<tr>
<th>Density (gm/cc)</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.643</td>
<td>0.4</td>
</tr>
<tr>
<td>0.654</td>
<td>0.6</td>
</tr>
<tr>
<td>0.665</td>
<td>0.4</td>
</tr>
<tr>
<td>0.676</td>
<td>0.2</td>
</tr>
<tr>
<td>0.686</td>
<td>0.9</td>
</tr>
<tr>
<td>0.698</td>
<td>1.7</td>
</tr>
<tr>
<td>0.709</td>
<td>0.9</td>
</tr>
<tr>
<td>0.720</td>
<td>1.5</td>
</tr>
<tr>
<td>0.731</td>
<td>1.3</td>
</tr>
<tr>
<td>0.742</td>
<td>1.7</td>
</tr>
<tr>
<td>0.753</td>
<td>1.9</td>
</tr>
<tr>
<td>0.764</td>
<td>1.9</td>
</tr>
<tr>
<td>0.770</td>
<td>0.4</td>
</tr>
<tr>
<td>0.776</td>
<td>2.3</td>
</tr>
<tr>
<td>0.787</td>
<td>2.8</td>
</tr>
<tr>
<td>0.798</td>
<td>3.8</td>
</tr>
<tr>
<td>0.809</td>
<td>4.9</td>
</tr>
<tr>
<td>0.820</td>
<td>3.6</td>
</tr>
<tr>
<td>0.831</td>
<td>4.7</td>
</tr>
<tr>
<td>0.841</td>
<td>4.9</td>
</tr>
<tr>
<td>0.853</td>
<td>6.4</td>
</tr>
<tr>
<td>0.864</td>
<td>4.3</td>
</tr>
<tr>
<td>0.875</td>
<td>5.3</td>
</tr>
<tr>
<td>0.886</td>
<td>4.3</td>
</tr>
<tr>
<td>0.897</td>
<td>3.4</td>
</tr>
<tr>
<td>0.908</td>
<td>6.2</td>
</tr>
<tr>
<td>0.919</td>
<td>6.4</td>
</tr>
<tr>
<td>0.930</td>
<td>4.3</td>
</tr>
<tr>
<td>0.941</td>
<td>3.8</td>
</tr>
<tr>
<td>0.952</td>
<td>3.6</td>
</tr>
<tr>
<td>0.963</td>
<td>1.5</td>
</tr>
<tr>
<td>0.973</td>
<td>2.6</td>
</tr>
<tr>
<td>0.984</td>
<td>1.9</td>
</tr>
<tr>
<td>0.995</td>
<td>1.1</td>
</tr>
<tr>
<td>1.006</td>
<td>1.9</td>
</tr>
<tr>
<td>1.018</td>
<td>0.6</td>
</tr>
<tr>
<td>1.029</td>
<td>0.4</td>
</tr>
<tr>
<td>1.040</td>
<td>0.2</td>
</tr>
<tr>
<td>1.051</td>
<td>0.2</td>
</tr>
<tr>
<td>1.062</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Mean**: 0.861 gm/cc  
**Standard Deviation**: 0.083 gm/cc

**Figure 17.** The Distribution of Bulk Density Values for all Seven Coke Batches.
Figure 18a. A Summary of Mean Bulk Density Values for all Seven Coke Batches.
Figure 18b. Bulk Density versus Oven Wall Pressure
(Points for industrial oven cokes estimated the using linear line and bulk density values).
3.2.2 TRUE DENSITY

The true densities of all seven coke batches have been determined. These values are presented in Table IX. There is no apparent correlation between the true density and the oven wall pressure (or static load). The true density values of all seven cokes vary within five percent of each other. These values are lower than that of graphite (2.266 gm/cm$^3$ (40)) which indicate that these cokes are not well graphitized. Since CPR-270 is the wharf coke, it would require a large number of true density measurements to get a representative value for all wharf coke, so its true density was calculated from the average of CPR-267, CPR-268 and CPR-269 true density values.

3.3 MICROSTRUCTURE

The microstructure of the seven coke batches used in this project was examined quantitatively using a Leitz TAS PLUS image analyzer, as discussed in section 2.5.2. Since this analysis was performed on two dimensional photographs with the intention of representing a three dimensional system, an effort was made toward improving the accuracy of the method employed. This includes determining the sensitivity of the results towards the number of fields (photographs of circular faces) analyzed and assessing the effect of large pores crossing the outside boundaries of the fields. The analysis of the porous structure proceeded in the following manner: 1) the sensitivity analysis was performed to
<table>
<thead>
<tr>
<th>Coke Type</th>
<th>Depth Below Coal Line (m)</th>
<th>Estimated Static Load Pressure (kPa)</th>
<th>Mean Bulk Density gm/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPR-267</td>
<td>5.0</td>
<td>10.2</td>
<td>0.919</td>
</tr>
<tr>
<td>CPR-268</td>
<td>3.3</td>
<td>4.9</td>
<td>0.884</td>
</tr>
<tr>
<td>CPR-269</td>
<td>0.8</td>
<td>5.4($10^{-1}$)</td>
<td>0.779</td>
</tr>
</tbody>
</table>

Table VIII. Estimated Variation of Mean Bulk Density and Oven Wall Pressure with Depth Below The Coal Line.

<table>
<thead>
<tr>
<th>Coke Type</th>
<th>Depth Below Coal Line (m)</th>
<th>Oven Wall Pressure (kPa)</th>
<th>True Density gm/cm$^3$</th>
<th>Standard Deviation gm/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPR-264</td>
<td>-</td>
<td>3.2</td>
<td>1.9672</td>
<td>0.0784</td>
</tr>
<tr>
<td>CPR-265</td>
<td>-</td>
<td>5.9</td>
<td>2.0229</td>
<td>0.0918</td>
</tr>
<tr>
<td>CPR-266</td>
<td>-</td>
<td>17.8</td>
<td>1.9009</td>
<td>0.0729</td>
</tr>
<tr>
<td>CPR-267</td>
<td>5.0</td>
<td>10.2*</td>
<td>1.9167</td>
<td>0.0326</td>
</tr>
<tr>
<td>CPR-268</td>
<td>3.3</td>
<td>4.9*</td>
<td>2.0163</td>
<td>0.0216</td>
</tr>
<tr>
<td>CPR-269</td>
<td>0.8</td>
<td>5.4($10^{-1}$)*</td>
<td>1.9194</td>
<td>0.0640</td>
</tr>
<tr>
<td>CPR-270</td>
<td>Warf</td>
<td>-</td>
<td>1.9470**</td>
<td>0.0621</td>
</tr>
</tbody>
</table>

Table IX. Variation of True Density as a Function of Coking Conditions.

* Calculated.
** Average of true densities of CPR-267, 268 and 269.
determine the minimum number of fields required to represent the whole microstructure; 2) the effect of pores situated on the borders of the field was assessed; 3) distributions of pore area, equivalent diameter, mean chord length, form factor \((4\pi(area)/(perimeter)^2)\), pore perimeter, maximum and minimum Feret's diameters along with a mean chord sizing of coke cell walls were determined; and 4) a statistical analysis was performed on the results.

3.3.1 SENSITIVITY

Table X shows the measured parameters obtained from measuring 4, 10, 20 and 40 fields (photographs) of a batch of coke. As shown, some variables are more sensitive to the number of fields analyzed than others with pore perimeter being the most sensitive, while the mean chord length (averaged over three orientations) varying the least.

The values appear to converge when more than twenty fields of view have been analyzed. Therefore, it was decided that an analysis of thirty or more fields of view would represent each coke batch adequately.

The porosity was also measured using the same software. These values are compared in Table XI, with those calculated from the measured bulk and true density values. The values obtained from the image analyzer were consistently higher
<table>
<thead>
<tr>
<th>Number of Fields Analyzed</th>
<th>Number of Pore Area (mm²)</th>
<th>Equivalent Diameter (mm)</th>
<th>Mean Chord Length (mm)</th>
<th>Form Factor</th>
<th>Pore Perimeter (mm)</th>
<th>Maximum Feret’s Diameter (mm)</th>
<th>Minimum Feret’s Diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.174</td>
<td>0.298</td>
<td>0.178</td>
<td>0.858</td>
<td>1.483</td>
<td>0.427</td>
<td>0.273</td>
</tr>
<tr>
<td>10</td>
<td>0.180</td>
<td>0.310</td>
<td>0.178</td>
<td>0.847</td>
<td>1.596</td>
<td>0.449</td>
<td>0.283</td>
</tr>
<tr>
<td>20</td>
<td>0.133</td>
<td>0.281</td>
<td>0.176</td>
<td>0.879</td>
<td>1.251</td>
<td>0.403</td>
<td>0.250</td>
</tr>
<tr>
<td>40</td>
<td>0.130</td>
<td>0.285</td>
<td>0.177</td>
<td>0.877</td>
<td>1.248</td>
<td>0.404</td>
<td>0.253</td>
</tr>
</tbody>
</table>

Table X. Variation of The Arithmetic Mean Values of The Pore-parameters Measured Using The Leitz TAS PLUS Image Analyzer for CPR-264 as a Function of Number of Fields Analyzed.
<table>
<thead>
<tr>
<th>Coke Type</th>
<th>Number of Frames from CPR-Analyzed Image Analyzer</th>
<th>Porosity from Pycnometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>264</td>
<td>40</td>
<td>60.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55.50</td>
</tr>
<tr>
<td>265</td>
<td>33</td>
<td>59.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>54.32</td>
</tr>
<tr>
<td>266</td>
<td>40</td>
<td>56.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>51.34</td>
</tr>
<tr>
<td>267</td>
<td>40</td>
<td>57.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>52.05</td>
</tr>
<tr>
<td>268</td>
<td>40</td>
<td>57.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>56.16</td>
</tr>
<tr>
<td>269</td>
<td>40</td>
<td>59.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59.41</td>
</tr>
<tr>
<td>270</td>
<td>40</td>
<td>57.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55.88</td>
</tr>
</tbody>
</table>

Table XI  Comparison of Porosity Values as Measured using the Image Analyzer with Those Values Obtained From Pycnometry.
than those found by pycnometry. The differences between the two methods follow the best fit relationship:

\[ \varepsilon_p = 0.944\epsilon_I - 0.023 \quad r=0.994 \]  

where \( \varepsilon_p \) and \( \epsilon_I \) are the porosities (in percent) measured by pycnometry and by the image analyzer, respectively. In order to calculate the porosities of the test-oven cokes (CPR-264 to CPR-266) a single averaged true density value was used. This average true density was obtained from eighteen different true density measurements of all three cokes. The justification in using such a method is that the oven wall pressure should not affect the true density of the coke (5).

3.3.2 EDGE EFFECTS

One form of inaccuracy, that affects the optical methods of quantitatively characterizing microstructure, is the effect of edges. Often, large features cross over the boundaries of the photographs. This allows only a fraction of their size to be analyzed. The Leitz TAS PLUS image analyzer has the capability of eliminating features which cross the boundaries of the frame being analyzed. This effect was examined by analyzing four and twenty fields. The arithmetic mean values of seven parameters are listed in Table XII. The mean values for all seven microstructural parameters are consistently lower for the data obtained in the absence of features bordering the field edges as
<table>
<thead>
<tr>
<th>Parameter</th>
<th>4 Fields Edge Pores</th>
<th>4 Fields Containing Edge Pores</th>
<th>20 Fields Edge Pores Eliminated</th>
<th>20 Fields Edge Pores Eliminated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mm)</td>
<td>0.085</td>
<td>0.174</td>
<td>0.073</td>
<td>0.133</td>
</tr>
<tr>
<td>Equivalent Dia. (mm)</td>
<td>0.258</td>
<td>0.298</td>
<td>0.241</td>
<td>0.281</td>
</tr>
<tr>
<td>Mean Chord Length (mm)</td>
<td>0.170</td>
<td>0.178</td>
<td>0.162</td>
<td>0.175</td>
</tr>
<tr>
<td>Form Factor</td>
<td>0.894</td>
<td>0.858</td>
<td>0.913</td>
<td>0.879</td>
</tr>
<tr>
<td>Pore Perimeter</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mm)</td>
<td>1.016</td>
<td>1.483</td>
<td>0.925</td>
<td>1.251</td>
</tr>
<tr>
<td>Max. Feret's Dia (mm)</td>
<td>0.352</td>
<td>0.427</td>
<td>0.330</td>
<td>0.403</td>
</tr>
<tr>
<td>Min. Feret's Dia (mm)</td>
<td>0.174</td>
<td>0.273</td>
<td>0.178</td>
<td>0.250</td>
</tr>
</tbody>
</table>

**Table XII.** The Effect of Edges on Microstructural Parameters of CPR-264.
compared to those values obtained when edge features are included. This is not surprising as the larger features are expected to be more frequently intercepted by the field boundaries than the smaller ones. Since larger pores are considered likely to be the cause for mechanical failure in coke, it was decided that further microstructural analysis would be carried out including all the edge pores. This decision is based on the assumption that edge effects will be similar for all seven coke batches and, therefore, the results produced by the image analyzer will be relatively consistent.

3.3.3 CELL WALL SIZE

The thickness of the cell wall was determined using the image analyzer to perform intercept sizing. This method is similar to the manual technique but is performed on a series of lines oriented at 0°, 60°, and 120° relative to the horizontal axis. The mean chord length is found by counting the number of intercepts of each line and dividing the length of each line by the number of intercepts for each of the three angles. The final value results from an average of the chord sizing of the three orientations. The wall size values of the seven coke batches are listed in Table XIII. The cell wall width of the cokes produced in 460mm test-oven are thinner than those for the cokes produced in the 5m industrial coke-oven.
<table>
<thead>
<tr>
<th>coke Type</th>
<th>CPR-264</th>
<th>CPR-265</th>
<th>CPR-266</th>
<th>CPR-267</th>
<th>CPR-268</th>
<th>CPR-269</th>
<th>CPR-270</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Size (mm)</td>
<td>0.131</td>
<td>0.122</td>
<td>0.131</td>
<td>0.154</td>
<td>0.152</td>
<td>0.168</td>
<td>0.169</td>
</tr>
</tbody>
</table>

**Table XIII.** Comparison of Cell Wall Size Values for Different Cokes.
3.3.4 PORE SIZE AND GEOMETRY

The analysis of pore size and geometry was carried out by measuring all seven parameters of each pore on all photographs. The number of pores analyzed per coke batch ranged between 3500 and 5500 depending on the coke being analyzed. The seven pore-parameters which were expected to have an influence on coke mechanical properties are listed in section 2.5.2. Each pore measurement has been classified into histograms and the distribution statistics were calculated using the PDP-11 computer attached with the image analyzer. In addition, all pore measurements were transferred to the main AMDAHL computer for further statistical analysis.

The calculated mean values and their corresponding standard deviations are listed on Table XIV and the histograms for CPR-264 are included in Appendix B as an example. There is a general decrease in the pore dimension values from CPR-264 to CPR-266 for the test-oven cokes while an increase in pore dimensions is observed from CPR-267 to CPR-269. The mean pore size (as described by equivalent diameter, mean chord, maximum and minimum Feret's diameters) is found to be larger for the commercially produced coke than that for the test-oven cokes. The standard deviations of each parameter is shown to be larger than the arithmetic mean values. This is characteristic of heavily skewed distributions. The histograms shown in the appendix are seen to have a positive skewness (there is a very large number of
## Table XIV

Mean ($\mu$) and Standard Deviations ($\sigma$) of the Coke Porous Parameters for all Seven Coke Batches.

<table>
<thead>
<tr>
<th>Coke CPR-</th>
<th>Pore Area ($\text{mm}^2$)</th>
<th>Equivalent Diameter (mm)</th>
<th>Mean Chord Length (mm)</th>
<th>Form Factor</th>
<th>Pore Perimeter (mm)</th>
<th>Maximum Feret's Diameter (mm)</th>
<th>Minimum Feret's Diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>264</td>
<td>0.130</td>
<td>0.285</td>
<td>0.177</td>
<td>0.877</td>
<td>1.248</td>
<td>0.404</td>
<td>0.299</td>
</tr>
<tr>
<td>265</td>
<td>0.105</td>
<td>0.270</td>
<td>0.173</td>
<td>0.885</td>
<td>1.116</td>
<td>0.376</td>
<td>0.252</td>
</tr>
<tr>
<td>266</td>
<td>0.100</td>
<td>0.269</td>
<td>0.170</td>
<td>0.874</td>
<td>1.140</td>
<td>0.378</td>
<td>0.239</td>
</tr>
<tr>
<td>267</td>
<td>0.128</td>
<td>0.287</td>
<td>0.180</td>
<td>0.877</td>
<td>1.244</td>
<td>0.407</td>
<td>0.255</td>
</tr>
<tr>
<td>268</td>
<td>0.150</td>
<td>0.307</td>
<td>0.189</td>
<td>0.867</td>
<td>1.350</td>
<td>0.435</td>
<td>0.274</td>
</tr>
<tr>
<td>269</td>
<td>0.184</td>
<td>0.323</td>
<td>0.196</td>
<td>0.862</td>
<td>1.446</td>
<td>0.463</td>
<td>0.289</td>
</tr>
<tr>
<td>270</td>
<td>0.164</td>
<td>0.314</td>
<td>0.193</td>
<td>0.866</td>
<td>1.380</td>
<td>0.440</td>
<td>0.278</td>
</tr>
</tbody>
</table>
small pores). This raises doubt as to the validity of using the arithmetic mean as a representative value.

3.3.5 **REPRESENTATION OF PORE SIZE AND GEOMETRY**

The statistical problems (associated with skewed distributions) mentioned in section 3.3.4 can be avoided by considering cumulative distributions. For the purpose of this project, the seven parameters used to characterize coke structures were represented arbitrarily by the cumulative 80% finer values (values at which 80% are smaller). The cumulative 80% finer values at the 95% confidence limit are shown in Table XV. The values shown for Form Factor all exceed the theoretical maximum of 1.0 (for a circle) and therefore can not be relied upon. With this in mind, the ratio of maximum Feret's diameter to minimum Feret's diameter was used to characterize pore shape as previously suggested by other workers (32-36). CPR-265 exhibits the smallest pore dimensions of the test oven cokes, whereas CPR-267 exhibits the same (i.e. smallest pore dimensions) for the cokes produced in the 5m industrial coke-oven. Another parameter which has been considered important is the number of pores per field (see Table XV). It can be seen the test-oven cokes contain a larger number of smaller pores when compared with cokes produced at Algoma.
<table>
<thead>
<tr>
<th>Coke Type</th>
<th>Number of Pores per Field</th>
<th>Pore Area ((\text{mm}^2))</th>
<th>Equivalent Diameter ((\text{mm}))</th>
<th>Mean Chord Length ((\text{mm}))</th>
<th>Form Factor</th>
<th>Pore Perimeter ((\text{mm}))</th>
<th>Maximum Feret's Diameter ((\text{mm}))</th>
<th>Minimum Feret's Diameter ((\text{mm}))</th>
<th>Ratio of Max to Min Feret's Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>264</td>
<td>121</td>
<td>0.104</td>
<td>0.363</td>
<td>0.229</td>
<td>1.10</td>
<td>1.378</td>
<td>0.518</td>
<td>0.310</td>
<td>1.771</td>
</tr>
<tr>
<td>265</td>
<td>140</td>
<td>0.093</td>
<td>0.343</td>
<td>0.222</td>
<td>1.10</td>
<td>1.290</td>
<td>0.482</td>
<td>0.301</td>
<td>1.714</td>
</tr>
<tr>
<td>266</td>
<td>126</td>
<td>0.098</td>
<td>0.353</td>
<td>0.224</td>
<td>1.10</td>
<td>1.345</td>
<td>0.506</td>
<td>0.310</td>
<td>1.755</td>
</tr>
<tr>
<td>267</td>
<td>115</td>
<td>0.105</td>
<td>0.365</td>
<td>0.231</td>
<td>1.10</td>
<td>1.410</td>
<td>0.530</td>
<td>0.310</td>
<td>1.749</td>
</tr>
<tr>
<td>268</td>
<td>101</td>
<td>0.105</td>
<td>0.365</td>
<td>0.231</td>
<td>1.10</td>
<td>1.574</td>
<td>0.573</td>
<td>0.352</td>
<td>1.754</td>
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<tr>
<td>269</td>
<td>89</td>
<td>0.134</td>
<td>0.413</td>
<td>0.255</td>
<td>1.10</td>
<td>1.629</td>
<td>0.603</td>
<td>0.352</td>
<td>1.766</td>
</tr>
<tr>
<td>270</td>
<td>97</td>
<td>0.125</td>
<td>0.399</td>
<td>0.251</td>
<td>1.09</td>
<td>1.531</td>
<td>0.566</td>
<td>0.350</td>
<td>1.766</td>
</tr>
</tbody>
</table>

Table XV  Cumulative 80% Finer Values of the Seven Pore Parameters for the Seven Coke Batches.
3.4 COMPRRESSIVE STRENGTH OF COKE BATCHES

Table XVI includes the mean compressive strength values of the seven coke batches, both at ambient temperature and at 1400°C. Also given are their standard deviation values.

Several conclusions can be drawn from this data:
1. Coke is stronger at high temperature,
2. Test-oven cokes (CPR-264 to CPR-266) are stronger than the Algoma cokes, and
3. The standard deviation for each mean strength value is large (up to 50% of the mean strength).

The large standard deviations show the large variation in coke strength values within each coke batch. This scatter in the data will be described in more detail in section 3.4.5.

3.4.1 COKE STRENGTH AS A FUNCTION OF VARIABLES

The independent variables used to characterize ambient and high temperature coke strength have been listed in section 2.0. The effects of these variables on coke strength are illustrated in Figures 19-21 (a-g). All strength results show a significant amount of scatter which is associated with the heterogenous nature of coke.

3.4.2 BULK DENSITY

The position of coke in the Algoma coke-oven with respect to height was found to affect the bulk density of the final coke product (section 3.2.1). The results show that bulk density rises with increasing depth in the
<table>
<thead>
<tr>
<th>Coke Type</th>
<th>Mean Strength at Ambient Temperature (MPa)</th>
<th>Standard Deviation (MPa)</th>
<th>Mean Strength at 1400°C (MPa)</th>
<th>Standard Deviation (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPR-264</td>
<td>12.76</td>
<td>4.09</td>
<td>16.41</td>
<td>5.06</td>
</tr>
<tr>
<td>CPR-265</td>
<td>14.34</td>
<td>6.26</td>
<td>17.81</td>
<td>7.17</td>
</tr>
<tr>
<td>CPR-266</td>
<td>17.57</td>
<td>6.90</td>
<td>18.72</td>
<td>7.71</td>
</tr>
<tr>
<td>CPR-267</td>
<td>10.72</td>
<td>4.74</td>
<td>13.32</td>
<td>5.41</td>
</tr>
<tr>
<td>CPR-268</td>
<td>10.64</td>
<td>5.95</td>
<td>13.84</td>
<td>7.55</td>
</tr>
<tr>
<td>CPR-269</td>
<td>8.16</td>
<td>4.06</td>
<td>6.29</td>
<td>2.40</td>
</tr>
<tr>
<td>CPR-270</td>
<td>9.93</td>
<td>3.56</td>
<td>11.35</td>
<td>5.78</td>
</tr>
</tbody>
</table>

Table XVI. Mean Compressive Strength Values for the Seven Coke Batches at Both Ambient Temperature and at 1400°C.
coke-oven. Figure 19a shows the effect of mean bulk density on mean compressive strength. There was no correlation found between the strength of individual specimens, within a coke batch, and their respective bulk densities as shown in Figure 19b. Figure 19b shows the strength versus bulk density for the range of bulk density values (mean ± standard deviation) chosen for this strength study. This further confirms the need for a statistical approach to the treatment of coke strength data. The error bar in Figure 19a represents the 95% confidence limit for estimating the mean strength. Despite the large scatter, definite trends are noticeable as indicated by the "best fit" lines. The results suggest a linear relationship between bulk density and strength for the range of cokes studied. The coke strength appears to be greater for cokes extracted from the lower regions of the Algoma coke-oven than those sampled from the top of the oven.

3.4.3 POROSITY

Porosity has previously been reported to affect the strength of materials (28). Figure 20 is the relationship between strength and porosity. The strength was found to decrease with increasing porosity. Two empirical relationships, as postulated previously, were used to test the data:

\[ \sigma = -n \varepsilon_p + b \]

and \[ \sigma = \sigma_0 \exp(-b\varepsilon_p) \] (ref 28)
Figure 19a. Mean Compression Strength versus Mean Bulk Density.
Figure 19b. Compressive Strength vs Bulk Density for CPR-264 at Ambient Temperature.
Figure 20. Mean Compressive Strength versus Coke Porosity.
where $\varepsilon_p$ is the porosity, $\sigma$ is the compressive strength and $\sigma_0$ is an empirical constant. The empirical parameters of these equations are shown in Tables XVII and XVIII, respectively. Judging by the values of the correlation coefficients, the linear relationship more accurately described the variation of compressive strength with porosity than the exponential equation proposed by Knudsen (28).

3.4.4 MICROSTRUCTURE

It is obvious from section 3.4.3 that the correlation between compressive strength and porosity is significant but not very satisfactory (as indicated by the correlation coefficients). So, to obtain a better correlation between the strength and some microstructural features, attempts have been made to test the dependence of the strength data on the parameter values determined using the image analyzer.

3.4.4.1 Cell Wall Size

The effect of cell wall size on the compressive strength value is shown in Figure 21a, for the data both at ambient temperature and at 1400°C. Error bars are not shown since the 95% confidence limits for mean compressive strength are the same as in Figures 19 and 20. There is a significant negative correlation between the strength and the cell wall size as shown by the calculated linear regression lines. These results are in disagreement with Patrick et al (32) who found a
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Test Oven Cokes, Ambient Temp.</td>
<td>1.14</td>
<td>76.25</td>
<td>-0.999</td>
</tr>
<tr>
<td>Test Oven Cokes, 1400°C</td>
<td>0.51</td>
<td>44.92</td>
<td>-0.934</td>
</tr>
<tr>
<td>Algoma Cokes, Ambient Temp.</td>
<td>0.33</td>
<td>28.50</td>
<td>-0.845</td>
</tr>
<tr>
<td>Algoma Cokes, 1400°C</td>
<td>0.91</td>
<td>61.94</td>
<td>-0.794</td>
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</table>

Table XVII Parameters for the Equation: \( \sigma = n \sigma + b \).

<table>
<thead>
<tr>
<th>Testing Condition</th>
<th>( \sigma_0 )</th>
<th>b</th>
<th>Corr. Coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Oven Cokes, Ambient Temp.</td>
<td>837.98</td>
<td>0.075</td>
<td>-0.996</td>
</tr>
<tr>
<td>Test Oven Cokes, 1400°C</td>
<td>82.85</td>
<td>0.029</td>
<td>-0.927</td>
</tr>
<tr>
<td>Algoma Cokes, Ambient Temp.</td>
<td>71.45</td>
<td>0.036</td>
<td>-0.842</td>
</tr>
<tr>
<td>Algoma Cokes, 1400°C</td>
<td>2435.73</td>
<td>0.097</td>
<td>-0.801</td>
</tr>
</tbody>
</table>

Table XVIII Parameters for the Equation: \( \sigma = \sigma_0 \exp(-b \tau) \).
Figure 21a. Mean Compressive Strength versus Cell Wall Size (mm)
positive correlation between cell wall thickness and tensile strength.

3.4.4.2 Pore Size

The pore structure was represented by five different parameters: pore area, equivalent diameter, mean chord length, and maximum and minimum Feret's diameters. Plots of compressive strength versus these parameters are shown in Figures 21(b-e). The effect of minimum Feret's diameter on strength was not plotted due to the small variation of values between the seven coke batches. In Figures 21(b-e), error bars representing the 95% confidence interval of the 80% cumulative finer values are only shown for the ambient temperature points since these intervals are the same for the high temperature data as well. The "best fit" lines represent the general trends of the data. From these plots, it is apparent that the strength decreased with increasing pore area and pore size, but the linear correlations obtained in all four plots are poor. Similar trends have been observed in previous studies (32-36).

3.4.4.3 Number of Pores

Larger pore and wall size have been found to decrease the compressive strength of coke. It is apparent, therefore, that the number of pores per unit volume might also correlate with strength. This relationship is shown in Figure 21f. In this figure, the
Figure 21b. Mean Compressive Strength Versus Pore Area

- R. T. (T = 0.824)
- 1400°C (T = 0.863)
Figure 21c. Mean Compressive Strength versus Pore Equivalent Diameter.
Figure 21d. Mean Compressive Strength versus Pore Mean Chord Length.
Figure 21e. Mean Compressive Strength versus Pore Maximum Feret's Diameter.
Figure 21f. Mean Compressive Strength versus Number of Pores per Field.
coke strength appears to rise with increasing number of pores per field. This result agrees with previous observations (32-36).

3.4.4.4 Pore Perimeter

The compressive strength has been shown in the past (32-36) to be a function of the pore perimeter. This parameter is thought to represent the pore surface area. Plotting mean compressive strength versus pore perimeter (see Figure 21g), yields a negative correlation indicating that strength decreased with increasing pore perimeter. However, this correlation does not describe the coke strength more accurately than other correlations shown in Figures 21(a-f).

3.4.5 STATISTICAL ASPECTS OF COKE FRACTURE

The Weibull statistics have provided a useful tool to test the strength data of brittle solids. An attempt has been made to assess the variability of compressive strength values of coke (that has been encountered in this study for different coke batches) using the Weibull model of failure. The failure behaviour is represented by a probability curve, which is expressed mathematically as:

\[ P(\sigma) = 1 - \exp[-K\sigma^m] \]  

(10)

where \( P \) is the probability of failure, \( \sigma \) is the failure stress, \( K \) is an empirical constant and \( m \) is the Weibull
Figure 21g. Mean Compressive Strength versus Pore Perimeter.
modulus (also an empirical constant).

Theoretically, this equation was developed from the weakest link theory (18) and, therefore, was not truly meant to be applied to compressive strength data of coke where the failure mechanism may be a progressive cooperation of flaws. However, equation 10 can be used as a cumulative distribution function of the probability of failure versus failure stress to describe the variations of strength between coke specimens.

Figures 22(a-g) are the Weibull distribution plots of compressive strength for all seven coke types both at ambient and at high temperatures. The distribution of coke strength is large and sometimes varies by an order of magnitude (normal for brittle solids). The parameter of the Weibull function which most accurately describes the variation in strength values is the Weibull modulus ($m$) (slope of the Weibull plot). These values were calculated using linear regression and are compared in Table XIX. For tests at ambient temperature, the Weibull modulus values of the test-oven cokes (CPR-264 to CPR-266) are consistently higher than those values found for the Algoma oven cokes. This shows that the test-oven cokes appear to be slightly more uniform in strength properties at ambient temperature than those of the Algoma cokes. This pattern, however, does not apply to the data at 1400°C. All values of the Weibull modulus found in this project fall within the range reported in the literature (18).
Figure 22a. Weibull Distribution Plot of CPR-264 Mean Compressive Strength Values.
Figure 22b. Weibull Distribution Plot of CPR-265 Mean Compressive Strength Values.
Figure 22c. Weibull Distribution Plot of CPR-266 Mean Compressive Strength Values.
Figure 22d. Weibull Distribution Plot of CPR-267 Mean Compressive Strength Values.
Figure 22e. Weibull Distribution Plot of CPR-268 Mean Compressive Strength Values.
Figure 22f. Weibull Distribution Plot of CPR-269 Mean Compressive Strength Values.
Figure 22g. Weibull Distribution Plot of CPR-270 Mean Compressive Strength Values.
Table XIX  Weibull Modulus Values of Seven Coke Batches at Ambient Temperature and at 1400°C.
3.4.6 THEORETICAL ASPECTS OF COKE FRACTURE

The empirical correlations between coke strength and a number of microstructural parameters have been discussed above. The trends show that a number of structural parameters together may determine the coke strength.

Patrick et al (35) and other workers at the BCRA (34) proposed an equation (equation 5):

$$\sigma = 450(F_{\text{max}})^{-0.5}\exp[-2(F_{\text{max}}/F_{\text{min}})^{0.5}\varepsilon_p]$$  \hspace{1cm} (5)

where $F_{\text{max}}$ is the mean maximum Feret's diameter which is treated as the critical flaw size, and the term $2(F_{\text{max}}/F_{\text{min}})^{0.5}$ is the stress concentration factor. Using the data generated in this study, equation 5 was tested (see Figure 23) where $F_{\text{max}}$ and $(F_{\text{max}}/F_{\text{min}})$ are the 80 percentile values. It was assumed that all failure was in tension during the compression tests (24) which justifies the use of equation 5 for these tests. The slope of the plots are 2385 and 3331 MPa for room temperature and 1400°C, respectively, which is higher than 450MPa, reported by Patrick et al (35). It should be realized, however, that the nominal compressive strength of brittle solids are always higher than the tensile strength (theoretically 8 times greater (24)). Although Patrick's equation did not correlate any better than plotting strength vs individual porous parameters, it has the merit of predicting the observed order of mean strength values for the coke batches.

According to the theory of fracture mechanics, the failure stress of a material is governed by its critical
Figure 23. Mean Compressive Strength versus 

\[ F = \left( \frac{F_{\text{max}}}{F_{\text{min}}} \right)^{-0.5} \exp\left(-2\left( \frac{F_{\text{max}}}{F_{\text{min}}} \right)^{0.5} \right) \]

\[ F_{\text{max}}^{-0.5} \exp\left[-2(F_{\text{max}}/F_{\text{min}})^{0.5} p\right] \]
flaw size, and hence, its critical stress intensity factor (41). The stress intensity factor \( K \) is a function of the nominal stress applied and the flaw size, and when \( K \) reaches the critical stress intensity factor, \( K_{IC} \), failure occurs.

Nied and Arin (42) developed a model for ceramics which treated small pores as spherical flaws and developed a relationship to calculate the stress intensity factors by accounting for the interaction of stress trajectories in three dimensions:

\[
K = 2/\pi \left\{ \frac{1}{V_f} \tan\left(\frac{\pi}{2} V_f\right) \right\}^{1/2} \sigma_0 \sqrt{2a}
\]  

(11)

where \( a \) is the pore radius, \( V_f \) is the volume fraction of porosity, and \( \sigma_0 \) is the nominal applied stress. The critical stress intensity factors (\( K_{IC} \)) for the seven coke batches are shown in Table XX as calculated using equation 11. The values of \( K_{IC} \) for cokes produced in the experimental test-oven are higher than those for Algoma cokes. It has been suggested previously that pore shape influences the stress intensity factor (32-36), but equation 11 makes no account for flaw shape. The flaw shape, however, is difficult to assess statistically in a material, such as coke, owing to the complex system of pores.

It is interesting to note that the calculated values of the critical stress intensity factors are similar to those values calculated for coke batches of the same origin (ie. test-oven cokes have critical stress intensity factor values close to one another as do those of Algoma cokes). This
### Coke Porosity Max. Feret's K_{IC}

<table>
<thead>
<tr>
<th>Type</th>
<th>Porosity</th>
<th>Max. Feret's Dia, 2a</th>
<th>K_{IC}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V_f</td>
<td>(mm)</td>
<td>A.T.</td>
</tr>
<tr>
<td>CPR-264</td>
<td>0.555</td>
<td>0.518</td>
<td>8.560</td>
</tr>
<tr>
<td>CPR-265</td>
<td>0.543</td>
<td>0.482</td>
<td>9.205</td>
</tr>
<tr>
<td>CPR-266</td>
<td>0.513</td>
<td>0.506</td>
<td>11.341</td>
</tr>
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<td>CPR-267</td>
<td>0.521</td>
<td>0.530</td>
<td>7.112</td>
</tr>
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<td>CPR-268</td>
<td>0.562</td>
<td>0.573</td>
<td>7.542</td>
</tr>
<tr>
<td>CPR-269</td>
<td>0.594</td>
<td>0.603</td>
<td>6.081</td>
</tr>
<tr>
<td>CPR-270</td>
<td>0.559</td>
<td>0.566</td>
<td>6.980</td>
</tr>
</tbody>
</table>

**Table XX.** Calculated Critical Stress Intensity Factors Using a Multiple Flaw Model.
suggests that the textural characteristics (pore size) have a significant influence on the mechanical behaviour of coke (see section 4.5.2). Figures 24(a & b) illustrate the variation of the calculated $K_{IC}$ values amongst the coke batches tested at room temperature and 1400°C, respectively. The error bars represent the range of $K_{IC}$ values that would occur from the mean stress range calculated previously at the 95% confidence limit. The test-oven coke $K_{IC}$ values increase with increasing oven pressure, but this trend could not be found for the Algoma cokes. CPR-269 recorded the lowest $K_{IC}$ values at both temperatures.

3.4.7 STABILITY AND HARDNESS

Coke strength is traditionally assessed in North America in accordance with the ASTM stability and hardness standard (43). This standard has been presented previously in Table III (13). It is therefore desirable to attempt to develop a relationship describing stability and hardness using compressive strength values.

Figure 25 shows stability and hardness (measured at CANMET) versus the mean compressive strength values at room temperature. No correlation could be observed between the stability and hardness and the compressive strength data obtained in this project.
Figure 24a. Calculated Critical Stress Intensity Factors using Ambient Temperature Compressive Strength Data.
Figure 24b. Calculated Critical Stress Intensity Factors using Compressive Strength Data Obtained at 1400°C.
Figure 25. Stability and Hardness versus Mean Compressive Strength.
3.5 HIGH TEMPERATURE CREEP

A literature survey revealed no reference on the plastic behaviour of blast furnace coke. However, because of the existence of ash having low melting temperature constituents such as Na\textsubscript{2}O, SiO\textsubscript{2}, K\textsubscript{2}O, etc. (and their eutectics); some plastic deformation can be expected to occur when the specimens are heated to temperatures greater than 1000°C and subjected to a load. In this project, constant load experiments were performed at varying temperatures (greater than 1000°C) and pressures to determine if coke exhibits any high temperature plasticity. Such experiments were found to be difficult to perform as most of the specimens failed (collapsed) during loading to the desired stress for testing.

However, a few creep experiments were carried out under a constant load and isothermal conditions. In order to estimate the dimensional change, which specimens may undergo due to continued graphitization above the final coking temperature, graphitization tests were also performed. This was necessary to ensure that dimensional change during creep testing was not caused by graphitization.

3.5.1 GRAPHITIZATION

The maximum temperature encountered in a normal coke-oven is in the order of 1250°C, so it is quite natural that when coke is subjected to a temperature higher than this and for a prolonged period of time, the specimens would
graphitize resulting in an increase in density with an associated shrinkage.

In order to determine the extent of shrinkage due to graphitization, coke specimens were heat treated at 1400°C as described in section 2.7. The maximum linear shrinkage encountered in these experiments was in the range 0.96 to 1.33%, which agrees with dilatometer results obtained by other workers (3,23,26,27), who reported values in the range of 0.70 to 1.0% at temperatures reaching 1400°C.

3.5.2 ISOTHERMAL CONSTANT LOAD TESTS

The constant load tests were performed at temperatures ranging between 1000 and 1600°C with stresses ranging from 5.0 to 13.0MPa on the four Algoma cokes (CPR-267 to CPR-270). Such tests could not be carried out on the test-oven cokes as their sample sizes were not sufficiently large to produce enough cylindrical specimens to do both strength and creep studies.

The constant load tests were performed using the heating and loading conditions described in section 2.6.2. The deflection was recorded as a function of time and was corrected for elastic strain, obtained by removing the load at the end of the creep experiments and noting the magnitude of the elastic "spring back".

The first set of experiments performed was to determine the reproducibility of the creep curves. Three "so-called" similar specimens from one batch of coke (CPR-269) were
creep tested under isothermal conditions (1500°C) and pressure (6.0MPa). The normalized creep curves are shown in Figure 26. Unfortunately, the creep curves are not very reproducible. Similar randomness in creep behavior was encountered in almost all other cases. Because of the lack of availability of a large number of specimens having identical bulk density and properties, no extensive creep testing could be carried out in this program.

The test conditions and total strain for all creep experiments are listed in Table XXI. It is obvious (from Figure 26) that specimens were undergoing plastic deformation at temperatures ≥1000°C and the total maximum strain that could be introduced was in the order of 6 to 8% (not taking into consideration shrinkage due to graphitization of ≈1%). Due to the qualitative nature of this part of the study, it was considered unnecessary to account for graphitization shrinkage which could be very difficult to measure during the creep experiments. Most of the creep curves are shown in Appendix C, except those of CPR-270, which were selected for further analysis.

The creep curves of CPR-270 showed normal creep behavior with respect to temperature and stress (Figures 27(a-b)). Increasing the temperature and pressure of testing should produce a higher total strain, if the assumption that the melting of ash controls the plastic behavior of coke is correct. Both the concentration of the glassy phase (ash) and its viscosity should be affected by temperature and
Figure 26. Normalized Creep Curves Produced at 1500°C and 6.0MPa.
<table>
<thead>
<tr>
<th>Coke Type</th>
<th>Temperature of Tests (°C)</th>
<th>Applied Stress During Tests (MPa)</th>
<th>Total Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPR-267</td>
<td>1000</td>
<td>12.6</td>
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</tr>
<tr>
<td></td>
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<td>8.52</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>12.6</td>
<td>6.42</td>
</tr>
<tr>
<td>CPR-268</td>
<td>1200</td>
<td>9.69</td>
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<td>6.0</td>
<td>4.90</td>
</tr>
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<td>1500</td>
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<tr>
<td></td>
<td>1500</td>
<td>13.0</td>
<td>4.03</td>
</tr>
</tbody>
</table>

**Table XXI.** Conditions for Creep Tests.
Figure 27a. Creep of CPR-270 at 1500°C Under Varying Conditions of Applied Stress.
Figure 27b. Creep of CPR-270 at 9.29MPa Under Varying Conditions of Temperature.
pressure. Raising the temperature of coke should have the effect of increasing the concentration of glassy phase and decreasing its viscosity. Deviations from this behavior can be attributed to the very complex nature of coke texture (large variations were encountered even in the same batch).

An interesting observation that could be made from these creep curves is that the temperature was found to affect the shape of the curves. Creep curves generated at lower temperatures (1000-1200°C) were found to reach their final strain values (leveled off) more quickly than those produced at higher temperatures. This indicates a viscous type flow (similar to glass) at higher temperatures which supports the contention that it is the melting of ash components which produced the plastic strain.

3.5.3 CREEP BEHAVIOUR OF COKE

The determination of the mechanisms of the creep behaviour of coke is beyond the scope of this investigation and requires more extensive study. However, the shape of the creep curves was found to be similar to creep curves of refractories (44,45).

The creep behavior of refractories are often analyzed by visco-elastic models as the systems are too complex to be analyzed using any atomistic mechanisms. In almost all cases, the creep of refractories is due to the formation of a glassy phase produced by low melting temperature constituents (45). Furthermore, it was reported that an
increase in porosity reduces the ability of refractories to resist creep (45). Since coke is a highly porous solid containing low melting temperature phases (ash constituents), it is natural that an attempt be made to analyze the creep data of coke using a visco-elastic model. Also, the complex nature of the coke structure does not permit any interpretation of the creep of coke using any atomistic model.

3.5.4 VISCO-ELASTIC MODELS

Three models are considered for the analysis of the creep behavior of coke. These are a single-Kelvin unit (Figure 28a), an interactive double-Kelvin element unit (46,47) (Figure 28b) and three-non-interactive-Kelvin units (48) (Figure 28c). Of these three models, only the interactive double-Kelvin element model is found to adequately describe the response of coke subject to constant load tests.

3.5.5 ANALYSIS OF CREEP DATA

The analysis of the creep data was carried out using a visco-elastic model derived previously (46,47) for hot-pressing of ceramic powders. In Figures 27(a & b), the
Figure 28a. Single-Kelvin Unit.
Figure 28b. Interactive-double-Kelvin Unit.
Figure 28c. Three-non-interactive-Kelvin Units.
points correspond to experimental data and the lines as drawn can be represented by an equation as follows:

\[ \epsilon = \frac{\Delta L}{L_0} = K(1 - Ae^{-at} - Be^{-\beta t}) \]  

(12)

The parameters \( K, A, B, a \) and \( \beta \) can be determined by digitizing experimental curves and then, using a computer, fitting the data to equation 12. It is also possible to fit the creep curves to a sixth order polynomial (46), but such an equation would not lend itself to the development of a visco-elastic model.

The problem can be represented using system dynamics (47) where a step input stress:

\[ \sigma = \sigma_0 U_C(t) \]  

(13)

where

\[ U_C(t) = \begin{cases} 
0 & \text{for } t < 0 \\
1 & \text{for } t > 0 
\end{cases} \]  

(14)

produces a strain output (equation 12). Therefore, the strain can be represented by the product of stress and the system transfer function:

\[ \epsilon = \chi \sigma \]  

(15)

where \( \chi \) is a transfer function.
A differential equation for the system can be found by applying the Laplace transform to equation 15 (51) (represented by capital letters):

\[ E = X \Sigma \]  \hspace{1cm} (16)

where

\[ E = \mathcal{L}(\epsilon(t)) = \frac{K}{s} - \frac{KA}{s+a} - \frac{KB}{s+\beta} = \frac{K(s+a)(s+\beta)-KAs(s+\beta)-KBs(s+a)}{s(s+a)(s+\beta)} \]

and

\[ \Sigma = \mathcal{L}(U_c(t)) = 1/s \]

Therefore, the Laplace transform of the transfer function is found to be (taking into consideration that at \( t=0, \epsilon(t) = 0 \), therefore, \( A+B=1 \)):

\[ \frac{E}{\Sigma} = sK(Aa+B\beta)+K\alpha \]

\[ \frac{1}{s^2+(a+\beta)s+a\beta} \] \hspace{1cm} (17)

which can be arranged to give:

\[ E[s^2+(a+\beta)s+a\beta] = \Sigma[sK(Aa+B\beta)+K\alpha] \] \hspace{1cm} (18)

Taking the inverse Laplace transform of equation 18 produces the differential equation:

\[ \frac{d^2\epsilon}{dt^2} + (a+\beta)\frac{d\epsilon}{dt} + a\beta \epsilon = K(Aa+B\beta)\frac{d\sigma}{dt} + K\alpha \sigma \] \hspace{1cm} (19a)

This differential equation is similar to that which
describes the behavior of the two interactive Kelvin elements shown in Figure 28b (46,47):

\[
\frac{d^2 \varepsilon}{dt^2} + \left[ \eta_2 (M_1 + M_2) + M_2 \eta_1 \right] \frac{d\varepsilon}{dt} + \left[ M_1 M_2 \right] \varepsilon = \frac{1}{\eta_2} \frac{d\sigma}{dt} + \frac{[M_1 M_2]}{[\eta_1 \eta_2]} \sigma
\]

(19b)

The spring constants and the dashpot viscosities have been shown to be related to K, A, B, a, and β by:

\[
\eta_2 = \frac{1}{K[Aa + B\beta]}
\]

(20)

\[
M_2 = \eta_2 [a + \beta - Ka\beta \eta_2]
\]

(21)

\[
\eta_1 = \frac{M_2^2}{\eta_2 [Ka\beta M_2 - a\beta]}
\]

(22)

\[
M_1 = \frac{\eta_1 \eta_2 a\beta}{M_2}
\]

(23)

This mechanical analogue was used to describe the components of creep strain for the coke samples tested under a constant load, and under isothermal conditions.

The values of these mechanical parameters are calculated using the values of K, A, B, a, β of the experimental curves and are shown in the Appendix C. The temperature and stress dependence of \( \eta_1, \eta_2, M_1, M_2 \) are illustrated in Figures 29 (a & b), respectively. In both figures, the viscosity parameter \( \eta_1 \) has much higher values than those of \( \eta_2, M_1, \) and \( M_2 \). The parameter, \( \eta_1 \), also appears to be both temperature and stress sensitive whereas the other three parameters are relatively insensitive. The significance of this behaviour with respect to temperature
Figure 29a. Variation in Visco-Elastic Model Mechanical Parameters as a Function of Temperature for CPR-270.
Figure 29b. Variation in Visco-Elastic Mechanical Parameters as a Function of Applied Pressure for CPR-270.
and pressure cannot be explained at present. However, any resistance to flow implies that very high viscosity in the system and the reduction of values of $\eta$, with temperature may be associated with the increasing flow properties of coke.
4. DISCUSSION

In the previous chapter, the results obtained in this study have been analyzed. However, it is worthwhile to critically evaluate some of the attempted correlations already made. Before doing this evaluation, the total efforts will be summarized first.

As outlined in section 1.6, an effort has been made to study the variation of coke properties (microstructure and strength both at ambient and high temperatures) as a function of position (height) in a coke-oven battery. Secondly, a wharf coke sample to represent the oven-coke, as a whole, was also used as the control sample. This was done in order to compare this wharf coke with cokes extracted from various heights in Algoma's 5m coke-oven. Furthermore, three test-oven samples made from the same coal blend but prepared under varying coking conditions were also tested for further comparison with the commercially produced samples.

The experimental program involved quantifying the microstructure of the coke using an automated image analyzer and correlating the microstructural parameters with compressive strength values obtained both at ambient and high temperatures. Lastly, the plastic behaviour of the industrial coke samples was qualitatively evaluated at temperatures above 1000°C.
4.1 BULK DENSITY
Initially, the bulk density of the coke samples was considered as a major parameter for distinguishing each of the seven coke batches (CPR-264 to CPR-270). The bulk density of coke depends on its ash content, the carbonaceous product, its true density, and its porosity. Since these coke samples were produced from the same coal blend, their ash content should be similar if not the same. For this reason, the bulk density was considered a good parameter for distinguishing the coke batches.

4.1.1 RELIABILITY OF BULK DENSITY RESULTS
According to the ASTM standards (57), a 50 pound sample of wharf coke must be used when determining the sample bulk density. Such a large sample size is normally considered necessary to get a representative value. However, this was not possible for the purpose of this project since the large sample sizes needed and the necessary equipment were not available. The bulk density was therefore determined by measuring the volume of near-perfect drill-core specimens and their respective weights. The results showed considerable scatter as represented in Figure 18a by the error bars (standard deviation).

The number of specimens measured in this way ranged between 32(CPR-265) and 131(CPR-269), which was governed by the size of the sample batches supplied by CANMET. There is a considerable "overlap" of the bulk density ranges (error
bars) of the seven coke batches. This raised concern about the possibility that population mean bulk densities could be the same. An analysis of variance of the bulk density values using the One-Way Classification technique (29) was employed at 99% confidence to test this possibility. The results showed that at least two sample mean bulk density values differed. A more in depth analysis (single-degree-of-freedom comparisons (29)) revealed that the individual mean bulk densities do in fact differ from one another in most cases. Table XXII shows the probability that individual comparisons have the same mean bulk density. Blank spaces in the table indicate that there is no significant difference between the two coke batches. The coke batches CPR-264, CPR-265, CPR-268 and CPR-270 possess similar mean bulk density values when compared at a level of significance of 0.01. An interesting result of this analysis is that the mean bulk density value of CPR-270 (wharf coke) is representative of the combination of bulk density values obtained from CPR-267, CPR-268, and CPR-269 (Algoma cokes) but is not representative of the test-oven cokes. Furthermore, the mean bulk density values of CPR-264, CPR-265, and CPR-266 as a group do not represent those of CPR-267, CPR-268, and CPR-269 which they were initially intended to do (see Appendix D).

4.1.2 OVEN PRESSURE

Bulk density was shown to be affected by the pressure

\[ \text{All pressures existing in a battery (static or other) are referred to as oven pressures.} \]
<table>
<thead>
<tr>
<th></th>
<th>264</th>
<th>265</th>
<th>266</th>
<th>267</th>
<th>268</th>
<th>269</th>
<th>270</th>
</tr>
</thead>
<tbody>
<tr>
<td>264</td>
<td>-</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>265</td>
<td></td>
<td>-</td>
<td>0.01</td>
<td>0.05</td>
<td>0.01</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>266</td>
<td>0.01</td>
<td>0.01</td>
<td>-</td>
<td>0.05</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>267</td>
<td>0.01</td>
<td>0.05</td>
<td>0.05</td>
<td>-</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>268</td>
<td></td>
<td>0.01</td>
<td>0.01</td>
<td>-</td>
<td>0.01</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>269</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>270</td>
<td>0.05</td>
<td>0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>0.01</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Table XXII. Probability that The Assumption of Differing Bulk Densities is Erroneous for Comparisons Between Coke Batches.
of the oven walls during coking in the test-ovens (Figure 18b). The relationship between the bulk density and the oven wall pressure existing in the coke-oven was found to be:

\[ \rho_b (\text{gm/cm}^3) = 0.11 \log_{10} P(KP_a) + 0.808 \]

This equation, however, was derived using only three data points (from test-oven cokes) since it was impossible to determine the pressure in an operating industrial coke-oven. Shown also in Figure 18b are the estimated points for the three Algoma cokes based on their bulk density values. The difference in coking pressure in the industrial coke-oven can be attributed to the static load existing on the charge. It should be mentioned, however, that there may be other variables (such as vertical temperature gradients) affecting the final bulk density of the Algoma coke. Figure 30 illustrates the variation of temperatures as a function of time in the Algoma No. 9 battery for the three positions from where cokes CPR-267(sole) to CPR-269(top) were sampled (49). The temperature histories of the three positions are somewhat varied with final temperatures being 935°C, 1195°C, and 1262°C for the top, middle, and sole positions, respectively. The effect of final coking temperature on the coke bulk density is uncertain but it is possible that the temperature effect may be significant.

4.1.3 **TRUE DENSITY**

The true density of all seven coke batches was determined from the samples taken 2cm from the cauliflour
Figure 30. Temperature Histories Measured in the Algoma No. 9 Coke-oven Battery at the Top, Middle and Sole Positions.
edge. This was necessary as a precaution against possible true density variation as a function of position along the oven width. Two fluids were used in the pycnometric determination of true density giving six measurements for each of the seven coke types. From Table IX, the standard deviation ranged between 1.1% (CPR-268) and 4.5% (CPR-265). The variation (i.e., standard deviation) between measurements was seen to be greater for the test-oven cokes than those encountered for the Algoma cokes. The true density values followed no particular trend. Theoretically, the test-oven coke should all have similar true density values since they were produced under similar conditions of coking time and temperature (5). Algoma coke was expected to show increasing true density values toward the sole of the coke-oven as the temperature was higher in this region. For the wharf coke (CPR-270), the true density value was calculated as an average of CPR-267, CPR-268 and CPR-269, since the sample required to achieve a representative value would have to be extremely large.

4.2 MICROSTRUCTURE

Two sources of error are possible when making quantitative microstructural analysis from photographs:

1. Inaccuracies associated with representing a three
dimensional system using a two dimensional photographs, and

2. The effect of large pores crossing the boundaries of the measurable area.

The first problem is easily taken care of by increasing the area of analysis (i.e. increasing the number of photographs). However, the problem of large pores crossing the boundaries of the measurable area is less easily solved.

Table XII shows the differences between the mean values of seven microstructural parameters with and without "edge" pores. The results show a significant decrease in mean values when edge pores are eliminated. Decreasing the magnification of the photographs could reduce this effect but would decrease the accuracy of such measurements, since the measurements are only as accurate as the smallest "pixel point" on the T.V. monitor, and are, therefore, resolution dependent. Since small pores are difficult to resolve, the magnification of each photograph was set at 12X. In addition, it was decided that edge pores would also be included in the analysis because it is the largest pore (or pores) which is expected to have the greatest influence on coke mechanical behaviour.

Comparison between porosity values measured using both pycnometry and image analysis is made in Table XI. The image analyzer consistently produced higher porosity values than those obtained by pycnometry. This can be attributed to dark areas present in the pore walls caused by insufficient
polishing (i.e. areas with rough surface).

Although the porosity values obtained using pycnometry and those obtained by the image analyzer differ, they do show essentially the same relative variation between the different coke batches and this is shown by equation 9 (section 3.3.1). The porosity values calculated using the results of bulk density and true density varied linearly with those values determined using the image analyzer. This justified the assumption that the image analyzer described the microstructures of the various coke batches relative to one another. This is important, since most of the effort was directed more toward variation between coke texture and its effect on the compressive strength than on the acquisition of absolute values of microstructural parameters.

4.3 EFFECT OF COKING CONDITIONS ON MICROSTRUCTURE

The coke samples used in this study were all produced from the same coal blend, but under a variety of coking conditions. The effects of different coking conditions on the pore structure of coke are described below.

4.3.1 CELL WALL THICKNESS

Table XIII summarizes the measured cell wall size of all seven coke batches. It is immediately apparent that the cokes produced in the 460mm test-oven possess thinner cell walls than those produced in Algoma. This is contrary to the results of the BCRA (31), where they claimed to find no
significant effect of oven size on the cell wall thickness. However, their results showed cell wall sizes of 0.125, 0.134, and 0.137 mm for the 250 kg, 350 kg, and 17 tonnes ovens, respectively. This may indicate that there was an oven-size effect in their results.

The variation in the final coking temperature as a function of height in an Algoma coke-oven, has been illustrated in Figure 30. As can be seen in Table XXIII, no direct dependence of cell wall size on estimated final coking temperature was observed. Perch (5), also reported that cell wall size was independent of final carbonizing temperature for coals carbonized above the resolidification temperature.

Coke-oven pressure and coal moisture content showed no apparent effect on cell wall size of the cokes examined. In contrast, it has been well documented that preheating (drying) coal prior to charging has resulted in a finer pore-wall thickness (31, 50).

4.3.2 PORE SIZE AND GEOMETRY

The pore size and geometry values of the seven coke batches with their respective coking conditions are summerized in Table XXIV. For the purpose of this discussion, pore size is represented as the 80% cummulative finer mean chord length, and geometry is represented as the ratio of the maximum to minimum Feret's diameters.
<table>
<thead>
<tr>
<th>Coke Sample</th>
<th>Oven Pressure (kPa)</th>
<th>Estimated Coking Temperature (°C)</th>
<th>Charge Moisture Content (%)</th>
<th>Cell Wall Size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPR-264</td>
<td>3.2</td>
<td>1250</td>
<td>5.9</td>
<td>0.131</td>
</tr>
<tr>
<td>CPR-265</td>
<td>5.9</td>
<td>1250</td>
<td>4.1</td>
<td>0.122</td>
</tr>
<tr>
<td>CPR-266</td>
<td>17.8</td>
<td>1250</td>
<td>1.2</td>
<td>0.131</td>
</tr>
<tr>
<td>CPR-267</td>
<td>10.2</td>
<td>1260</td>
<td>N/A</td>
<td>0.154</td>
</tr>
<tr>
<td>CPR-268</td>
<td>4.9</td>
<td>1200</td>
<td>N/A</td>
<td>0.152</td>
</tr>
<tr>
<td>CPR-269</td>
<td>0.54</td>
<td>940</td>
<td>N/A</td>
<td>0.168</td>
</tr>
<tr>
<td>CPR-270</td>
<td>-</td>
<td>-</td>
<td>N/A</td>
<td>0.169</td>
</tr>
</tbody>
</table>

**Table XXIII.** Cell Wall Size Values as a Function of Coking Conditions (Oven pressure estimated for Algoma Coke).
<table>
<thead>
<tr>
<th>Coke Batch</th>
<th>Oven Pressure (kPa)</th>
<th>Estimated Coking Temperature (°C)</th>
<th>Coal Charge Moisture (%)</th>
<th>Mean Chord Length (mm)</th>
<th>Fmax</th>
<th>Fmin</th>
<th>Number of Pores per Field</th>
</tr>
</thead>
<tbody>
<tr>
<td>264</td>
<td>3.2</td>
<td>1250</td>
<td>5.9</td>
<td>0.229</td>
<td>1.771</td>
<td>121</td>
<td></td>
</tr>
<tr>
<td>265</td>
<td>5.9</td>
<td>1250</td>
<td>4.1</td>
<td>0.222</td>
<td>1.714</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>266</td>
<td>17.8</td>
<td>1250</td>
<td>1.2</td>
<td>0.224</td>
<td>1.755</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>267</td>
<td>10.2</td>
<td>1260</td>
<td>N/A</td>
<td>0.231</td>
<td>1.749</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>268</td>
<td>4.9</td>
<td>1200</td>
<td>N/A</td>
<td>0.243</td>
<td>1.754</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>269</td>
<td>0.54</td>
<td>940</td>
<td>N/A</td>
<td>0.255</td>
<td>1.766</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>270</td>
<td>—</td>
<td>—</td>
<td>N/A</td>
<td>0.251</td>
<td>1.766</td>
<td>97</td>
<td></td>
</tr>
</tbody>
</table>

Table XXIV. Pore Size and Geometry Values as a Function of Coking Conditions.
Figures 31a and b illustrate the relationship between the pore size as a function of the estimated coking temperature and oven pressure, respectively. It appears that pore size decreases with increasing temperature and oven pressure.

The existence of oven wall pressure during the production of the test-oven cokes seems to be positively correlated to the coal-charge bulk density (see table IV). This agrees with the observations of other workers (5,31) who have observed a similar decrease in the pore size resulting from an increase in the coal charge bulk density.

The value of $(F_{\text{max}}/F_{\text{min}})$ did not show much variation between coke batches with values ranging between 1.7 and 1.766. This compares with values between 1.7 and 1.9 reported by Patrick (31-36) and other BCRA workers. Their studies showed that the value of the shape factor was found to be dependent on the number of orientations performed on each measurement. The BCRA (34) studies showed that the error for measuring maximum Feret's diameter ranged between 8.3% for four orientations, and 0.5% for sixteen orientations. In this study, twelve measurements at 15° intervals were made to obtain the maximum and minimum Feret's diameters since this was the maximum number of orientations that could be performed using the Leitz TAS PLUS image analyzer. A statistical analysis performed by BCRA (34) showed that the probable error of estimate for the determination of maximum Feret's diameter using twelve
Figure 31a. Pore Size as a Function of Estimated Coking Temperature.
Figure 31b. Pore Size as a Function of Estimated Oven Pressure.
orientations was approximately 1%.

The average number of pores per field of view is also listed in Table XXIV for each of the seven coke batches studied. In general, cokes with smaller pores had a larger total number of pores than cokes containing larger pores. Thus, these values appear to be related to coking conditions where the number of pores is found to increase with coking temperature and oven pressure.

4.3.3 SUMMARY OF MICROSTRUCTURAL DEPENDENCE ON COKING CONDITIONS

It can be concluded from the above, that the cell wall thickness is not greatly dependent on the conditions of coking. However, cell wall thickness was found to be greater for cokes produced in the Algoma coke-oven than those of the test-oven cokes.

In contrast, the pore size was shown to increase at a lower final carbonization temperature and lower oven pressure (or lower coal charge bulk density). The temperature of coking and the existing oven pressure are lower near the coal line of a commercial coke-oven which results in coke products exhibiting larger pores.

4.4 COKE STRENGTH

The importance of coke strength on the efficiency of a blast furnace has already been outlined. One of the main objectives of this project is to determine the factors which
influence the coke strength and to relate these to current coke production practices.

4.4.1 EFFECT OF TEMPERATURE

Table XVI includes the mean compressive strength values for the seven coke batches both at ambient temperature and at 1400°C. The coke strength increased in every case except with the coke batch CPR-269 when tested at 1400°C. The cause of this discrepancy (CPR-269) can not be explained but may be due to a non-representative sample used in this investigation.

A similar effect of increasing strength at high temperature has also been observed by previous workers studying coke (19) and graphite (40). The increase in coke strength when heated above the carbonization temperature is explained by its continued graphitization above the coking temperatures. In graphite, this strength increase at higher temperatures has been attributed to relieving the residual stresses formed during the initial graphitization and subsequent cooling (40).

The high temperature strength tests performed in this project were only carried out in an inert gas (Ar). It is probable that the increase in strength would be affected or even non-existent if these tests were performed in a CO₂ atmosphere, since the pore walls would be subjected to attack by the Boudouard reaction. No such experiments have yet been reported in the literature.
4.4.2 EFFECT OF MICROSTRUCTURE

As with most porous solids, the strength has been shown to be reduced with increasing porosity (Figure 20) and conversely the strength increased linearly with bulk density (Figure 19a). These trends have been extensively studied in the past, particularly in the field of ceramics. Though these parameters (porosity and bulk density) generally have provided a qualitative correlation with coke strength, it is important to explore the cause of these observed variations in coke strength. It has been demonstrated in section 4.1.1 that the coke batches CPR-264, CPR-265, CPR-268, and CPR-270 have similar bulk densities (using one-degree-of-freedom comparisons) but they vary in compressive strength both at ambient and high temperatures. These differences may be caused by variations in pore size distributions and pore geometry.

Figures 22(a-g) show that a rise in compressive strength correlates with decreasing cell wall size, pore size, and with increasing number of pores. It is surprising that strength rises with decreasing cell wall size and increasing number of pores, but this effect can be explained by considering the pore size to be the dominant factor affecting the strength. For example, if two cokes have the same porosity, the coke with larger pores will contain a smaller number of pores which are, on average, more widely spaced than a coke with smaller pores. Figure 32 illustrates how the cell wall size and the number of pores per field are
Figure 32. Cell Wall Size and Number of Pores per Field as a Function of Pore Size.
just a consequence of the pore size. This observation disagrees with the implications of Patrick's equation (equation 4, section 1.5.3) that pore size, cell wall size and the number of pores per field are independent of one another (37,42). It can be concluded, therefore, that the pore size has perhaps the greatest effect on coke strength compared with all other pore parameters. This supports the argument that the critical flaw size governing failure may be related to pore size.

Patrick et al (35) also proposed an equation which suggests that there is a strength dependence on the pore shape factor (equation 5). This equation was tested with the present data (Figure 23) and, as can be seen, the correlation was poor. This may be due to the difficulty of statistically describing the shape of the pores. Furthermore, no interaction of stress around pores was considered in the derivation equation 5. For this reason, it was decided to apply an equation developed by Neid and Arin (42) which is a multiple flaw model that can predict the critical stress intensity factor \( K_{IC} \) for porous materials. Using porosity values and maximum Feret's diameter as the flaw size, the values of \( K_{IC} \) were calculated for all seven coke batches.

Judging by the compressive strength values of coke, quality of coke in the Algoma coke-oven is better for samples extracted from the sole region of the oven than those obtained at higher positions. This may be due to both
the effect of a less porous product, and smaller pores in cokes produced at the sole level. Porosity and pore size appear to be affected by the following factors: static load (oven pressure), final coking temperature and oven size. To produce a stronger coke, it is best to increase the static load on the charge and increase the final coking temperature.

4.5 CREEP OF COKE

A preliminary study on the plastic flow behaviour of coke above 1000°C has been carried out. From the knowledge of the fact that ash is made up of low melting point constituents which are likely to melt at temperatures encountered at the tuyere region of the blast furnace, it is expected that coke should deform plastically, as do refractories. Thus, the formation of a glassy phase should decrease the load bearing capacity of coke, which may result in creep.

The complex structure of coke prohibits any interpretation of the creep data in any fundamental way. For this reason, a viso-elastic model was used to describe the creep behaviour of coke above 1000°C. It was found that an interactive double-Kelvin-element model (Figure 28b) described the behaviour most accurately.

Figures 29(a-b) illustrates the effect of temperature and applied pressure on the mechanical parameters \( \eta_1, M_1, \eta_2, M_2 \) of the two interactive Kelvin element model. Only the parameter, \( \eta_1 \), varied with temperature and pressure and it
had very high values when compared with the other three parameters: $M_1$, $\eta_2$ and $M_2$. If it is considered that the resistance to deformation can be attributed to the very high values of the viscous parameter, $\eta_1$, (as the other parameters have low values) the temperature effect on this parameter should be the controlling factor describing the viscous deformation of coke at high temperatures (>1000°C). Thus, $\eta_1$, may represent the effective viscosity of the glassy phase (ash) controlling the flow behaviour of the system. The parameters, $M_1$, $M_2$, and $\eta_2$, may somehow be related with the carbon structure and/or the machine response which explains their relative insensitivity to temperature and applied pressure.

As expected, the viscosity $\eta_1$, is lowered when the temperature rises. This is typical of most glassy materials and it should result in a decrease in the load bearing capabilities of coke at higher temperatures. There is also a definite dependence of the viscosity, $\eta_1$, on the applied pressure which is shown to decrease with a rise in the applied stress. This is characteristic of a non-Newtonian fluid.

In summary, a time dependent strain has been observed at temperatures greater than 1000°C. This behaviour has been described using an interactive-double-Kelvin element visco-elastic model.

It should be noted that some of the ash constituents, such as $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, and $\text{SiO}_2$, should also vaporize in the
highly reducing atmosphere existing in the blast furnace (6). This may somehow counteract the weakening of coke due to melting of ash. In addition, the loss of carbon from coke by the Boudouard reaction should be taken into consideration when determining the strength properties of coke, as that would relate more closely to blast furnace conditions.
5. CONCLUSION

In this project, seven coke batches specially prepared by CANMET were studied. These samples originated from three sources:

1. Three coke batches were prepared in a 460mm test-oven, each with different coke-oven pressures.
2. Three coke batches were sampled from three different positions, with respect to height, in a 5m coke-oven at Algoma Steel Corporation.
3. A warf coke sample was prepared to be compared with the other six batches.

The experimental program was carried out in four major steps:

1. Bulk and true density determinations,
2. Quantitative microstructural analyses,
3. Compressive strength value determinations for all seven coke batches at ambient temperature and at 1400°C (these values were then related to coking conditions and to the microstructural results), and
4. Creep test experiments above 1000°C.

The following conclusions can be made from this study:

1. The bulk density of the Algoma cokes was higher for cokes extracted from the bottom of the coke-oven than those sampled close to the top. This increase in density can be attributed to an increase in static load, due to the weight of the burden, which was greatest at the oven sole. This effect may also have been aided by the higher
final coking temperatures near the bottom of the coke-oven, but there is insufficient evidence to make a definite comment.

2. Coke pore and wall size were also found to be affected by coking conditions. The pore and wall size were smaller in test-oven cokes than those in Algoma cokes. This implies that there is an oven size affect on the microstructure of coke. Furthermore, an increase in pore size was observed with height in the Algoma coke-oven. No apparent trend could be established between cell wall size and height.

3. The coke compressive strength was found to be greater for the specimens obtained from regions close to the sole of the 5m Algoma oven. Cokes produced at the sole region exhibited lower porosity values and smaller pores than the cokes situated higher in the oven. This resulted in a stronger coke for the samples produced at the sole of the coke-oven. Coke batches produced in the test-ovens were always stronger than the Algoma cokes and were also more uniform in properties (ie. higher Weibull modulus values) at ambient temperature. Coke strength was shown to be higher at 1400°C than at room temperature for six of the seven coke batches. This was thought to be due to continued graphitization after the coke exceeded its final coking temperature.

4. The critical stress intensity factor values ($K_{IC}$) of the test-oven coke batches were shown to increase with oven
wall pressure, but this trend was not so apparent for values of $K_{IC}$ obtained from the strength data of the Algoma coke batches. It was concluded that since $K_{IC}$ is a material property, the differences in these values may be due to variations in the mechanical properties of the solid coke (i.e. pore walls) and to large hidden fissures that may have been present inside some of the samples. However, these differences were slight and, therefore, it is probable the coke mechanical behaviour is largely governed by the porous structure.

5. The coke exhibited plastic flow behaviour when subject to a constant load at temperatures greater than 1000°C. The creep data were interpreted by using an interactive-double-Kelvin element visco-elastic model. The value of the dashpot viscosity, $\eta_1$, was decreased with increasing temperature. The viscosity of this dashpot is thought to be related with the presence of a glassy phase (ash) in coke which may govern its creep behavior.
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