THE EFFECTS OF SOME INERT CARBONACEOUS ADDITIVES ON THE MECHANICAL AND OPTICAL PROPERTIES OF COKE.

By

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EFFECTS OF INERT CARBONACEOUS ADDITIVES ON COKE PROPERTIES.

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ABSTRACT

The objectives of the present study were to investigate, under laboratory conditions, the strength of coke as a function of some of the key variables in the carbonization process, including the addition of some inert carbonaceous materials, and to analyze the effects of these additions on the optical properties of a particular high fluidity coal (Devco). Three coals were selected; Devco, a Canadian coal, and Madison and Chisholm both of which are American coals. Three inert carbonaceous additives were used; Devco semicoke (carbonized at 500°C), low temperature Devco coke (carbonized at 700°C), and coke breeze.

The experimental work was divided into two parts. In the first part, a full factorial design was planned and the blends of Devco coal were carbonized according to it. The variables investigated were: heating rate, size, amount, and 'type' of the inert carbonaceous blended. The dependent variable was the microstrength index (MSI). It was found that the 'type of inert' had the largest statistical weight on the results. The content and mean particle size of the additive in the blend and their interactions with the 'type' were also very significant in the strength. An empirical equation was obtained to express MSI as a function of these variables. In the second part, the blends of the three coals were carbonized according to another statistical design to investigate the following variables: heating rate, type of coal and type of inert. The 'type of coal' was found to be the most statistically

significant variable. Nevertheless, the type of inert changed drastically the mechanical properties.

In single coal experiments the blending of Devco semicoke-500°C increased the MSI (i.e., 10% addition raised the index in Madison by 28%, Chisholm by 28% and Devco by 18%). On the other hand, the blending of coke breeze caused the MSI to drop (10% addition reduced the index in Madison by 29%, Chisholm by 22% and Devco by 19%). The type of inert was characterized by its microhardness, true specific gravity, and ash and volatile matter contents. The type of coal was described by an empirical function derived from accepted industrial correlations.

A relationship has been established between microstrength index and tensile strength based on data of the present work. Several samples of cokes were analyzed under the SEM and the optical microscope. It was observed that the addition of Devco semicoke-500° and low temperature Devco coke-700°C reduced the amount of isotropic carbon present in the structure; these blends also had the higher strength.

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CHAPTER 1

INTRODUCTION

For many years, the techniques used for the selection of coals to prepare blends which could produce a good coke for the blast furnace, were based on a trial and error type of approach. Many investigators tried to relate the chemical properties of the coal to the mechanical properties of the coke, but not a single adequate correlation was found.

The prediction of the coke strength using the information from a petrographic analysis was studied and developed by Ammossov (1957), Schapiro (1960), Bennedict (1966) and others. The system worked very well for the Appalachian region coals which had similar coking characteristics to the Eastern Canadian coals.

The blend charged to a conventional coke-oven is prepared by mixing low, medium and high volatile coals in order to get a coke of required properties suitable for the blast furnace. Recently, research has been oriented to the reduction or substitution of the expensive low-volatile coal by new components in the blend which can give an equally strong coke. The objectives of this project were:

1) To investigate, under laboratory conditions, the strength of coke as a function of some of the key variables in the carbonization process, including the addition of some inert carbonaceous materials, and

2) to analyze the effect of these additions on the optical properties of a particular high fluidity coal (Devco).

The low volatile coals, which are in short supply, could be substituted totally or partially by inerts which could be produced from high volatile coals. Some properties of these inerts determined their assimilation in the coke matrix. This information is also relevant for the formed coke processes; in this case, briquettes are made from blends containing a low amount of good coking coals, and non-coking coals, and sometimes inerts.

The experimental work was divided into two parts. In the first part, three types of inert (Devco semicoke carbonized at 500°C, low temperature Devco coke carbonized at 700°C, and crushed industrial coke from Stelco) were blended to a high fluidity and high volatile coal (Devco, from Cape Breton, N.S.). Four variables were considered important in this carbonization study: a) heating rate, b) type of inert, c) amount, and d) particle size of the inert.

In the second part, two additional coals (Madison and Chisholm, which are American coals used in blends by Canadian Steel industries) were blended with the same type of inerts used in part 1. The variables studied were: a) heating rate, b) type of inert, and c) type of coal.

An empirical mathematical model to express coke strength as a function of the significative variables was found in each part. These correlations can be improved by the inclusion of other carbonaceous additives such as petroleum coke, brown coals, and anthracite. Coke is a very heterogeneous material which could contain all types of carbon in small areas. It is possible to estimate the content of each structure, under the optical microscope using polarized light, from samples prepared for this analysis.

It is known that at high temperatures the isotropic form of carbon is very reactive to CO_2. Metallurgical coke used in blast furnaces has to fulfill certain requirements in chemical and mechanical properties in order to produce pig iron smoothly and at a minimum cost. The type of carbon (i.e. isotropic and anisotropic) present in the wall structure of coke is an important parameter which influences the strength and the chemical reactivity of coke. At the present time, there are no correlations between the strength and the type of carbon for industrial coke. It has been observed that a prime coking coal produces a coke with better mechanical as well as chemical properties and a larger content of anisotropic carbon than a low rank coal.

The current trend in coke research is toward clarifying the conditions for promoting and controlling the anisotropic development in conventional and formed coke. Some investigators have studied the carbonization of pitch and several chemical compounds such as fluorene, carbazole, naphthalene, anthracene, etc. for their relative simplicity, but the complexity and variety of the coal structure make the findings more difficult to generalize. It is expected that this type of research will be increased in the near future since its direct application on carbonization technology will allow the use of abundant, domestic and cheap non-coking coals in conventional oven and formed coke processes.

CHAPTER 2

LITERATURE REVIEW

Summary

This chapter introduces a general background on the nature of coal, its microscopically recognizable constituents and the use of petrographic analysis for predicting the mechanical properties of the coke produced from it.

It also describes some experimental techniques used in the study of the transformation of coal into coke.

The mechanical properties of coke can be assessed by means of a tumbler test. Although other tests, such as tensile strength and shatter tests have been used, the tumbling seems to be the most reliable method to predict the mechanical behaviour of coke in the iron blast furnace.

One section of this chapter is dedicated to the study of the effect of inert additions, as reported by the literature found in this field.

In the last part of this review the optical anisotropy of coke is discussed. Many researchers have tried to study the influence of the carbonization conditions on the development of the anisotropy.

2.1 The Nature of Coal

As a result of the accumulation of dead plants, the transformation of the vegetable material began initially in the presence of a deficient supply of oxygen,in the presence of moisture, and subsequently altogether out of contact with air, under water. In the first stage of coal formation, the plants were converted to peat with an accumulation of humid acids in the material (humidification).

The second stage - the conversion of peat to bituminous coal occurred after the accumulations had been covered by mineral sediments deposited by water which periodically inundated the lowlands. Depending on the conditions (salinity of water, depth of reservoir, and possibility of aeration), the activity of microorganisms - aerobic (in the presence of oxygen) or anaerobic (in the absence of oxygen) - began. Usually, anaerobic microorganisms do not cease their activity even when the coal seams become covered by deposits of considerable thickness. Finally, all transformations of the second stage increased the carbon content and reduced the oxygen content. The conversion of peat to coal and further transformation of the coal are known as carbonification or coalification.

The gradual transitions from peat to anthracite occurring in nature can be arranged in a definite sequence according to the degree of coalification, as shown in Table 2.1.

Coals of equal degree of carbonification may differ in their properties because of the difference in the condition of the material prior to the beginning of the metamorphism proper.

TABLE 2.1

Average elementary composition of different fuels in relation to the degree of coalification(1)

Fuel	Elementary composition of organic mass, %		
	C	H	O+N
Wood	44	6.0	50.0
Peat	59	6.0	35.0
Brown coal and lignites	70	5.5	24.5
Bituminous coal	82	5.5	13.0
Anthracite	95	2.0	3.0

Humic acids are present in coals in the initial stages of their metamorphism. Their chemical structure is principally aromatic. Their molecules may contain carboxyl (COOH), phenolic (C_6H_5OH), and methoxyl (OCH_3) groups at the same time. The carbon content in humic acids varies from 56 to 64%, that of hydrogen from 3 to 6%. Their average molecular weight is about 400. Apparently the molecular weight of coal is above 2500 (2).

2.2 The microscopically recognizable constituents of coal.

2.2.1 The concept of 'macerals'.

Coal is a heterogeneous substance consisting of various constituents. In the same way as inorganic rocks are composed of minerals, coal consists of macerals. A maceral of coal varies widely in its chemical composition and physical properties and is not crystalline. Stopes used the term 'maceral' for the first time in 1935 for the constituent of coal isolated by maceration. (This word is derived from the Latin verb "macerare" which means "to soften"). As used at present, the term describes at the same time both the shape and the nature of the microscopically recognizable constituents of the coal (3).

2.2.2 The three maceral groups.

All macerals have been classified in three groups: (a) Vitrinite; (b) Exinite (or Liptinite), and (c) Inertinite. Inorganic materials in coal consist primarily of mineral matter, among them chiefly clay minerals, carbonates, sulfides, and sulfates, and many others in relatively small quantities. The total inorganic material in coal ranges from a few percent to more than 50%. If the inorganic constituent is greater than 50% by weight, it is classified as carbonaceous shale. The three maceral groups are characterized by their chemical composition. If one compares isometamorphic maceral groups (groups of the same rank or class), the vitrinite contains relatively more oxygen, the exinite more hydrogen and the inertinite more carbon. The volatile-matter yield also is highest in the exinite, amounting in a particular coal to 66.7% as against 35.2% in the vitrinite and 22.9% in the inertinite.

Coal petrologists and coal chemists have established the existence of a distinct relation between the reflectance of a maceral and its carbon or volatile-matter yield. This fact allows the exact determination of the rank of a coal by measuring its reflectance on a polished surface. In determining the character of maceral fragments, the property of colour can be useful. The 'internal' reflexions are indicative of certain maceral types. In low rank coals, for instance, the internal reflexion imparts to the sporinite a golden yellow appearance under oil immersion , whereas semifusinite appears white and fusinite frequently yellowish.

2.2.2.1 The vitrinite group.

Vitrinite is the most frequent and the most important maceral group occurring in bituminous coal. Three different macerals can be distinguished in the vitrinite: telinite, collinite and vitrodetrinite.

Telinite (which constitutes the cell walls of cellular structures) and vitrinite generally originate from trunks, branches, stems, leaves and roots. Collinite is the structureless constituent of vitrinite. In vitrinite showing structure, the cells are frequently filled with collinite. Vitrodetrinite is a rare maceral. It can occur in the form of detritus. These fragments mostly originate from plants or humic-peat particles which were degraded at a very early stage.

Table 2.2 shows the chemical composition (expressed in weight percent of carbon and in the atomic ratios H/C, O/C and N/C) and the densities of several vitrinites of different rank.

TABLE 2.2

Chemical composition and densities of some vitrinites of different ranks

C	H/C	O/C	N/C	d_4^{20} (g/cm^3)
70.5	0.862	0.247	0.015	1.425
75.5	0.789	0.181	0.015	1.385
81.5	0.753	0.108	0.017	1.320
85.0	0.757	0.071	0.016	1.283
87.0	0.733	0.050	0.018	1.274
89.0	0.683	0.034	0.018	1.296
90.0	0.656	0.027	0.018	1.319
91.2	0.594	0.021	0.015	1.352
92.5	0.509	0.016	0.015	1.400
93.4	0.440	0.013	0.015	1.452
94.2	0.379	0.011	0.013	1.511
95.0	0.307	0.009	0.013	1.587
96.0	0.223	0.007	0.012	1.698

In the form of vitrain layers, vitrinite fractures angularly and conchoidally. The surface fractures exhibit a glassy or pitchy lustre. In anthracite a metallic yellowish lustre may appear.

If the reflectance of a maceral is measured in various optical media, e.g. air, water, oil or methylene iodide, the refractive index and the absorption index can be calculated. Table 2.3 shows some values calculated by van Krevelen using vertically incident light and air and cedar oil as media.

TABLE 2.3

Optical constants of vitrinites at 5460Å (5)

C	Reflectance in cedar oil		Reflectance in air		Refractive Index		Absorption Index	
	max.	min.	max.	min.	max.	min.	max.	min.
58.0	0.26	0.26	6.40	6.40	1.680	1.680	0.01	0.01
70.5	0.32	0.32	6.70	6.70	1.700	1.700	0.011	0.011
75.5	0.48	0.48	7.21	7.21	1.732	1.732	0.027	0.027
81.5	0.74	0.71	8.00	7.93	1.781	1.777	0.048	0.048
83.0	0.83	0.78	8.25	8.12	1.795	1.788	0.054	0.054
84.0	0.90	0.83	8.41	8.26	1.806	1.796	0.059	0.059
85.0	0.96	0.89	8.60	8.40	1.816	1.805	0.063	0.063
86.0	1.04	0.95	8.81	8.57	1.828	1.815	0.070	0.068
87.0	1.13	1.02	9.01	8.80	1.843	1.825	0.077	0.073
88.0	1.25	1.11	9.28	8.92	1.859	1.837	0.084	0.080
89.0	1.40	1.22	9.61	9.13	1.881	1.851	0.093	0.088
90.0	1.60	1.35	10.09	9.44	1.907	1.869	0.104	0.097
91.2	2.00	1.56	10.8	9.90	1.940	1.890	0.130	0.111
92.5	2.81	1.97	12.12	10.62	1.977	1.911	0.186	0.140
93.4	3.61	2.32	13.20	11.13	2.005	1.923	0.227	0.166
94.2	4.24	2.66	14.18	11.60	2.025	1.933	0.265	0.191
95.0	5.03	3.02	15.21	12.10	2.043	1.942	0.301	0.217
96.0	6.09	3.47	16.55	12.73	2.058	1.950	0.351	0.249

Vitrinite is composed of various humins which consist of an aromatic nucleus surrounded by peripheral aliphatic groups. With increasing rank the peripheral groups (OH, COOH, CH_3) are lost and the aromatic nuclei become larger.

In Table 2.4 some vitrinites are listed in order of increasing rank.

TABLE 2.4 (6)

Chemical composition of vitrinites from bituminous and anthracite coal grouped by rank. (Weight percent)

No.	C	H	O	N	S	H/C*	O/C*	Vol. matter
1	81.5	5.15	11.7	1.25	0.4	0.753	0.108	39
2	85.0	5.4	8.0	1.2	0.4	0.757	0.071	34
3	87.0	5.35	5.9	1.25	0.5	0.732	0.051	30
4	89.0	5.1	4.0	1.3	0.6	0.683	0.034	26
5	90.0	4.94	3.2	1.35	0.5	0.655	0.027	23
6	91.2	4.55	2.6	1.15	0.5	0.594	0.021	8

*These values represent atomic ratio.

2.2.2.2 The Exinite group

This group comprises the macerals sporinite, cutinite, suberinite, resinite, alginite and liptodetrinite. These macerals consist of sporine, cutine, suberine, resins, waxes, fats and oil of vegetable origin. In coals of low rank the exinites are distinguished from the vitrinites by a higher hydrogen content. On carbonization they yield much tar and gas; a higher stage of rank (below 28% of volatile matter) they yield much less tar and gas.

2.2.2.3 The inertinite group

The word 'inert' is applied in coal petrography to certain constituents of coal which are more or less non-reactive in a particular sense. The macerals of the vitrinite and exinite groups in coking coals will soften during the carbonization process, the fusibility of the inertinite maceral is very weak or nil. Only micrinite is not inert;

it differs in its origin from the rest of the inertinites.

One characteristic of this group is its high reflectance. The macerals belonging to the inertinite group are micrinite, macrinite, semifusinite, fusinite, sclerotinite and inertodetrinite. Fusinite is the richest in carbon of all the constituents of coal. It frequently originates from charcoal.

2.3 Petrography of Coal

There are two methods of approach for petrographic analysis of coal: the reflected light and the transmitted light techniques. The reflected (incident) light technique requires that the coal samples be optically polished and free of scratches; the samples are studied with the aid of an incident light microscope using either oil immersion or dry objectives. The reflected light method is the most widely used technique at the present time because of the relative ease of sample preparation; the resolution of polished surface, particularly in oil immersion, is much better than in the thin section technique, the quantitative count of maceral is more accurate, and the ability to measure the reflectance of the maceral is enhanced.

2.3.1 Prediction of coke properties

The coking power of a coal depends mainly on its inherent properties, but it can be influenced by external factors, such as size distribution, bulk density and heating rate. The coking power of maceral or maceral groups as a function of rank was determined by many researchers. Different attempts have been made to predict or calculate the properties of a high temperature coke from the results of microscopic analysis. In all proposed methods the macerals or microlithotype analytical data are summed and grouped in two categories - reactive constituent and inert constituents. All 'reactive' constituents of coals suitable for carbonization pass through the plastic state, the inerts do not. The three most important methods proposed are: (a) The method of Brown, Taylor and Cook; (b) The method of Ammosov et al. and Schapiro et al.; (c) The method of Simonis and Mackowsky(7).

2.3.2 The method of Ammosov et al. and Schapiro et al.

Previous experience has shown that the coking characteristics of a coal cannot be predicted from its chemical composition, not any other property currently measured in routine tests. Ammosov, Eremin, Sukhenko and Oshurkova in 1957 proposed a method which was further developed by N. Schapiro, R.J. Gray and G.R. Ausner (1961) working at the Applied Research Laboratory of the United States Steel Corporation. Investigations have shown that the petrographic composition is the fundamental factor that controls the chemical composition, rank and carbonization characteristics of a coal.

Table 2.5 shows the division of the different entities. The letter and number designation of the entity type can be translated directly into reflectance. For example, vitrinoid type (V7) has a reflectance range of 0.70 to 0.79 percent reflectance in oil (photometric measurements are used to determine the reflectance of each entity).

Higher rank coals have more reflectance vitrinoids and less volatile matter than the lower rank coals. Usually more than one vitri-

TABLE 2.5

Classification of coal entities (8)

General	Qualitative entities	Quantitative entities
Reactives	Fusible vitrinoids	V0 to V21
	Fusible semifusinoids	SF0 to SF21
	Exinoids	E0 to E15
	Resinoids	R0 to R15
Inerts	Inert vitrinoids	V22 to V70
	Inert semifusinoids	SF22to SF40
	Micronoids	M18 to M70
	Fusinoids	F40 to F70
	Mineral Matter	

noid type occurs in a coal. Figure 2.1 shows the optimum reaction-inert ratio which will give a maximum strength for each vitrinoid type from V3 through V21, found from micro-oven carbonization tests by Schapiro and co-workers. In routine petrographic analysis, relative abundances of macerals are obtained by the point-count method, reported as volume percent. A reflected light microscope (with polarized light) a mechanical stage and an eyepiece reticule are required for petrographic analysis. Within each field of view the maceral is identified and counted. The following macerals are usually reported: vitrinite (V), pseudovitrinite (PV), exinite (E), resinite (R), micrinite (M), fusinite (F), and semifusinite (SF), (9).

The Composition Balance Index of a coal is determined by dividing the inerts present in the coal by the optimum amount of inerts. This composition balance index (also called "Inert Index") can be calculated using the formula 2-1 which is valid either for single coals or blends.

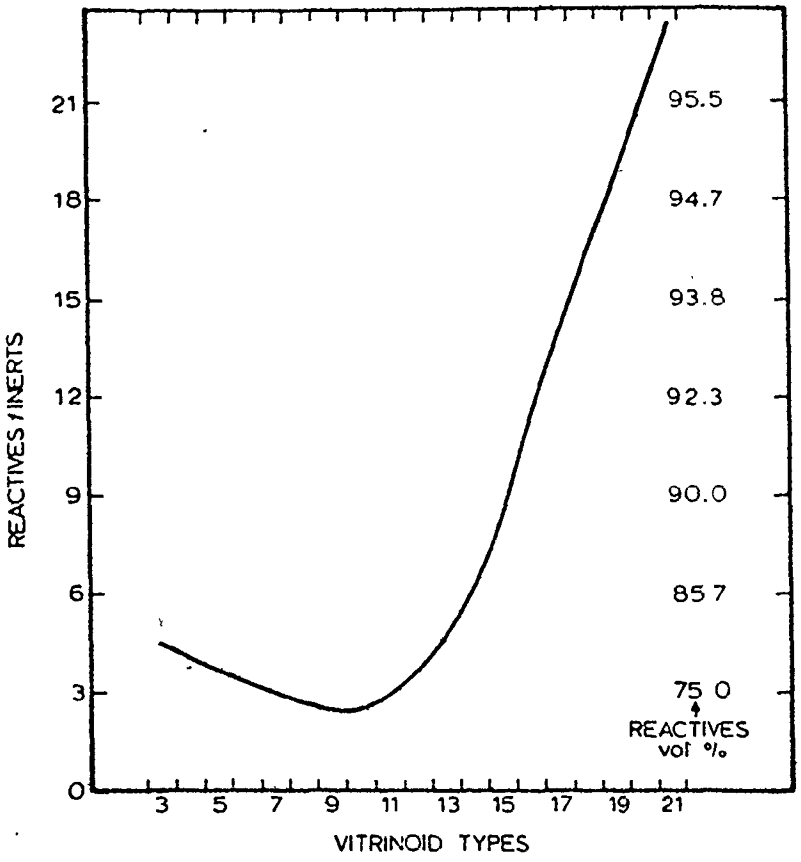


Figure 2.1: Optimum ratio of reactives to inerts for each vitrinoid type. (Ref.10,15)

$$\text{Comp.Bal.Index} = \frac{\text{Total inerts in Blend}}{\dfrac{\text{Total React}(\text{vt}^1)}{\text{Opt.}\frac{R}{I}\text{ ratio}(\text{vt}^1)} + \dfrac{\text{Total React}(\text{vt}^2)}{\text{Opt.}\frac{R}{I}\text{ ratio}(\text{vt}^2)} + \dfrac{\text{Total React}(\text{vt}^{21})}{\text{Opt}\frac{R}{I}\text{ ratio}(\text{vt}^{21})}} \qquad \ldots\ldots (2\text{-}1)$$

Total inerts = Micrinite + macrinite + sclerotinite + fusinite +
2/3 semifusinite.

If the Composition Balance Index is less than 1, the proportion of inerts falls short of the maximum value and coke strength is decreased because there was not enough aggregate to depress the development of large vacuoles and add strength to the coke-cell walls. If it is larger than 1 there is an excess of inerts which cannot be bonded properly by the reactive entities.

Both Ammosov et al. and Schapiro et al. have derived a 'strength index (K)' for each V-step as a function of the inerts content. As a rule this is determined by an ASTM tumbler test on coke produced from coking blends charged in a 500 lb oven with the following characteristics. Coals are dried to less than 2 percent moisture and crushed to 80 percent minues 1/8 in (3 mm) which results in an oven bulk density of about 55 lb/ft^3 (88 kg/m^3). The coking rate used is 1 in/hr and the ash yield for each coal was not larger than 12 percent.

The strength index SI_{blend} for each mixture (single coal or blend) has to be calculated using the formula

$$SI_{(\text{blend})} = \frac{(K_{(\text{vt}^1)} \times \text{Reactives}_{(\text{vt}^1)} + (K_{(\text{vt}^2)} \times R_{(\text{vt}^2)}) + \ldots + (K_{(\text{vt}^{21})} \times R_{(\text{vt}^{21})})}{\text{Total Reactives in Blend}} \qquad \ldots\ldots (2\text{-}2)$$

$K_{vt(1...21)}$ are the strength indices of the succesive V-steps. The reactions Vt 1-21 comprise the vitrinite in the succesive V-steps and the prorated amount of the exinite on the basis of the quantity of each V-step present plus 1/3 of the semifusinite.

Figure 2.2 shows the relation among the strength index for the indicated vitrinoid types and amount of inerts. Figure 2.3 shows the curves of isostability as a function of the composition balance index and the strength index. The use of the isostability graph permits the selection of coals in order to achieve a predetermined coke stability. Schapiro and Gray also found some relation between the petrographic data and the results of some physical and chemical tests (10).

L.G. Benedict and R.R. Thompson working at Bethlehem Steel Corporation were able to identify and describe as "pseudovitrinoid" a group of constituents which had previously been classed with reactive vitrinoids but were now seen to be semi-inert to inert in the cooking process. They developed correlations for predicting the coke stability taking into account that some particles of pseudovitrinoid can be highly altered whereas others can be slightly altered (11,12,13).

2.4 The Transformation of Coal into Coke (Carbonization).

When coal is heated without the access of air, it decomposes with the formation of volatile and non-volatile products. The former are eliminated from the coal in the form of gases and vapours. The liberation of gases begins approximately at 250°C. At around 300°C the liberation of tar vapours begins and there is a simultaneous forma-

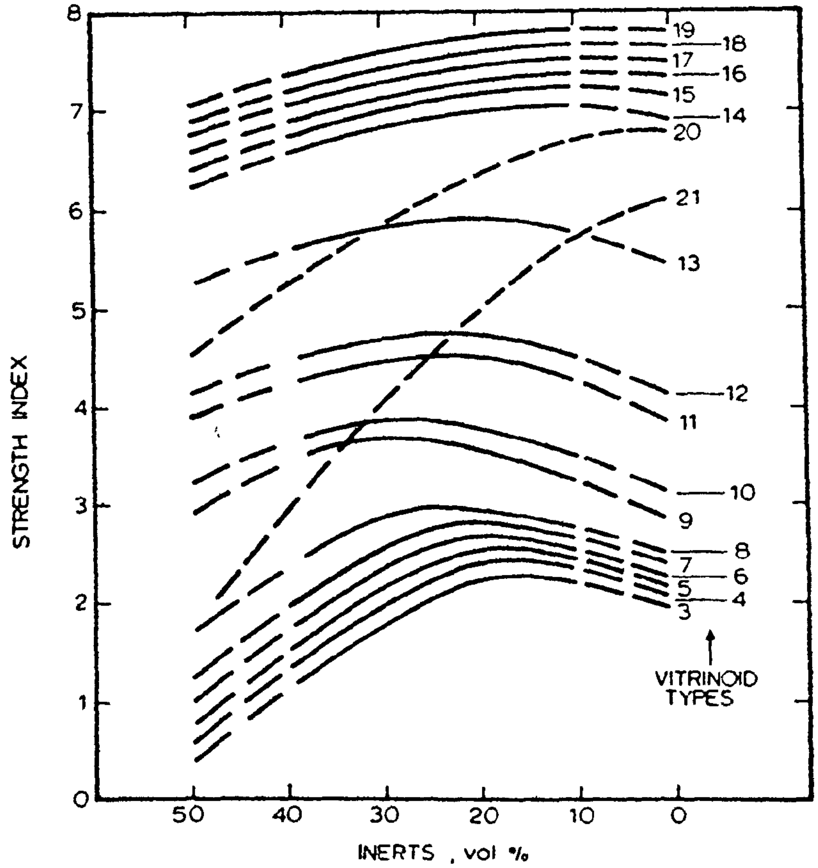


Figure 2.2: Relation among the strength index, the vitrinoid types and the inerts volume. (Ref. 10,15).

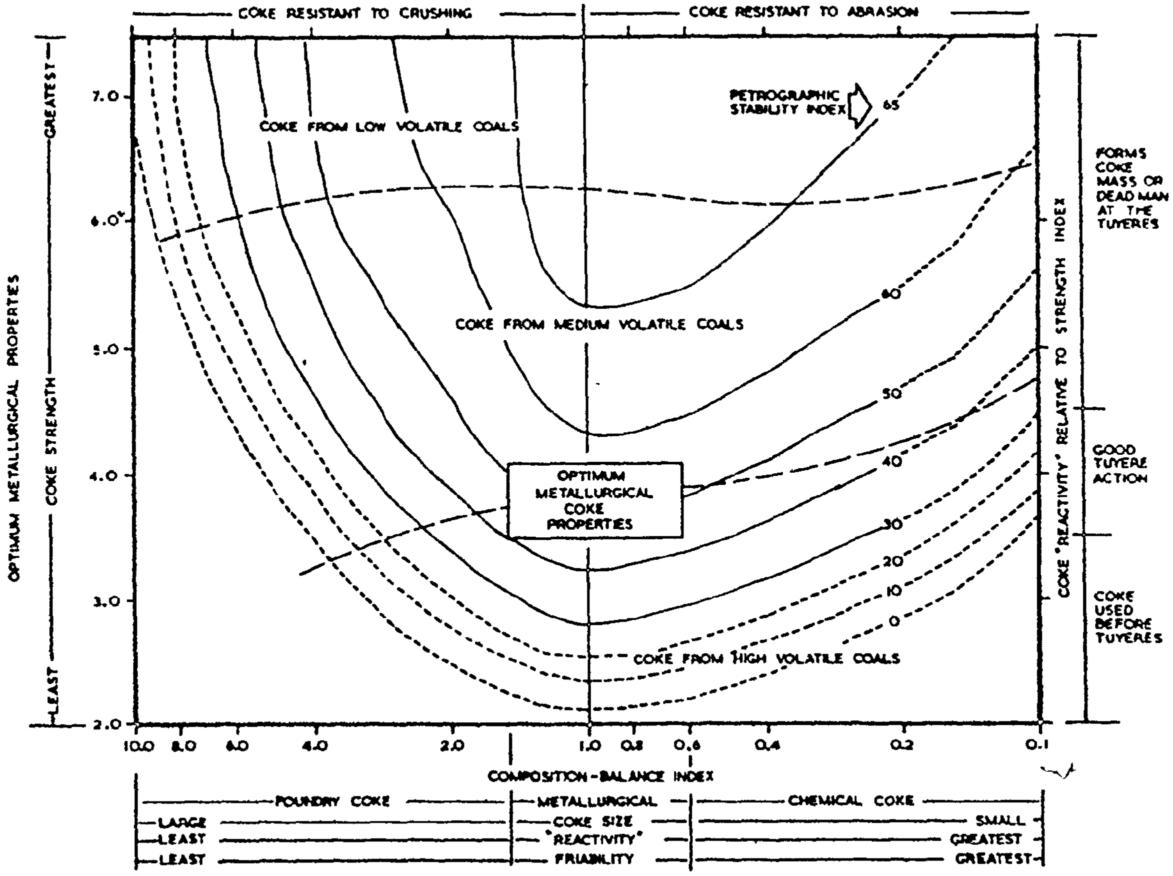


Figure 2.3: Composition balance-index, strength index and empirically determined isostability line. (Ref. 10,15).

tion of appreciable amounts of water. The formation of tar ends at about 550°C.

Coking coal heated in the absence of air, softens between 350 and 500°C. The thermal decomposition of the coal substance with the formation of new compounds, produces the liquid plastic phase. At around 500°C there is solidification of the plastic phase producing a more or less homogeneous fused mass, which is coke (14). Softening, devolatilization, swelling and resolidification are closely related. However, these phenomena depend to a very large degree on the heating rate.

Plotting the weight of coal heated at an adjustable rate against temperature allows one to observe two peaks: one in the temperature range 250-500°C and one near 700°C. The initial peak is correlated with the primary devolatilization in which compounds containing carbon, hydrogen and oxygen are released. The second peak is caused by the secondary degasification in which mainly methane and hydrogen are removed.

2.4.1 Experimental techniques in carbonization research.

The more important techniques in carbonization research are:

1. Thermogravimetric investigations by determining:
   a) the rate of loss in weight as a function of time, at constant temperatures (with temperature as the variable parameter),
   b) the rate of loss in weight as a function of temperature at constant heating rate (with heating rate as the variable parameter).

In both methods the rank of coal and its petrographic composition are independent variables. When a coal is heated at a constant heating rate, the devolatilization rate passes through a maximum. Of the petrographic components exinite shows the largest loss in weight, micrinite the smallest.

2. Thermovolumetric investigations.

At constant heating rate the rate of generation of each of the gases of interest is measured.

3. Plastometric investigations.

The Gieseler Plastomer is the most common of a number of instruments measuring a property, plasticity, which is analogous to viscosity. It consists of a crucible containing coal packed around a stirrer with rabble arms. The stirrer is attached to a constant torque motor adjusted to rotate at a constant rate of 280 rpm in the empty crucible. A disc attached to the stirrer is divided into one hundred dial divisions; the maximum speed of the stirrer is 28000 dial divisions per minute (ddm). The heating rate of the crucible is 3°C/min and the movement of the stirrer under constant torque is registered as a function of temperature. Five characteristic temperatures are noted:

a) Initial softening temperature - the one at which the disc attached to the stirrer rotates at 1 ddm.

b) Fusion temperature - the one at which the dial reading is 5 ddm

c) Maximum fluid temperature - the one at which the dial movement is at its maximum ddm reading.

d) Final temperature - the one at which the dial movement returns to 1.0 ddm.

e) Solidification temperature - the one at which the dial movement ceases.

The fluid range of the coal is the difference between the initial softening and final temperature readings.

4. Dilatometric measurements.

The Ruhr Dilatometer is the most popular. A 'pencil' of standard dimensions is formed from pulverized coal under pressure, removed from the mold and heated in a vertical tube at 3°C/min. A piston resting on the 'pencil' traces a record of the contraction and dilatation of the sample during the heating cycle. Three temperatures are noted from each test:

a) the initial softening temperature (contraction starts).

b) the temperature of maximum contraction.

c) the temperature of maximum dilatation.

The dilatation of a coal measures its coking capacity, and its ability to absorb inert coals or carbonaceous additives. Table 2.6 shows the coking capacity of bituminous coals according to dilatation.

TABLE 2.6
Grouping of Bituminois coal by Dilatometer

Dilatometer Results	Degree of coking (sub-groups)	Designation of coking capacity.
No softening	0	Non-coking
Contraction only	1	Very slightly coking
<0% dilatation ("negative"dilatation)	2	Slightly coking
>0% to 50% dilatation	3	Average coking
>50% to 140% dilatation	4	Good coking
>140% Dilatation	5	Surplus coking capacity

Bituminous coals demonstrate a distinctive property; they leave a coherent residue after the volatile matter is driven off. They are charged to a conventional coke oven for production of coke for the reduction of iron ore in a blast furnace (15).

5. Differential thermal analysis.

The heat effects produced by the decompositions are registered by plotting the temperature difference between the sample and an inert medium, both being heated at constant rate, as a function of the temperature prevailing in the inert medium. The thermogram thus obtained is characteristic of the sample examined; the areas under the peaks are proportional to the amounts of active material present.

Glass (16) found that heating of bituminous coals produces three successive endothermic reactions in the coal mass, represented by peaks in the thermogram. The initial peak, caused by removal of water, lies in the vicinity of 150°C, except in the meta-anthracite range where no thermal effect is observed at this temperature. The second peak is related to chemical decomposition of the coal and occurs in the temperature range 350-550°C, which is the range of primary devolatilization. The 600-700°C peak is a measure of the secondary degasification, which is also highly endothermic.

There is an interruption in the primary devolatilization peak due to an intermediate exothermic reaction caused by resolidification (with condensation of aromatic structures) at about 500°C.

6. Solvent extraction after pre-heating (Thermosolvolysis).

Dryden and Pankhurst found that chloroform is an extremely suitable solvent for preheated (to 420°C) coal. That solubility appears to be associated with the development of plasticity in the coal.

7. Vacuum Pyrolisis.

Juettner and Howard were the first to construct a still for the pyrolisis of coal at temperatures up to 525°C and pressures down to 10^{-3} mm. Orning and Greiger used an improved apparatus. The pyrolisis products were condensed just above the coal sample. After vacuum pyrolisis the residual char strongly resembled the original coal; there was, however, no coking, no agglomeration and practically no swelling of the particles.

2.4.2 Phenomenological theory of carbonization.

The "Metaplast" Theory: Fitzgerald, Chermin and Van Krevelen gave a quantitative description of experimental results. These authors proceeded from earlier assumptions that the decomposition may be distinguished into three successive reactions: formation of an unstable intermediate phase (metaplast) partly responsible for the plastification, and transformation of this intermediary into semicoke and finally into coke.

$$\text{I. Coking coal (P)} \xrightarrow{k_1} \text{metaplast (M)}$$

$$\text{II. Metaplast (M)} \xrightarrow{k_2} \text{semicoke (R)+primary volatiles}(G_1)$$

$$\text{III. Semicoke(R)} \xrightarrow{k_3} \text{coke(S) + secondary gas } (G_2)$$

k_1, k_2 and k_3 denote the respective reaction velocity constants.

Reaction I is a depolymerization reaction. An unstable intermediate phase - metaplast - is formed. Reaction II represent a cracking process. Tar is vaporized and non-aromatic groups are split off. There is recondensation and formation of semicoke. Reaction III is a secondary degasification reaction. Evolution of methane and hydrogen welded together semicoke units to yield a real coke.

The book by Van Krevelen (Chapter XIV) presents the mathematical treatment of the kinetics of the carbonization assuming that it is described by the three following equations and that the third reaction is a first-order reaction.

$$-\frac{dP}{dt} = k_1 P \qquad (2\text{-}3)$$

$$\frac{dM}{dt} = k_1 P - k_2 M \qquad (2\text{-}4)$$

$$\frac{dG}{dt} = \frac{dG_1}{dt} + \frac{dG_2}{dt} = k_2 M + k_3 R \qquad (2\text{-}5)$$

where t is time and P, M, G and R are the amounts by weight of coking coal (P), metaplast (M) and the reaction products gas (G) and semicoke (R).

Heating of coal at constant temperature is represented by the following solutions to the former equations:

$$P = P_0 e^{-kt} \qquad (2\text{-}6)$$

$$M = P_0 k te^{-kt} \qquad (2\text{-}7)$$

$$G = P_0 [1 - (kt + 1) e^{-kt}] \qquad (2\text{-}8)$$

At constant heating rate the amounts by weight of the products are:

$$P = P_0 e^{-\bar{k}t} \qquad (2\text{-}9)$$

$$M = P_0 \bar{k} te^{-\bar{k}t} \qquad (2\text{-}10)$$

$$G = P_0 [1 - (\bar{k}t + 1) e^{-\bar{k}t}] \qquad (2\text{-}11)$$

2.5 Coal and Coke Properties for Iron Making

2.5.1 Coal quality

A good coal for production of blast furnace coke must meet four properties: (a) have coking ability to yield a strong coke alone or in blends with other coals; (b) must be uniformly low in ash and sulfur content, and (d) must become plastic or fluid during its thermal decomposition (caking properties).

In blends, high volatile bituminous coking coals generally serve as the base coal to which small amounts of low and medium volatile coals are added. Actually, coals used for coke making cover a wide range in chemical composition and physical properties; ash content from 3.5% to over 12% and sulfur content from 0.3% to as much as 2% (17). The stability factor for the coke produced ranges from 44 to 60. This value can be predicted using the petrographic information, so it is possible to blend the coals in the right proportion.

A typical coal blend which should produce coke of good quality has the following properties:

TABLE 2.7 (18)

Properties of a Typical Coal Blend

Grade	Limits
Ash	6.0%
Volatile Matter	28-31%
Sulfur	0.8%
Phosphorous	0.09
Alkalis	0.19
Mean reflectance (R_o)	1.10-1.25
Caking Properties	
Free Swelling Index (FSI)	6
Plasticity (Gieseler)	60-1000 dd/m
Dilation (Ruhr)	50-140%
Coking Properties	
Stability Factor (ASTM)	55%
Operational properties	
Max. wall pressure	< 2.0 psi
Expansion/contraction	- 6%

The penalties for high and variable ash and sulphur contents in coke in blast-furnace operations are additional slag volume, increased coke consumption, decreased production and difficulty of furnace control.

2.5.2 Coke Quality

A good blast furnace coke has the following properties:

Analysis	Limits
Ash	8.0%
Volatile Matter	1.0%
Sulphur	0.7%
Alkali oxide in coke	0.2%
Phosphorous pentoxide in coke	0.27%
Stability Factor (ASTM)	55

Several mechanical tests which measure coke strength have been developed in order to predict its behaviour in the blast furnace. The most common of these are:

ASTM - Tumbler Test
ISO - Micum Tumbler
JIS - Drum Test
ASTM - Drop Shatter Test
Tensile Strength

2.5.2.1 The ASTM Stability Factor

The ASTM Stability Factor is an index obtained from a Tumbler Test carried out under standard conditions (A STM Standard D3402). It represents a relative measure of the resistance of coke to degradation by impact and abrasion. Twenty-two pounds (10 kg) of dried coke which will pass a 3-inch (75 mm) and be retained on a 2-inch (50 mm) square mesh sieve are required for every test. The sample is placed in a motor-driven, circular steel drum; 36 inches (91.44 cm) inside diameter and 18 inches (45.72 cm) long, equipped with equally-spaced steel angles. The drum is rotated at 24 r.p.m. for 1400 revolutions, with the resultant product being screened at 2, 1-1/2, 1, 1/2 and 1/4 inch. The percentage retained on the 1 inch screen will give the "stability factor"; the plus 1/4 inch screen percentage is called the "hardness factor" (19).

2.5.2.2 The Microstrength Index (MSI)

This test was developed at the Northern Coke Research Laboratories in England, and it is described by Blayden et al. (20,21) in a paper published in 1937. It is suitable for analysis under laboratory conditions where only small samples can be obtained. The apparatus employed for the assessment of the mechanical strength of the cokes is shown in Figure 2.4.

Two stainless steel tubes, 1 inch (2.54 cm) in internal diameter and 12 inch (30.48 cm) long, were fitted with steel caps which could be screwed down to give a dust-proof joint. The two tubes were mounted firmly in a frame, which could be rotated at 24 r.p.m. by means of an electric motor, for 800 revolutions. Two grammes of the coke, graded between 16(1.19 mm) and 30(595 microns) mesh on Canadian Standard Sieves, are placed in the tubes together with twelve steel balls (0.79 cm in diameter). The amount of breakage is determined by a careful sieve analysis of the resulting material. The mean percentage weights of the original material which remained on the 70 mesh (0.212 mm) is recorded as the Micro-Strength Index.

2.5.2.3 The Tensile Strength

The "Brazilian Test" has been used to determine the tensile strength of coal and coke in an indirect way. The method requires specimens of accurate dimensions and free from cracks. Figure 2.5 shows the stress developed in the diametrical compression of a disk. It is assumed that the test material behaves isotropically and elastically up to the limiting breakage stress. The compressive load is applied along a line at the opposite ends of the diameter of the disk; a uniform principal tensile stress is developed along the diameter at right angles to that along which the load is applied. The relationship between the compressive line load W (Newtons), and the tensile stress,

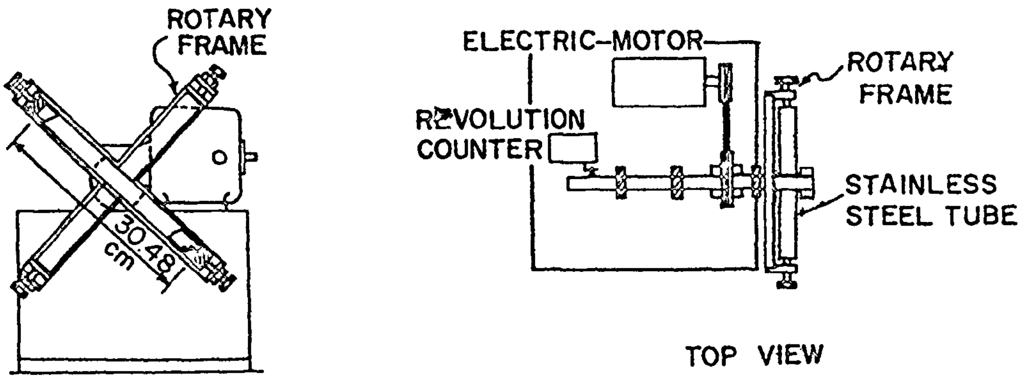


Figure 2.4: Tumbling machine.

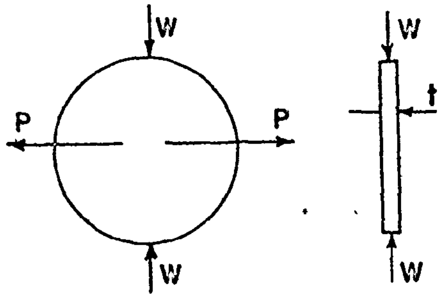


Figure 2.5: Disk under compressive load.

P(Newton/mm^2) is given by

$$P = \frac{2W}{\pi Dt} \qquad (2\text{-}12)$$

where D and t are the diameter and the thickness of the disk in millimeters. At the point of brittle fracture of the disk, P gives the tensile strength (22,23).

2.6 Behaviour of Coke in the Iron Blast Furnace

Coke plays five roles in the blast furnace (24):

1) It provides heat for the endothermic reactions and the melting of slag and metal.
2) It produces and regenerates the gases for the reduction of iron oxides.
3) It provides a permeable bed for the circulation of slag, metal and gases; coke occupies about half of the volume of the blast furnace.
4) It carbonizes the pig iron.
5) It is a dust filter and stores, for example, the soot produced by the incomplete burning of the injected oil.

Properties of coke such as size, strength and bulk density influence the gas flow and therefore the coke consumption.

The most important reactions taking place in the iron blast furnace are:

a) Indirect Reduction:

$$FeO + CO = Fe + CO_2$$

$$Fe_3O_4 + CO = 3FeO + CO_2$$

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$$

$3Fe + 2CO = Fe_3C + CO_2$ (Carburizing)

b) Direct Reduction: $CO_2 + C = 2CO$

$FeO + CO = Fe + CO_2$

$3Fe + C = Fe_3C$ (Carburizing)

At the tuyere level (2000-3000°C) the combustion of coke takes place:

$$C + O_2 \rightarrow CO_2$$

and followed by $CO_2 + C \rightarrow 2CO$

2.7 The Role of Inert additions

2.7.1 Properties of Canadian Coals

In general, Western Canadian coals are high in ash and low in sulphur; most of them have acceptable levels of alkali and phosphorous. Conversely, Eastern Canadian coals are very low in ash and high in sulphur; the phosphorous and alkali levels are also low.

Western Canadian coals generally exhibit poor rheological properties; they have low Gieseler fluidity and FSI and negative Ruhr dilatation. Devco which is an Eastern Canadian coal has excellent rheological properties (25). A good blend for producing a coke of acceptable qualities has the following composition: i) low volatile coal 15-25%; ii) medium-volatile coal 30-35%; iii) high volatile coal: the balance. There are two kinds of inert materials in a coal: a) organic, which are the carbonaceous constituents that do not become plastic, and b) inorganic or mineral matter. Anti-fissurants are defined as inert, non-caking, carbonaceous materials which are added to coke oven blends to:

1) reduce coke shrinkage rates. (Consequently, fissuring during carbonization is reduced so coke strength will be higher); 2) change the balance index for the blend since the ratio reactive/inert is modified. This effect will alter the microstructure of the coke. Table 2.8 shows the most important carbonaceous materials used as anti-fissurants:

TABLE 2.8 (26)

Carbonaceous anti-fissurants investigated.

1. Coke fines
2. Chars : non-coking coals
3. Coke fines + Char
4. Anthracites
5. Petroleum Coke
6. Blast Furnace Flue Dust
7. Rubber tires
8. Low and Medium Volatile Coals.

2.7.2 Fissuration Mechanism

Fissuring is influenced by a wide variety of factors and the entire sequence of events is still far from fully understood. No correlation has yet been established between the solid-state processes that take place in the developing coke and its degree of fissuring.

There is experimental proof that fissures develop in the solidified material and not in the plastic mass. Shrinkage is the cause of fissuring. Muchnik (27) has investigated the shrinkage dynamics in thin beds of coal during the carbonization process. The most important conclusions from his work are as follows: 1) Fissures develop in a semicoke layer between 530°C (start of shrinkage) and 620°C (first peak in a curve showing shrinkage rate). 2) Longitudinal fissures are formed.

by the same mechanism. 3) "Fissuring is brought about by the stresses set up as shrinkage is obstructed as a result of occurring at different rates at different temperatures". 4) Fissures develop where the stresses exceed the strength of the formation layer.

Figure 2.6 shows the contraction and rate of contraction of a high-volatile coal (26). The rate of contraction can be expressed as:

$$\alpha = \frac{1}{\ell_0} \frac{d\ell}{d\theta} \qquad (2\text{-}13)$$

where ℓ_0 = length of sample at the solidification temperature

ℓ = length at temperature θ

$d\ell/d\theta$ = slope of the curve of contraction at temperature θ

The tendency to fissuration increases as the magnitude of variations for the curve of rate of contraction increases. Figure 2.7 shows the effect of blending coke fines on the coefficient of contraction of a high-volatile coke. Addition of coke fines reduces the two coefficient of contraction peaks; increasing the mean size and the strength of the final coke. From the list of materials in Table 2.8, coke fines (Breeze) is the most effective in minimizing those two peaks.

2.7.3 Effect on the Stability Factor

The most common and cheapest antifissurant is coke breeze. Its use has to meet certain conditions of grinding and concentration. The use of breeze and chars in the production of foundry coke is well established and documented mainly in Europe. Little work has been done on the use of antifissurants for the production of blast furnace coke.

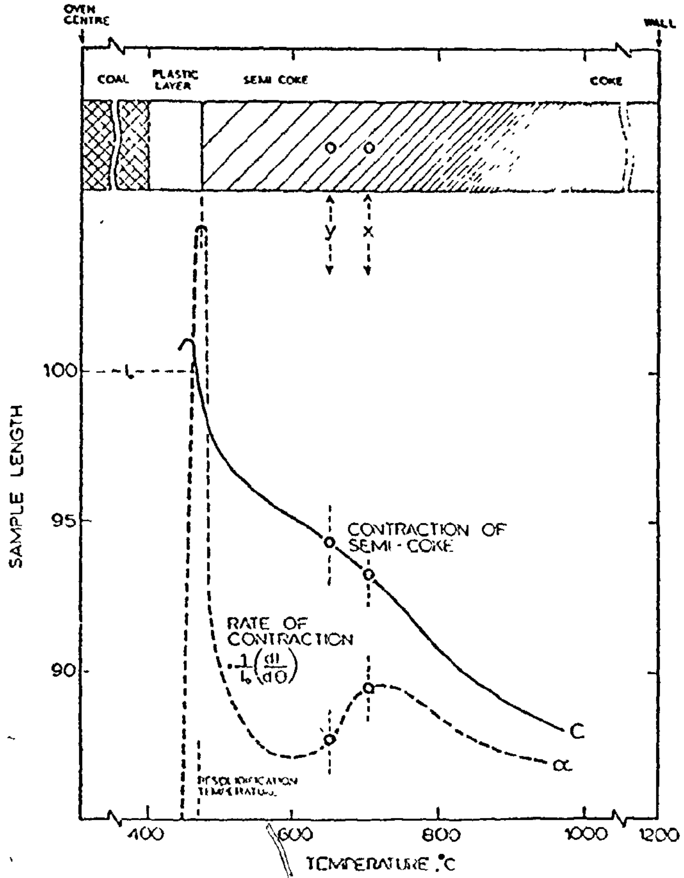


Figure 2.6: Contraction and rate of contraction of a high volatile coal. (Ref.26)

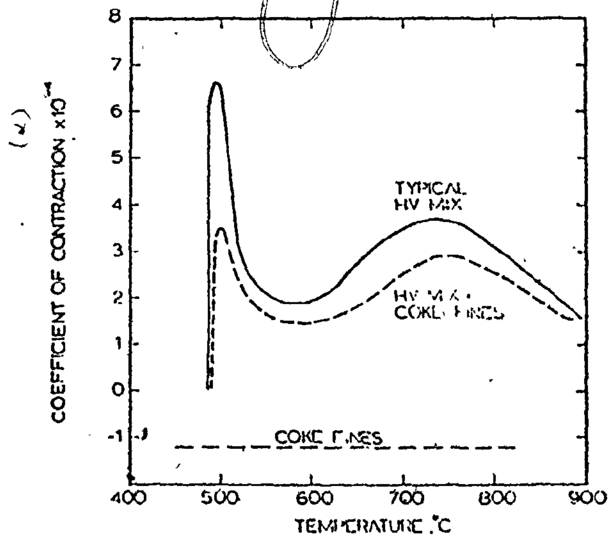


Figure 2.7: Influence of coke fine additions on the coefficient of contraction of a high volatile coal. (Ref.26).

Reeve and Paulencu (26) studied the effect of the addition of coke fines (minus 16,35,60 and 100 mesh) in blends prepared from eight different coals. They found that coke fines passing 6o mesh can be used to reduce the amount of low-volatile coals. Four to seven percent of breeze will not affect coke stability. Addition of minus 35 mesh maintained coke stability but reduced coke hardness.

Chars are produced by heating coals until the temperature ranges between 450 and 700°C in the absence of air. This low temperature carbonization is used mainly in Europe to give large yield of tar, a gas with a gross heating value of about 26000 kJ/m^3 (gross heating value for coke oven gas is about 20500 kJ/m^3) and a solid product, char or semicoke. Early in the nineteenth century, low temperature carbonization began to be developed.

Low temperature char has several applications. The first one is for domestic or industrial fuel. The second important use of chars is in blends for producing blast furnace coke. Wilson and Clendenin(28) listed some desirable characteristics of the char: 1) amount (less than 20%), 2) volatile content should preferably be between 15 and 20%, and 3) physical properties, especially surface condition. Reed and coworkers (28) found that the quality of the high volatile coal used for blending was of great importance but the percentage of char and the uniformity of its volatile matter content in the range studied were not critical.

After World War II Japanese investigators blended char to high volatile coals to produce good metallurgical coke (85 drum index value).

Char production is the first step in the manufacture of briquettes or formed coke. Price and Woody (29) reported the results of experiments carried out at Colorado Fuel and Iron Corporation. They produced char from a high volatile coal for substituting the low volatile coal in a blend. The most important information from the paper is that the strength of blends using char was higher than the one for blends using other additives (coke breeze and petroleum coke). Two variables were observed having importance in the coke strength: volatile matter and amount of char. The mechanism was not understood; even Price suggested that there was not wetting of the breeze particle by the plastic material as it occurred with the char particle. The paper written in 1944 showed the economic advantages of replacing low volatile coals for chars in regions where only high volatile coals are at hand.

Ignasiak and Berkowitz (30) have studied the behaviour of Western Canadian cretaceous coals and found that their petrographic composition did not afford a reliable basis for predicting coke stability. For carboniferous Eastern American and European coals, the correlations developed by Schapiro, Gray and Eusner have proved fairly successful. Ignasiak and Berkowitz blended a West Virginia high volatile coal (FSI 8, 18400 dd/m) with chars produced at different temperatures from a high volatile coal from Pennsulvania (FSI 2, 24 dd/m) and a low volatile coal from Alberta (FSI 6, 10 dd/m). For both cases they found that the optimum charring temperature was about 600°C for the first blend and 500°C for the second. At those temperatures the strength index increased. Beyond those temperatures the index declined because of the excessive differences in the coefficients of thermal contraction of the blend components. They also related the strength of indices of cokes from these binary blends to the concentrations of oxygen-bearing functional groups (-OH and =CO) in either or both blend components.

In a second paper (31), Ignasiak et al. found that "coke strength is more closely dependent on the distribution of 'reactive' oxygen in the parent coals than on their proximate, elemental or petrographic composition." They suggested that it was possible to qualitatively predict coke strength from information about reactive oxygen. A non-caking high volatile coal was freed of reactive oxygen by charring at different temperatures. Blending to other coal produced a strong coke; its strength may be further improved by modifying the size distribution of the semicoke and the rate at which it is charred.

2.7.4 Effect on the tensile strength

The Coke Research Report 31 by the British Coke Research Association (22) presented a complete study on the estimation of the tensile strength of coke (and how it is affected by different variables) for two British coals. Some conclusions of this study were:

1) The tensile strength of the carbonized product increased progressively with increasing carbonization temperature.
2) The effect of the heating rate was different for the two coals. In one case the tensile strength was higher at a higher heating rate; in the second case it was higher at a lower heating rate.

3) There is a general tendency for the tensile strength to increase with increasing apparent density of the specimen, which varies according to the position relative to the wall). The relationship was specific to each series of samples.
4) For a specific sample the carbonization temperature has a large effect on the apparent density, but the change of porosity is relatively small.

From the Report 65 by the British Coke Research Association(32) and Reference (33), one important conclusion is drawn; there is no direct correlation between the tensile strength of blast furnace cokes and micum strength indices, including non-standard indices.

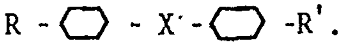
Patrick and Stacey (34) found that there is a dependence of the coke strength on the total porosity, the characteristic pore size as determined by mercury porosimetry and on the average thickness of the pore walls, but it is not possible to establish a correlation between the tensile strength of cokes in general and any of these parameters or various combinations of them. The nature of the carbon material forming the pore walls could be the key in explaining these observations.

The same investigators (35) prepared blends of two British coals (NCB class 501 and 401) with different amounts of breeze in the range from 10 to 18% by weight, which was ground at three different particle sizes. They found that breeze additions caused changes in the coke tensile strength in a non-systematic way and that decreasing the breeze particle size increased the tensile strength. These variations could not be related to changes observed in density, porosity, pore-wall thickness or mean pore size of the cokes. It was not possible to relate the tensile strength with the results of micum indices. Addition of 10% breeze produced the highest coke tensile strength. The carbonization was carried out in a 10-ton test oven in which the operating conditions were not very closely controlled. The same experiments were repeated (36) using a small-scale oven in order to obtain close control of the charge preparation and carbonization conditions. They found that increasing breeze content systematically reduced the tensile strength and that these changes correlated with variations in the apparent density and total porosity. The M10 micum index increased while M30 decreased when the breeze content was increased. Additions of petroleum-coke breeze (37) up to 50%, produced a coke with higher tensile strength than those manufactured blending breeze or silica sand. The addition of breeze was in the range 5-20%, while silica sand content was 5 and 15%.

2.8 Anisotropy of Coke

2.8.1 Basic Types and Structures of Liquid Crystals

'Liquid Crystals' is a term used to describe a state of matter intermediate between the solid crystalline and the ordinary (isotropic) liquid phases. Liquid crystals exhibit anisotropic properties as do solid crystals. They are also called mesophases or mesomorphic phases because of their intermediate nature. Several thousands of organic compounds form liquid crystals when the solid crystals are heated above their melting point.

Friedel proposed a classification of three basic types of liquid crystal; smectic, nematic and cholesteric. These mesophases differ in the orientational order of the long molecular axis; Figure 2.8 shows a schematic representation of the three types. Nematic liquid crystals differ from ordinary liquids by a long range orientational order of the long molecular axes which, averaged over time or space, are aligned parallel to a preferred direction $\vec{L}$. Mesomorphic behaviour is found in compounds with elongated molecules which, in most cases, consist of a conjugated aromatic system; many compounds forming nematic liquid crystals have the simple structure . Meir et al. in Application of Liquid Crystals (38) listed the most important groups X linking the two substituted phenyl rings; R and R' are small groups or rather short chains. Under the microscope using cross polars, the nematic type has a thread like appearance while the soap like is proper for the smetic type. The nematic mesophase may be distinguished from others in the way it separates from the isotropic liquid as spherical droplets, which eventually coalesce to give a nematic texture. These droplets are themselves anisotropic. Within the nematic phase there are a number of domains which possess the molecular orientation of Fig. 2.8, each domain having a different optical axial direction. Carbonization of coal produces a nematic system of liquid crystals. There are three important physical properties of this system which are relevant in carbonization: a) within domains, the orientational direction of the molecules is influenced significantly by surfaces of containing vessels or internal surfaces within the system; b) molecules which form nematic liquid crystals usually possess features of common geometry; and c) it is now recognized that limited additions of a solute that does not form liquid crystals can be accommodated by the liquid crystal structure(48).

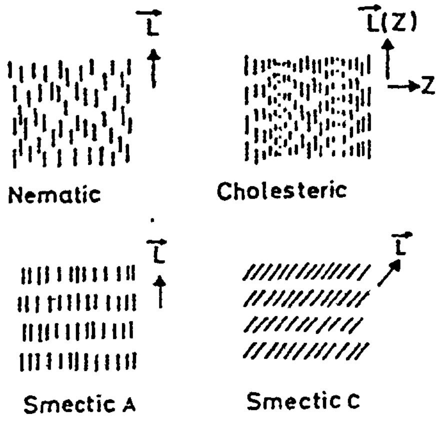


Figure 2.8: Structures of liquid crystals

2.8.2 Liquid Crystals and the Optical Anisotropy of Coke.

Ramdohr discovered in 1928 that coke may be optically isotropic or anisotropic in polarized light. Isotropic cokes are distinguished by higher reactivity; anisotropic cokes are less reactive, but are more easily graphitized (39). Under the microscope the isotropic coke, which has similar properties in all directions, showed a characteristic uniform colour. The anisotropic regions have optical properties varying according to the direction of light transmission at the surface, and show colours or tints which change when the analizer is rotated. Mackowsky and other investigators have confirmed the optical heterogeneity of coke.

The size and intensity of the anisotropic regions vary with the rank of the parent coal. The lower the plasticity of the softened coal, the lower also the degree of orientation of the aromatic nuclei; inversely, the higher the plasticity of the coal, the larger the zones of anisotropy. It has been established that variations in the rate of heating and soaking time at the final carbonization temperature have little influence on the anisotropy developed in high temperature cokes (40-44). Goodarzi and Murchison (45) studied the effect of increasing the heating rate from 1 to 60°C/min on six British vitrinites. The changes in anisotropism depends basically on the rank of the vitrinite.

In the isotropic liquid there are some nucleation points where the liquid crystals start to form. These structures grow by the diffusion in the isotropic liquid of newly-formed lamellar molecules, which then stack parallel to similar molecules.

The development of the liquid crystals in pitch was observed by many investigators. Brooks and Taylor (46) confirmed that spherical bodies were formed mainly in regions adjacent to insoluble particles which are not incorporated within the sphere but aggregate around the surface, impeding the symmetrical growth of the mesophase. The spheres can coalesce to give the anisotropic mosaic structure observed under the microscope.

Marsh and other investigators also studied the formation of the mesophase in pitch, some pure compounds, and two British and twelve American coals, in a pressurized system (200 MN/m^2). In some coal samples it was possible to observe relatively large spheres (5-10 μm), but in the most of the samples presenting anisotropism, this was of the fine grain mosaic type (47-51). Patrick et al.(52) studied the same phenomena at normal pressure and concluded that British coals form mosaic anisotropy without development of the spherical bodies observed in carbonization of pitch. Taylor (52) and Ihnatowicz had observed these spherical bodies in semicokes produced from Australian and French coals respectively.

CHAPTER 3

EXPERIMENTAL WORK

3.1 Introduction

Three coals were selected taking into consideration their properties. This work was divided into two parts. The first part deals with the effect of four variables on the mechanical strength of coke produced from one high volatile and high fluidity coal (Devco) to which three different inerts were added. In the second part, the effect of three variables on coke strength using three high volatile coals with different coking characteristics was analized.

After choosing the most suitable variables to be studied a statistical design of the experiment gave a better interpretation of the results.

3.2 Experimental Design

3.2.1 Selection of the Most Important Variables

The five most important variables in the process are the following: a) heating rate, b) grinding, c) amount of the inert added to the coal, d) nature of the coal, and e) nature of the inert. The final temperature and the bulk density were kept constant: 1000°C and 0.82 g/cm^3 (air-dried basis), respectively.

a) Heating Rate: An increase in the heating rate in the 0.5 to 10°C/min range produces several changes, namely: the softening point is slightly higher and the resolidification point shows a very definite increase; the broadening of the plastic range is the final result. According to Boyer (54), increasing the heating rate from 2 to 3°C/min increases the resolidification point from 12 to 14°C for medium volatile and from 15 to 20°C for high-volatile coals. Swelling and plasticity show an increase depending on the nature of the coal.

There is a correlation between the viscosity of the coal in its softened state and the size of the zones of optical anisotropy. For a given rank of coal, the degree of softening can be influenced by the heating rate during the carbonization. A sharp reduction to 0.5-1.0°C/min increases the viscosity and reduces the size of the zones of anisotropy and sometimes can result in isotropy (55).

Two levels of heating rate were chosen: 1.5 and 3°C/min. These two values were selected considering the limitations of the equipment. It was observed that at temperatures over 600°C, a steady heating rate greater than 3°C/min was not possible.

b) Particle Size: The coal had to be ground finely in order to obtain a representative sample for small scale equipment. The size distribution was kept constant. Very fine grinding of coal reduces its plastic properties (free swelling and plasticity), and the porosity of the coke also decreases. Although the quantity of gas released per unit volume and per unit time remains constant, the diffusion path becomes shorter, and the pressure gradient between the centre of the grain and the outer surface diminishes. Mackowsky and Wolff (56) studied these effects using single grains ranging from 5 to 0.2 mm.

The size distribution selected for the coal (100% passing the 0.3 mm sieve - the complete sieve analysis will be given later) is similar to the one used in the international standard ISO 502-1974$_{(E)}$ for determination of the caking power using the Gray-King coke test (57). (100% passing the 0.2 mm sieve), the ASTM Test Method for Free Swelling Index of coal (58) (100% passing a 0.25 mm sieve) and the ASTM standard for determination of plastic properties of coal by the Gieseler plastometer (59) (100% passing the 0.425 mm sieve).

In a small scale test, it is very difficult to study the effect of the particle size of coal. In the project, the effect of the size distribution of the inert blended to the coal was studied. This inert also has to be ground finely to generate a representative and homogeneous sample. The two sizes selected were as follows: a) 100% passing the 0.3 mm sieve and retained on the 0.125 mm sieve (mean particle size 0.20 mm), and b) 100% passing the 0.18 mm and retained on the 0.075 mm sieve (mean particle size 0.108 mm).

c) <u>Amount of additive</u>: It has been established (26) that additions up to 7% coke breeze could substitute some of the low volatile coal in blends; low temperature char could be added in proportions of 15 to 20% (28). The two levels selected were 10 and 20 percent.

d) <u>Nature of the coal</u>: The plastic properties vary considerably from one coal to another. The majority of the systems of coal classification, particularly the international classification, have adopted an index characteristic of the plastic properties and the volatile matter content.

Three coals were studied: (1) Devco and (2) Chisholm, which have similar volatile matter content and plastic properties but different coking characteristics, and (3) Madison which has poorest caking and coking properties. All the information about chemical and petrographic analysis for these coals are given in the Appendix B, as reported by Stelco.

e) Nature of the inert : Three types of organic inerts were added: (a) Devco semicoke produced at 500°C, (b) low temperature Devco coke produced at 700°C, and (c) crushed coke from Stelco which can be called coke breeze.

The properties of the inert considered in this study were microhardness, volatile matter (which directly affects the total contraction), the true specific gravity, and the mineral matter (60).

3.2.2 Statistical Design of the Experiments

3.2.2.1 Carbonization of Devco coal

The experiments were planned using a full factorial design with three variables at two levels, and one at three levels (the type of additive), that is, a 2 × 2 × 2 × 3 design. The variables were coded using the relation:

$$x = \frac{\text{Variable - Centre Point}}{\text{Range/2}}$$

a) Heating Rate: HR = Uncoded: 1.5°C/min, 3°C/min
Coded: -1 , +1
Centre point: (1.5 + 3)/2 = 2.25 Range/2: (3 - 1.5)/2 = 0.75

b) Mean size of inert: MS = Uncoded: 0.108 mm , 0.20 mm
Coded: -1 , +1
Centre point: 0.154; Range/2 = 0.046.

c) Amount of inert added: AI = Uncoded: 10% , 20%
Coded: -1 , +1
Centre point: 15%; Range/2 = 5

d) Type of inert: Uncoded: Devco semicoke (500°C)
Low temperature Devco coke (700°C)
Breeze

The dependent variable was the microstrength index (MSI). After the full factorial design was run, it was observed that, in the range studied, there is a relationship between MSI and the function:

$$F = \ln \left(\frac{A \times TD \times MH}{VM}\right)$$

where A = ash content of the inert
TD = true specific gravity of the inert
MH = microhardness of the inert
VM = volatile matter of the inert

Other functions were tested, but the one above gave the best correlation. The values of this function were used to define the type of inert used.

	Uncoded	Coded
Devco S.C. (500°C)	F = 3.558	-1
Low temp. Devco coke (700°C)	F = 4.978	-0.251
Breeze	F = 7.350	+1

Centre point = 5.494; Range/2 = 1.896

As an example, the coded variable for low temperature Devco coke - 700°C was calculated as follows:

$$x = \frac{4.978 - 5.494}{1.896} = -\,0.251$$

The general linear model for a 2 × 2 × 2 × 3 design is:

$$\begin{aligned} \mathrm{MSI}:&\beta_0+\beta_1x_1+\beta_2x_2 + \beta_3x_3 + \beta_4x_4 + \beta_5x_1x_2 + \beta_6x_1x_3 + \beta_7x_1x_4 + \beta_8x_2x_3 \\ &+ \beta_9x_2x_4 + \beta_{10}x_3x_4 + \beta_{11}x_1x_2x_3 + \beta_{12}x_1x_2x_4 + \beta_{13}x_1x_3x_4 + \beta_{14}x_2x_3x_4 \\ &+ \beta_{15}x_4^2 + \beta_{16}x_1x_4^2 + \beta_{17}x_2x_4^2 + \beta_{18}x_3x_4^2 + \beta_{19}x_1x_2x_4^2 + \beta_{20}x_1x_3x_4^2 \\ &+ \beta_{21}x_2x_3x_4^2 + \beta_{22}x_1x_2x_3x_4^2 + \beta_{23}x_1x_2x_3x_4 + \varepsilon \end{aligned} \qquad (3\text{-}1)$$

where: $\beta_0, \ldots ,\beta_{23}$ are the parameters

x_1, x_2, x_3, x_4 are the variables studied:
1) heating rate
2) size
3) amount
4) type of inert added.

Twenty four experiments and eight replicas were carried out.

3.2.2.2 Design using three coals

An additional study was performed using three coals with different properties (see Appendix B). From the analysis of the results for Devco coal it was concluded that the heating rate in the range 1.5 -

3°C/min was not a significant variable. The effects of heating rates on different types of coal (under different experimental conditions) have been reported. It was thought that changes would be apparent during the coking of coals of different caking capacity. Because of the time limitation, the number of variables studies were reduced and a $2 \times 3 \times 3$ full factorial design was chosen. The coded variables selected were:

a) Heating Rate: Uncoded: 1.5°C/min, 3°C/min

Coded: -1 +1

Centre point = 2.25, Range/2 = 0.75

b) Type of inert:

	Uncoded	Coded
Devo Semicoke (500°C)	F = 3.558	-1
Low temp. Devco coke (700°C)	F = 4.978	-0.251
Breeze	F = 7.350	+1

c) Type of coal:

The analysis of the values taken from the isostability chart by U. S. Steel (Fig.2.3) showed that at a strength index (SI) between 2.5 and 5, and a composition balance index (CBI) between 1 and 2, the petrographic stability index (St) could be calculated using the following expression.

$$St = (8.774\ \ell n\ SI - 25.306)\ CBI + 58.563\ \ell n\ SI - 15.194 \qquad \ldots (3\text{-}2)$$

Since the strength and composition balance indices depend on the particular coal or blend, their effect on the MSI should follow the same type of relationship as stated above. The effects due to heat distribution or heating surfaces for different ovens are not considered here. The dependency of MSI on the SI and CBI values, can be expressed as:

MSI = Function (SI, CBI, operational parameters)

Let us call $G = (8.774\ \ln SI - 25.306)\ CBI + 58.563\ \ln SI \quad (3\text{-}3)$

The value of G was used as the variable describing the type of coal blended. Appendix D shows the derivation of this function: Appendix C shows the method used to calculate the Strength Index and the composition balance index.

Coal	Uncoded	Coded
Madison	G = 57.87	1
Devco	G = 50.30	-0.0647
Chisholm	G = 43.65	-1

Center point = 50.76, Range/2 = 7.11

The general linear model to fit a 2 × 3 × 3 design is

$$\begin{aligned} MSI = {} & \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1 x_2 + \beta_5 x_1 x_3 \\ & + \beta_6 x_2 x_3 + \beta_7 x_1 x_2 x_3 + \beta_8 x_2^2 + \beta_9 x_3^2 + \beta_{10} x_1 x_2^2 \\ & + \beta_{11} x_1 x_3^2 + \beta_{12} x_2 x_3^2 + \beta_{13} x_2^2 x_3 + \beta_{14} x_2^2 x_3^2 + \beta_{15} x_1 x_2^2 x_3 \\ & + \beta_{16} x_1 x_2 x_3^2 + \beta_{17} x_1 x_2^2 x_3^2 + \varepsilon \end{aligned} \quad (3\text{-}4)$$

where $\beta_0, \ldots, \beta_{13}$ are the parameters of the model

x_1, x_2, x_3 are the variables studied:
(1) heating rate
(2) type of coal
(3) type of inert

The amount of the inert blended to the coal was 10%, its mean size was 0.20 mm, and the bulk density was 0.82 g/cm^3; these values were kept constant in the design. Eighteen experiments and nine replicas were conducted.

3.3 Experimental Technique

3.3.1 Description of the equipment

Figure 3.1 shows a schematic representation of the equipment used for the carbonization of the samples. The three zone Marshall furnace was built by Norton (Model 1127) and uses 110 volts per zone. The maximum temperature that can be reached is 1200°C. The power in each zone can be adjusted independently allowing the temperature profile to change. At a final temperature of 1000 °C and with the knobs in the positions - 60 for zone 1, 50 for zone 2 and 60 for zone 3, data was obtained which was used to plot the temperature profile shown in Figure 3.3. The furnace was placed in a vertical position and the crucible (which is approximately 26.7 cm long) was placed in the hot zone which was about ±18°C from the set point within a range of 28 cm. The temperature was controlled using a Model 32600-00-025 Program Controller manufactured by Thermo Electric. The automatic proportional "on-off" controller was provided with a programmer which allowed complete control of the heating rate from 6 up to 600°C/hour. The thermocouple used was made of chromel alumel. The temperatures, both above and below the crucible containing the sample, were measured using a Model 199 Omega digital temperature indicator.

The coal sample was placed in a stainless steel crucible which consisted of a tube with two threaded caps, one of which was provided

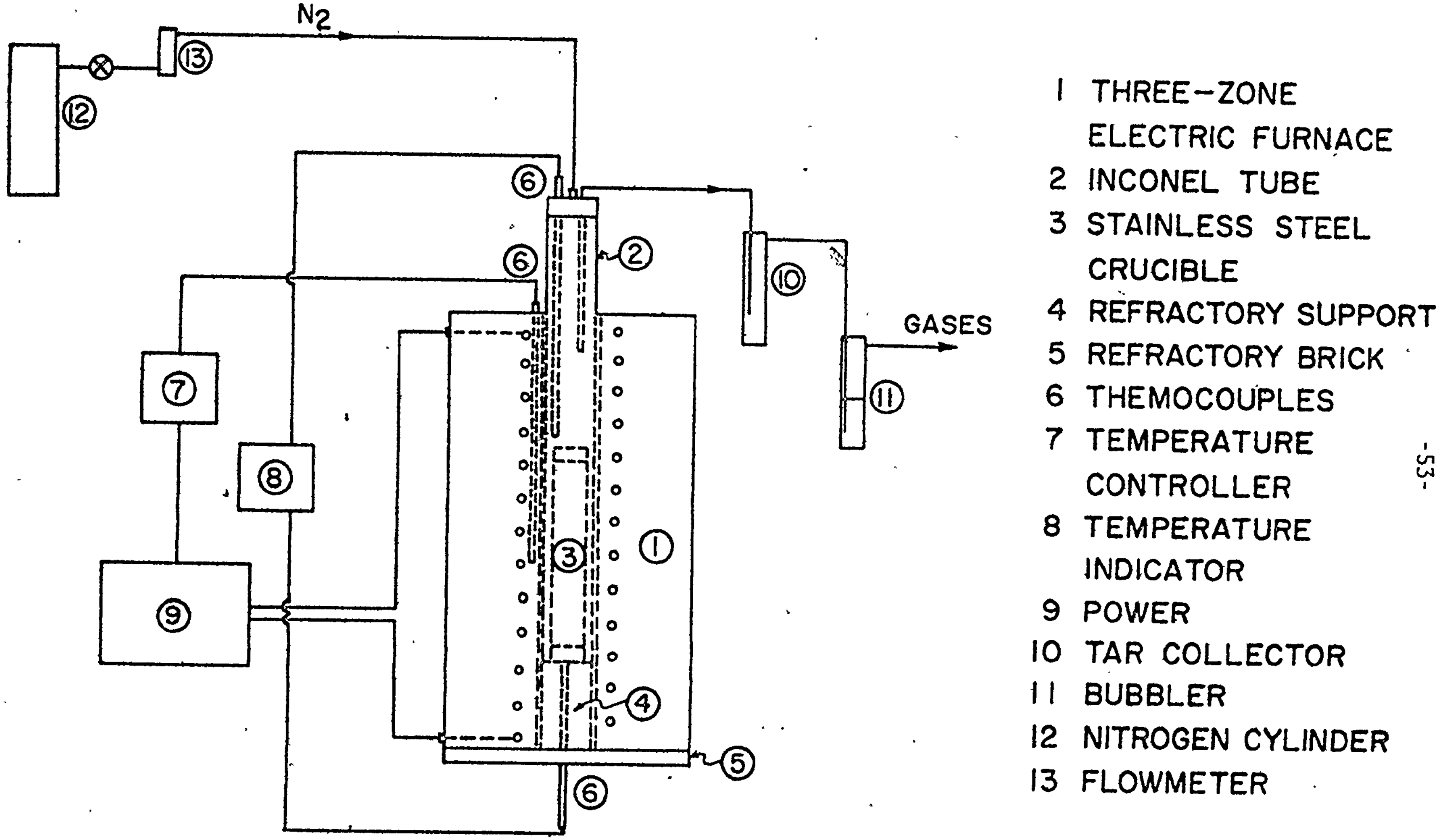


Figure 3.1: Schematic representation of the equipment.

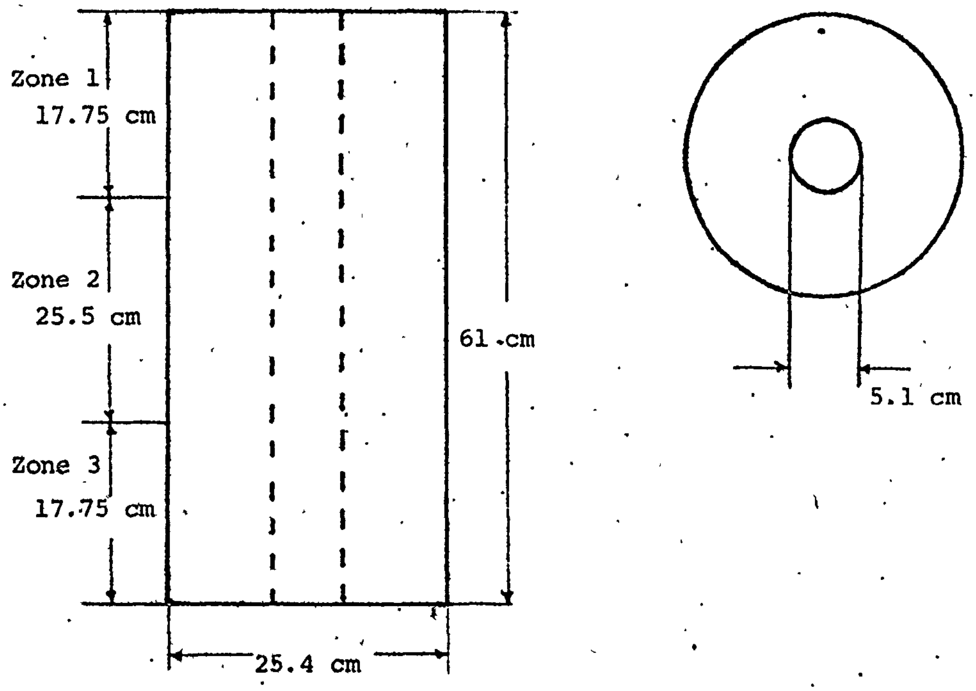


Figure 3.2: The three-zone furnace.

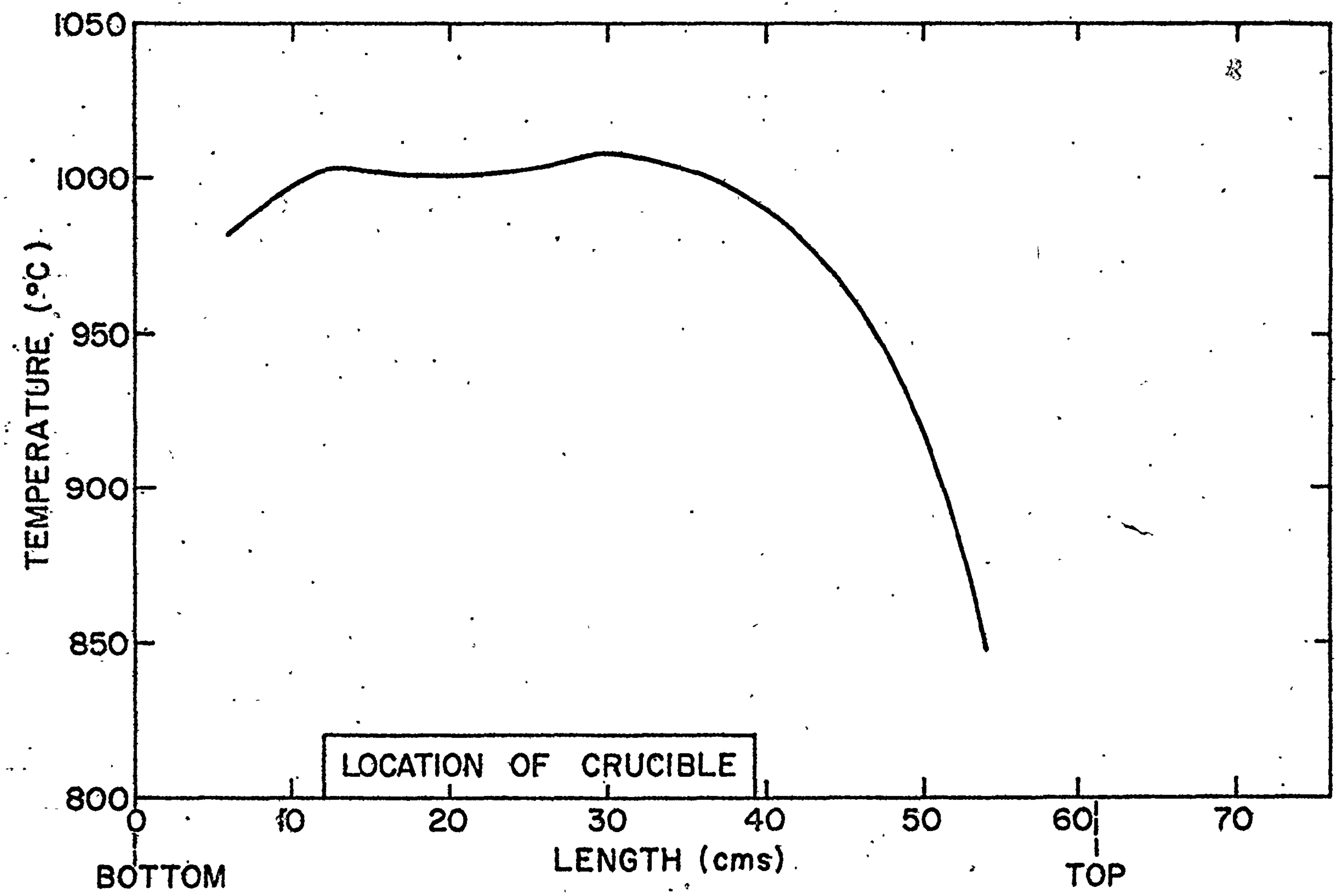


Figure 3.3: Temperature profile of the furnace

with four small holes for the exit of the gases. Three-fold sections of mesh 140 (0.106 mm) were used as a membrane between the coal and the holes, in order to prevent the flow of the viscous material out of the crucible. Figure 3.4 shows the dimensions of the crucible. The crucible was placed in an inconel tube closed at one end; a threaded cap at the other end was provided with an entrance for nitrogen, an exit for the gases, and one insulating tube for the thermocouple which was located in the inconel tube just above the crucible. Figure 3.5 shows the details of this assembly. A small cylinder of insulating material was placed inside the tube at the top of the furnace in order to reduce the losses by radiation.

3.3.2 Experimental Procedure

3.3.2.1 Coal preparation

The coals studied were obtained in plastic bags from the Steel Company of Canada. The total amount of each type of coal was divided and placed in several smaller plastic bags which were sealed and kept in a freezer.

Fractions of about 400 grams of coal were crushed and ground using a crusher and grinder respectively. The particles retained on mesh 50 (0.3 mm) were separated and ground again; this step was repeated until all the material passed through the above mesh number. An average sieve analysis of Devco coal which was ground in this way is as follows:

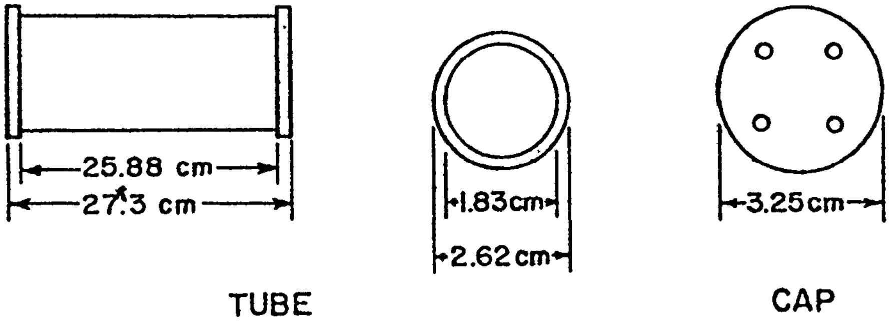


Figure 3.4: Stainless steel crucible

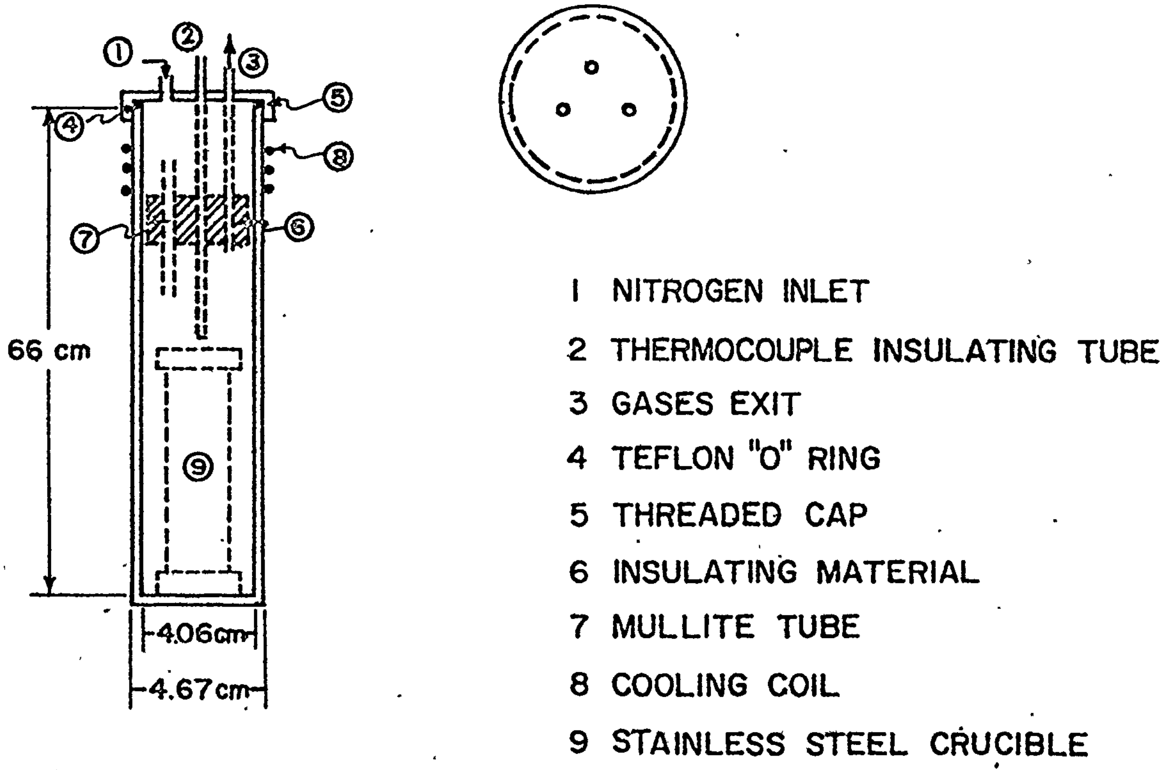


Figure 3.5: Details of the working tube

Sieve Size Mesh number	Coal retained on Sieve (Cumulative percentage)
50	0
80	56.9
100	65.3
120	76.1
140	82.6
200	95.4
Bottom	100.00

The total material was mixed thoroughly for 30 minutes using a V-blender and placed in bottles which were kept in a freezer to avoid oxidation. The volume of the crucible was 68.07 cm^3. The moisture content of the coals removed from the freezer was as follows: Madison 3%, Chisholm and Devco 1.9%. The coal and inert were dried for one hour by placing the sample in a thin layer so that the moisture content was approximately in equilibrium with the laboratory atmosphere. The sample dried in this way had a moisture content less than 1.5%.

Fifty-six grams of coal or blend were placed in the crucible; the bulk density was 0.82 g/cm^3 with a moisture content of less than 1.5%. The grinding of breeze was carried out using the same equipment as the one used for the grinding of coal. The semicoke and low temperature coke were ground using the crusher and a mortar. About fifteen runs for each of these inerts were carried out in order to prepare enough material for preparing the different blends. The products of the fifteen runs were mixed and ground as described above. The screened material was divided into two fractions having the following distribution:

TABLE 3.1

Size Distribution of the Inert

Fraction 1:

Mesh	Diameter mm	$\bar{d}$	Fraction retained on sieve (x)	Cumulative percentage
50	0.3	-	0	0
70	0.212	0.256	0.5	50
80	0.18	0.196	0.3	80
120	0.125	0.153	0.2	100

The mean volume diameter (d_v) was calculated using equation (3-5)

$$d_v = \frac{1}{\sqrt[3]{\sum \frac{x}{\bar{d}^3}}} \qquad (3\text{-}5)$$

$$d_v = 0.20 \text{ mm}$$

Fraction 2:

Mesh	Diameter mm	$\bar{d}$	Fraction retained on sieve (x)	Cumulative percentage
80	0.18	-	0	0
100	0.15	0.165	0.1	10
140	0.106	0.128	0.5	60
200	0.075	0.091	0.4	100

$$d_v = 0.108 \text{ mm} .$$

Blends were prepared by mixing the coal with the appropriate amount of inert (also previously air dried) in a V-blender for twenty minutes.

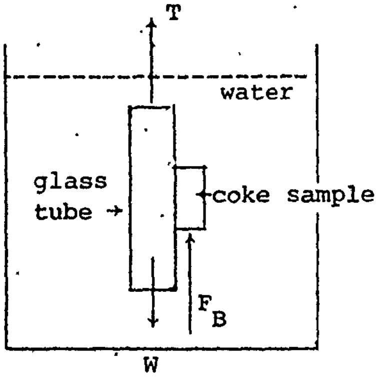
3.3.2.2 Carbonization procedure

The crucible containng the coal or blend was closed by screwing the top cap, together with the 'membrane' and placing it in the inconel tube. After closing, nitrogen was flushed at the rate of 0.40 cm^3/sec.

The heating rate (1.5°C/min or 3°C/min) and the maximum temperature (1000°C) were set in the program controller, and the furnace was turned on. After reaching the final temperature the sample was held for a soaking time of 45 minutes before the power was shut down. The system was allowed to cool down freely until it reached room temperature (about 15 hours). Semicoke and low temperature coke were produced from Devco coal following the same procedure, but the samples were carbonized at final temperatures of 500 and 700°C respectively, using a heating rate of 3°C/min.

3.3.2.3 Assessment of the apparent specific gravity

The apparent specific gravity was calculated by weighing the dried coke sample in air and in distilled water (in this case the sample remained in the water 1 min. before taking the reading). Since in many samples the density was smaller than 1 g/cm³, it was necessary to attach the coke to a small tube of glass to increase the total weight. Figure 3.6 shows a free body diagram for the determination.



T = Weight of coke sample, wire and small glass tube in water.

W = Weight of coke sample, wire and small glass tube in air.

F_{B_c} = Buoyant force due to coke.

F_{B_g} = Buoyant force due to glass and wire.

F_B = Total buoyant force

Figure 3.6

$$F_B = F_{B_c} + F_{g_c} \qquad (3\text{-}6)$$

$$W = T + F_B \qquad (3\text{-}7)$$

The specific gravity (at 20°C) for the coke was calculated using the relation

$$\text{Apparent Specific Gravity} = \frac{\text{Weight of coke sample}}{F_{B_C}} \qquad (3\text{-}8)$$

F_{B_C} = Weight of a volume of water equal to the volume of the coke sample.

The shapes of the samples after carbonization were rods approximately 1.5 cm in diameter and varied in length. Discs free of fissures and cracks were cut using a diamond wheel; their thickness was about 0.6 cm. The apparent specific gravity was determined for each disc and for some of the other small pieces such that the total weight was at least 65% of the total coke produced in that run. The average apparent specific gravity (A.S.G) was calculated by prorating these individual values.

3.3.2.4 Assessment of the Mechanical Properties

3.3.2.4.1 Compressive Test

The discs previously used in the density determination were dried at 105°C and allowed to cool. Only the material free of cracks and fissures was chosen for this test. Every disc was measured carefully and tested for compression in an Instron machine. The discs were approximately 1.5 cm in diameter and 0.6 cm thick. The cross-head speed was 0.1 in/min (0.254 cm/min). The load applied was registered on a chart and the tensile strength was calculated using the equation (2-12), as explained in Section 2.5.2.3.

3.3.2.4.2 Microstrength index

The broken specimens from the compression test were mixed with the other fraction of the coke. After selecting several small pieces for microscopic examination, the material was crushed to pass through mesh 6 (3.35 mm) and ground to pass through mesh 16 (1.18 mm). In this study, the Canadian Sieve Standard classification was followed (square mesh). The sample was ground in the same tumbler machine used for the MSI test, but the tubes were closed with caps which had openings in them covered with a stainless steel screen mesh 16 (See section 2.5.2.2). Six steel balls (0.95 cm in diameter) were placed in each tube, together with one of the two fractions of the previously divided sample. The tumbling process took from 2000 to 4000 revolutions for 99% of the material to fall out of the tube. The coke was placed on a stack of sieves (mesh 16, 18, 20, 30 and bottom, Canadian Standard) and shaken for seven minutes in a Ro-tap Testing sieve shaker.

Four samples weighing 2 grams and having the size distribution shown in Table 3.2, were prepared for each experiment. The sampling was done using a splitter.

TABLE 3.2

Size distribution of the sample for MSI test

Mesh	Cumulative Percentage (on sieve)
16	0
18	30
20	65
30	100

The samples were placed in the tube of the tumbler machine described in Section 2.5.2.2. There were two tubes screwed to a frame which rotated at 24 r.p.m., allowing two samples to be tested simultaneously. The samples were tumbled for 800 revolutions, as shown in the counter. The coke was placed on the following stack of sieves:

Mesh	Size (mm)
30	0.6
35	0.5
45	0.355
50	0.30
70	0.212
120	0.125
200	0.075
Bottom	

The sieves were 7.62 cm diameter and 5.08 cm deep and were supplied by the Taylor Company of Canada.

After shaking the stack for seven minutes, the coke on each sieve was weighed carefully. The cumulative percentage of the sample retained on the mesh 70 is the microstrength index (MSI).

3.3.2.5 Assessment of the true specific gravity and porosity

The true specific gravity was found using a method similar to the ASTM standard 167-73 (61); the amount of coke handled made it necessary to change the specification. The fraction used in the MSI test was mixed with the rest of the coke and an eight gram sample was pulverized to pass mesh 200 (0.075 mm).

A fraction of 2.5 grams of coke which was previously dried for one hour at 105°C was placed into a specific gravity bottle (capacity 25 ml) with distilled water. The bottle was put on a hot plate and the contents were kept boiling for one hour. After this time the bottle was allowed to cool to room temperature and fresh distilled water was added to fill the bottle. The true specific gravity (TSG) was calculated using the expression in eq. (3-9)

$$\text{T.S.G.} = \frac{W}{[W - (W' - B)]} \qquad (3\text{-}9)$$

where: W = weight in grams of dry coke

W' = weight in grams of the bottle and the dry coke and water required to fill it

B = weight in grams of the bottle and the water required to fill it.

The porosity was calculated using the relationship:

$$\text{Porosity} = 100 - 100(\text{apparent sp.gr./true sp.gr.}) \qquad (3\text{-}10)$$

Every determination was duplicated and the value reported was the average of them.

3.3.2.6 Properties of the inert materials

A proximate analysis and microhardness measurements were done on the semicoke, low temperature coke, and coke breeze in order to characterize each of them.

3.3.2.6.1 Proximate Analysis

The following standards were followed in the determination of the proximate analysis of the inerts (63):

Assay	ASTM Standard
Moisture	D3173-73 (62)

Assay	ASTM Standard
Ash	D3174-73 (63)
Volatile Matter	D3175-73 (64)
Fixed Carbon	D3172-73 (65)

3.3.2.6.2 Microhardness

The microhardness was determined with a diamond pyramid using a Tukon tester (Vickers test). The samples were mounted in resin and polished to get a flat surface. In order to have a better view of the indentation, the samples were covered with a solution of indigo carmine and allowed to dry.

The load applied in every test was 100 grams and 100 readings were taken using two samples in each determination.

3.4 Microscopic analysis of coke

Three kind of samples were prepared for studies with the microscope:

a) Small pieces of coke were impregnated under vacuum with Epofix resin and polished using abrasive paper 200, 400 and 600 grit. Finally, the sample was polished with 0.3 micron alumina slurry. These samples were analyzed under the optical microscope and some photographs were taken using polarized light, a gypsum plate and a green filter.

b) Small pieces without polishing were analyzed under the scanning electron microscope (Cambridge Instrument Co.).

c) A sample was taken from the material already ground which passed through mesh 30, to prepare briquettes with the same resin used in (a). After polishing the samples with the method described above, they were used for counting the type of carbon present, by means of polarized light and crossed polar position.

The samples of coke analyzed were produced from Devco coal alone and Devco blended with a 10 percent addition of the three inerts studied; all the samples were carbonized at 3°C/min and the mean diameter of the inert was 0.20 mm. Three hundred readings were done on each sample using a magnification of 1260x. The types of carbon were divided into three groups: (a) Isotropic, (b) Mosaic (fine, medium and coarse grain), (c) Flow type. After counting the material on each corner and the centre point of a square field, the sample was displaced 0.2 mm; this process was repeated until 1000 counts were recorded. For each count, an area of 36 μm^2 was assessed.

CHAPTER 4

RESULTS

4.1 Introduction

The amount of coke produced in a run depends on the blend composition; the weight was found to be between 30 and 40 grams. The overall product was used for all the tests performed, following the sequence: apparent specific gravity, compressive test, microstrength index and true specific gravity.

4.2 Carbonization of Blends of Devco Coal

4.2.1 Apparent and true specific gravity and porosity of the cokes

The Apparent Specific Gravity (ASG) and True Specific Gravity (TSG) were determined as described in Chapter 3. The Porosity (P) was calculated using the equation (3-10).

TABLE 4.1

ASG, TSG and P of coke and semicoke from Devco coal

Devco Coke:	ASG	TSG	P
Heating Rate: 3°C/min	0.95	1.90	50.0
Heating Rate: 1.5°C/min	0.90	1.88	52.1
Devco Semicoke (500°C)	0.71	1.49	52.3
Devco Low Temp. Coke (700°C)	0.83	1.66	50.2

TABLE 4.2

Binary Blends - Apparent and True Specific Gravity of the Cokes.

Mean particle size of additive	0.200 mm				0.108 mm			
Heating rate	3°C/min		1.5°C/min		3°C/min		1.5°C/min	
Blend	ASG	TSG	ASG	TSG	ASG	TSG	ASG	TSG
Devco coal + 10% Devco S.C.(500°C)	0.89	1.94	0.86	1.88	0.88	1.88	0.90	1.92
Devco coal + 20% Devco S.C.(500°C)	0.92	1.92	0.95	1.94	0.94	2.00	0.91	1.89
Devco coal + 10% LT.Devco C(700°C)	0.93	1.95	0.90	1.97	0.91	1.95	0.90	1.93
Devco coal + 20% LT.Devco C(700°C)	0.94	1.95	0.92	1.98	0.96	1.90	0.90	1.91
Devco coal + 10% Coke breeze	0.95	1.91	0.90	1.98	0.92	1.90	0.93	1.95
Devco coal + 20% Coke breeze	0.95	1.98	0.94	1.99	0.97	1.72	0.96	1.93

TABLE 4.3

Binary Blends - Porosity of the Cokes

Mean Particle Size of Additive	0.200 mm		0.108 mm	
Heating Rate	3°C/m	1.5°C/m	3°C/m	1.5°C/m
Blend.				
Devco coal + 10% Devco SC(500°C)	54.1	54.5	53.2	53.3
Devco coal + 20% Devco SC(500°C)	52.1	51.0	53.0	51.7
Devco coal + 10%LT.Devco C(700°C)	52.3	54.3	53.1	53.4
Devco coal + 20%LT.Devco C(700°C)	51.8	53.5	49.5	52.9
Devco coal + 10% Coke breeze,	50.3	54.5	51.6	52.3
Devco coal + 20% Coke breeze	52.0	52.8	43.6	50.3

4.2.2 Tensile strength

The tensile strength was calculated using the equation (2-12) and is expressed in M Newton/m^2. The values presented in Tables 4.4 and 4.5 were obtained following the factorial design.

TABLE 4.4

Binary Blends - Tensile Strength of the Cokes

Mean Particle diameter of additive = 0.20 mm

Heating Rate	3°C/min			1.5°C/min		
	No.of Samples	Mean (MN/m^2)	Standard deviations	No.of Samples	Mean (MN/m^2)	Standard deviations
Blend:						
Devco + 10% Devco SC(500°C	13	5.04	1.20	7	4.39	1.75
Devco + 20% Devco SC(500°C)	10	4.40	1.05	9	5.31	0.87
Devco + 10% LT.Devco C.(700°C)	21	4.49	0.90	11	4.06	1.38
Devco + 20% LT.Devco C.(700°C)	7	2.62	0.71	6	2.24	0.49
Devco + 10% Coke breeze	47	3.40	0.75	5	1.74	0.12
Devco + 20% Coke breeze	9	1.03	0.20	2	0.67	0.07

TABLE 4.5

Binary Blends - Tensile Strength of the Cokes

Mean Particle diameter of additive 0.108 mm

Heating Rate	3°C/min			1.5°C/min		
	No.of Samples	Mean (MN/m^2)	Standard deviations	No.of Samples	Mean (MN/m^2)	Standard deviations
Blend:						
Devco + 10% Devco SC(500°C)	4	3.31	1.31	8	6.43	1.26
Devco + 20% Devco SC(500°C)	6	5.02	0.99	7	6.43	1.50
Devco + 10% LT.Devco.C.(700°C)	10	5.01	0.84	10	3.93	1.90
Devco + 20% LT.Devco C.(700°C)	14	4.54	0.86	18	5.18	1.46
Devco + 10% Coke breeze	25	2.87	1.12	11	2.08	0.45
Devco + 20% Coke breeze	9	1.28	0.31	10	1.14	0.12

TABLE 4.6

Tensile Strength of some Additional Samples

Heating Rate	3°C/min			1.5°C/min		
	No.of Samples	Mean (MN/m^2)	Standard deviations	No.of Samples	Mean (MN/m^2)	Standard deviations
Blend:						
Devco	16	4.35	1.35	14	2.86	0.64
Devco Semi-coke (500°C)	6	1.89	0.61			
Low temp.Devco coke (700°C)	14	2.75	1.02			
Devco + 10% Madison coal	6	5.06	0.77			
Devco + 20% Madison coal	4	3.35	1.05	5	4.61	0.67
70% Devco + 10% Chisholm + 10% Madison + 10% Devco SC(500°C)	3	6.31	1.00			

4.2.3 Microstrength Index (MSI) of the cokes

The following list shows the microstrength index of the products of the carbonization of Devco coal. The final temperature is indicated in parentheses. The heating rate used was 3°C/min in all these cases.

Sample	MSI
Devco (1000°C)	38.9
Devco Semicoke (500°C)	17.2
Low temp. Devco coke (700°C)	22.0

TABLE 4.7
Binary Blends - Microstrength Index (MSI)

Mean Particle Size of inert	0.200 mm		0.108 mm	
Blend — Heating rate:	3°C	1.5°C	3°C	1.5°C
Devco + 10% Devco S.C.(500°)	44.9, 46.8 (Mean 45.9)	45.7	41.1	41.3
Devco + 20% Devco S.C.(500°)	48.7	48.3	45.5	45.1
Devco + 10% L.T.Devco Coke (700)	41.7, 38.5, 41.2 (Mean 40.5)	36.8	41.1	39.9
Devco + 20% L.T.Devco Coke (700)	30.5	29.4	44.5	35.1, 40.5 (Mean 37.8)
Devco + 10% coke breeze	30.9, 31.3, 31.7, 29.2, 34.2 (Mean 31.5)	30.6	31.6	30.2
Devco + 20% coke breeze	17.3	18.6	20.1	19.6

The following experiments were run several times in order to get a good estimate of the variance: a) all the blends with a 10% addition of inert carbonized at 3°C/min with the inert ground at 0.2 mm, and b) the blend prepared with devco coal and 20% of low temperature coke carbonized at 1.5°C/min with the inert ground at 0.108 mm. The analysis of the data was done with a computer program. Initially, the coded variables (see Section 3.2.2.1 and Appendix E) were arranged to fit the general model(3-1). The values of the parameters were taken from the print-out; those parameters that were not significantly different from zero were dropped from the general equation which can be reduced to the following relation:

$$MSI_C = 35.228 - 2.662x_1 - 10.328x_2 - 3.588x_1x_2 + 3.258x_3x_2^2 - 2.578x_3 \quad \ldots\ldots \qquad (4\text{-}1)$$

where x_1 = amount of inert coded = $\frac{AI - 15}{5}$

x_2 = type of inert coded = $\frac{F - 5.454}{1.896}$

x_3 = mean size of inert coded = $\frac{MS - 0.154}{0.046}$

where AI = amount of inert
MS = mean diameter of inert
F = function which numerically describes the type of inert.

The uncoded equation is as follows:

$$MSI_C = 1.53\ A.I. + 33.35\ F - 0.38\ A.I \times F + 19.71\ F^2 \times MS - 215.04\ F \times MS + 530.34\ MS - 3.04\ F^2 - 39.73 \qquad (4\text{-}2)$$

The analysis of variance showed that equation (4-1) (at a level α equal to 0.05) represented the data. Appendix E shows both the statistical analysis of the parameters of the general model and the analysis of variance for the model (4-1).

4.2.4 Plastic properties of some blends

This determination was done by Stelco using a Gieseler Plastomer

(59). The particle size of the samples used for this test and the one of the blends used in the carbonization test was the same. The results are shown in Table 4.8.

TABLE 4.8

Plastic Properties of Devco Coal and Some of its Blends

Mean Diameter of inert = 0.20 mm

Blend	Initial Temp. (°C)	Fusion Temp. (°C)	Maximum Fluid Temp(°C)	Final Temp. (°C)	Solidification Temp.(°C)	Melting Range (°C)	Maximum Fluidity ddm
Devco coal	397	413	450	481	484	84	23670
Devco coal + 10% D.semicoke	390	408	447	479	482	89	8760
Devco coal + 20% D. semicoke	391	409	446	478	482	87	6375
Devco coal + 10% low-temp.D.coke	394	410	446	478	481	84	N.A.
Devco coal + 20% low temp.D.coke	395	410	445	478	481	83	5960
Devco coal + 10% coke breeze	392	410	448	479	482	87	7830
Devco coal + 20% coke breeze	394	411	446	477	481	83	3975
Mean Diameter of inert = 0.108 mm							
Devco coal + 10% D. semicoke	392	409	443	477	481	85	8835
Devco coal + 20% D. semicoke	390	408	444	476	481	86	6110
Devco coal + 10%	396	409	446	477	481	81	6825
Devco + 20% coke breeze	394	410	445	479	482	85	4215

4.3 Properties of the Carbonaceous Inerts

The chemical and physical properties of the three inerts investigated and Madison semicoke-500°C are shown in the following tables.

TABLE 4.9

Proximate Analysis (Dry Basis)

Inert	Devco S.coke (500°C)	Low Temp. Devco coke (700°C)	Coke breeze	Madison S.C. (500°C)
Assay:				
Ash (A)	4.66	4.94	7.46	7.06
Volatile (VM)	9.89	6.89	1.84	11.31
Fixed Carbon	85.45	88.17	90.70	81.62

TABLE 4.10

Microhardness (MH) of the Inerts

Inert	136° Diamond Pyramid Hardness Number
Devco S.C. (500°C)	50
Low Temp. D.C. (700°C)	122
Coke breeze	192
Madison S.C. (500°C)	45

Calculation of F

The function F was introduced in Section 3.2.2.1 and was calculated using the following equation:

$$F = \ln\,(A \times T.S.G. \times M.H./VM)$$

TABLE 4.11

Values of the Function F

	True Specific Gravity (T.S.G)	F
Devco S.C. (500°C)	1.49	3.558
Low Temp.D.coke(700°C)	1.66	4.978
Coke breeze	2.00	7.350
Madison S.C. (500°C)	1.39	3.665

4.4 Carbonization of Madison Coal

4.4.1 Specific gravity and porosity data

TABLE 4.12

Binary Blends

Apparent and True Specific Gravity and Porosity of the Cokes

Mean Particle Size of Additive = 0.200 mm

Heating Rate:	3°C/min			1.5°C/min		
Blend	ASG	TSG	P	ASG	TSG	P
Madison + 10% Devco S.C. (500°C)	0.87	1.85	53.0	0.90	1.93	53.4
Madison + 10% LT.Devco C. (700°C)	0.87	1.82	52.2	0.87	1.87	53.5
Madison + 10% coke breeze	0.93	1.83	49.2	0.93	1.86	50.0
Madison + 20% Devco S.C. (500°C)	0.93	1.84	49.5			
Madison + 20% coke breeze	0.86	1.78	51.7			
Madison + 10% Madison SC (500°C)	0.85	1.84	53.8			

4.4.2 Mechanical properties of the cokes.

TABLE 4.13

Tensile Strength

Mean Particle Size of Additive: 0.200 mm

Heating Rate:	3°C/min			1.5°C/min		
Blend (Factorial Design)	No.of Samples	Mean (MN/m^2)	Standard deviation	No.of Samples	Mean (MN/m^2)	Standard deviation
Madison + 10% Devco SC (500°C)	-	-	-	4	5.89	2.51
Madison + 10% LT.Devco C. (700°C)	3	7.24	1.28	2	2.76	1.52
Madison + 10% coke breeze	10	2.02	0.66	12	3.75	1.13
Other samples						
Madison S.Coke (500°C)	18	2.03	0.65			
Madison	21	2.99	1.19			
Madison + 10% Madison S.C. (500°C)	5	3.41	1.13			
Madison + 20% Devco S.C. (500°C)	2	5.66	2.05			

TABLE 4.14

Microstrength Index (MSI)

Mean Particle Size of Inert: 0.200 mm

Heating Rate	3°C/min	1.5°C/min
Blend(Factorial Design)		
Madison + 10% D.S.C. (500°C)	36.1	34.3
Madison + 10% LT.Devco C.(700°C)	29.2	27.3, 28.5
Madison + 10% coke breeze	19.8	21.9
Other Samples		
Madison + 20% D.S.C. (500°C)	38.6	
Madison + 20% coke breeze	22.0	
Madison	28.2	

4.5 Carbonization of Chisholm Coal.

4.5.1 Specific gravity and porosity data.

TABLE 4.15

Apparent and True Specific Gravity and Porosity of the Cokes

Mean Particle Size of Inert	0.200 mm					
Heating Rate	3°C/min			1.5°C/min		
Blend (Factorial Design)	ASG	TSG	P	ASG	TSG	P
Chisholm + 10% Devco S.C. (500°C)	0.99	1.74	43.1	0.90	1.62	44.4
Chisholm + 10% LT.Devco C. (700°C)	0.91	1.74	47.7	0.87	1.77	49.7
Chisholm + 10% coke breeze	1.03	1.95	47.2	0.98	1.91	48.7
Other samples						
Chisholm + 20% D.S.C. (500°C)	1.00	1.88	46.8			
Chisholm + 20% coke breeze	1.09	1.93	43.5			
Chisholm	0.91	1.63	44.2			

4.5.2 Mechanical Properties of the cokes

TABLE 4.16

Tensile strength

Mean Particle size of inert	0.20 mm					
Heating Rate	3°C/min			1.5°C/min		
Blend	No.of Samples	Mean (MN/m^2)	Std. Dev.	No.of Samples	Mean (MN/m^2)	Std. Dev.
Chisholm+10%Devco SC(500°C)	4	6.53	3.05	5	5.25	0.83
Chisholm+10%LT.Devco C.(700°C)	8	7.08	1.47	7	4.92	1.07
Chisholm + 10% coke breeze	7	3.30	0.59	4	4.39	0.50
Other Samples						
Chisholm+20%Devco SC(500°C)	8	5.07	0.97			
Chisholm + 20% coke breeze	2	1.00	0.29			
Chisholm	6	3.96	1.18			

TABLE 4.17

Microstrength Index (MS)

Mean Particle Size of Inert 0.20 mm

Heating Rate	3°C/min	1.5°C/min
Blend		
Chisholm + 10% Devco S.C. (500°C)	51.0	47.5, 49.0
Chisholm + 10% LT.Devco C(700°C)	36.3	38.9
Chisholm + 10% coke breeze	31.1	32.6
Other Samples		
Chisholm + 20% D.S.C. (500°C)	52.0	
Chisholm + 20% coke breeze	25.8	
Chisholm	39.9	

4.6 A General Model for Predicting the Microstrength Index of Cokes Produced from Three Coals.

The design described in section 3.3.2.2 was analyzed using only the results of the MSI test for all the three coals which were blended with 10% of the three inerts with a mean diameter equal to 0.20 mm. These values are listed in Table 4.18.

TABLE 4.18

Carbonization of Blends from Three Coals - MSI Values

Coal	Madison (G=57.87)		Devco (G=50.30)		Chisholm (G=43.65)		
Heating Rate: per min	3°C	1.5°C	3°C	1.5°C	3°C	1.5°C	
Additive							F
10% Devco S.C.(500°C)	36.1	34.3	44.9 46.8	45.7	51.0	47.5 49.0	3.558
10% Low.Temp.Devco Coke (700°C)	29.2	27.3 28.5	41.7 38.5 41.2	36.8	36.3	38.9	4.978
10% coke breeze	19.8	21.9	30.9 31.3,31.7 29.2,34.2	30.6	31.1	32.6	7.350

The calculation of F was done in Section 4.3; the calculation of G was illustrated in Appendices C and D. The above data was used to find the parameters of the general linear model (3-4) by means of a computer program. After dropping the parameters which were not significantly different from zero the equation can be simplified to the following one:

$$MSI_C = 37.973 - 5.979x_1 - 7.476x_2 - 4.641x_1^2 \qquad (4\text{-}3)$$

where x_1 = type of coal = $\frac{G - 50.76}{7.11}$

x_2 = type of inert = $\frac{F - 5.454}{1.896}$

The uncoded equation is:

$$MSI_C = 8.48G - 0.09181G^2 - 3.943F - 134.40 \qquad (4\text{-}4)$$

The statistical analysis is shown in Appendix F.

4.7 Test of the Empirical Equations (4-2) and (4-4)

Several additional blends were carbonized at 1000°C using a heating rate of 3°C/min; the mean particle size of the inert was 0.2 mm. The measured microstrength index of the cokes was compared with that calculated from the empirical equations given in sections 4.2.3 and 4.6.

4.7.1 Carbonization of binary blends

a) Blend: Devco coal + 20% Madison semicoke 500°C.

F = 3.665

Observed MSI = 49.9

Calculated MSI = 45.8 (Equation (4-2))

The 95% confidence interval of the predicted value was: 45.8 ± 5.8.

b) Blend: Madison + 10% Madison semicoke-500°C

F = 3.665 G = 57.87

Observed MSI = 31.5

Calculated MSI = 34.4 (Equation (4-4))

95% Confidence interval = 34.4 ± 4.6

4.7.2 Carbonization of some blends containing more than one coal.

a) Blend: 10% Chicholm coal
10% Madison coal
70% Devco coal
10% Devco semicoke-500°C

F = 3.558 G = 52.25

Observed MSI = 43.7

Calculated MSI = 44.0 (Equation (4-4))

95% Confidence interval = 44.0 ± 4.6.

b) Blend: 20% Chisholm coal
20% Madison coal
50% Devco coal
10% Madison semicoke-500°C.

F = 3.665 G = 50.19

Observed MSI = 44.3

Calculated MSI = 45.5

95% Confidence interval = 45.5 ± 4.6.

4.8 Relationship Between MSI and Tensile Strength

The mean values of the microstrength index and the tensile strength of all the samples analyzed, were plotted in Figure 4.1. The microstrength index (MSI) can be expressed as a function of the tensile strength (T.S.) using the following polynomial expression fitted by regression analysis.

$$MSI_{TS} = 22.81 - 5.32T.S. + 4.01T.S^2 - 0.42T.S^3 \qquad (4\text{-}5)$$

The values of MSI_{TS} as a function of T.S. are shown in Figure 4.2. The experimental values of MSI are plotted against MSI_{TS} in Figure 4.3.

4.9 Microscopic Examination of the Cokes

The samples were carbonized at 1000°C using a heating rate of 3°C/min; the mean diameter of the inert was 0.20 mm.

The counting of the different types of carbon in the cokes was performed as it was described in section 3.4. The identication of the textures was done by following the classification used by the British Carbonization Research Association (40-44, 52).

TABLE 4.19

Analysis of Optical Anisotropy in Cokes

Blend:	Isotropic	Mosaic	Flow Type	Basic Anisotropy
Devco	17.2%	78.6%	3.9%	0.3%
Devco + 10% Devco S.C.(500°C)	11.5%	84.6%	3.8%	0.1%
Devco + 10% Low T.D.Coke(700°C)	11.3%	84.1%	4.4%	0.2%
Devco + 10% coke breeze	14.2%	82.1%	3.7%	-

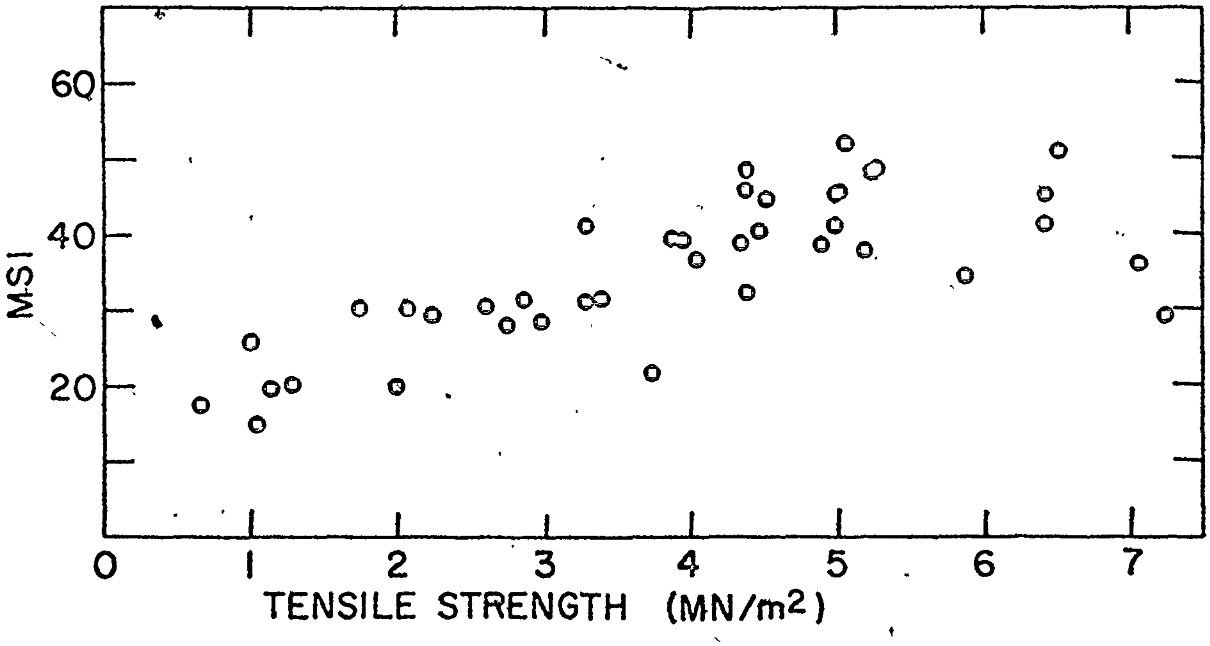


Figure 4.1: Relationship between MSI and Tensile Strength (T.S.)

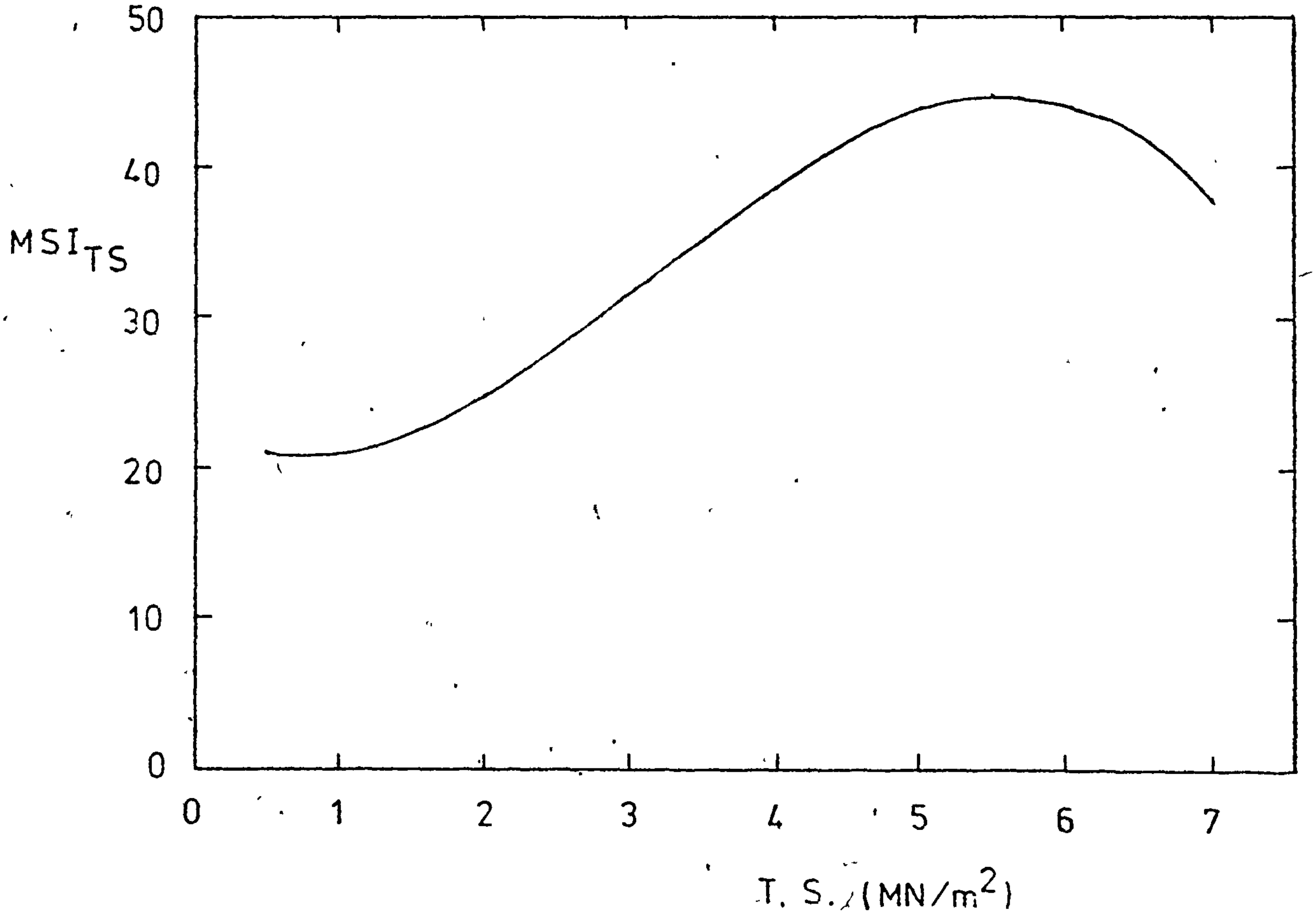


Figure 4.2: MSI as a function of T.S.

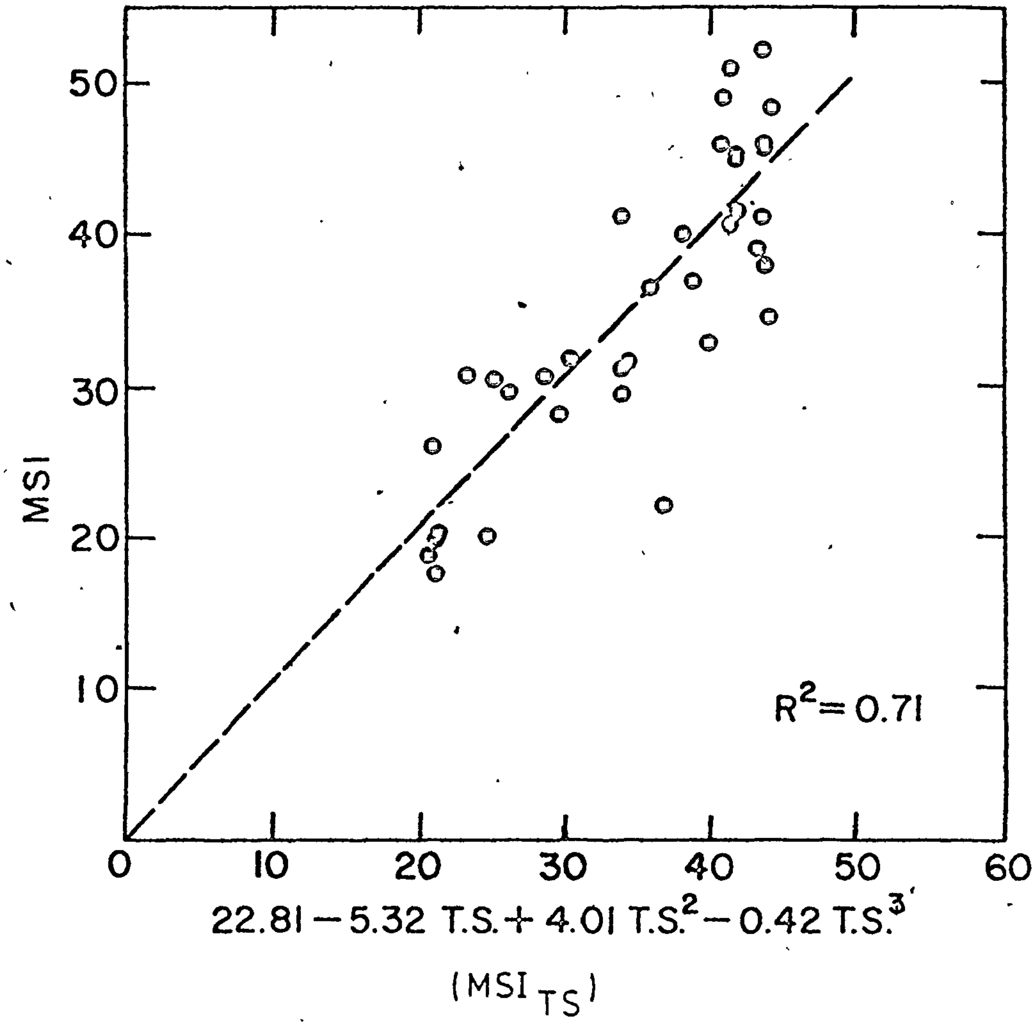


Figure 4.3: Correlation between MSI and $\mathrm{MSI}_{T.S.}$

CHAPTER 5

DISCUSSION.

5.1 Mechanical Properties of Coke

In single coal experiments, the blending of Devco semicoke carbonized at 500°C increased the microstrength index of the cokes produced by the following percentages:

	Increment of the MSI	
Coal	Addition of 10%	Addition of 20%
Devco	18%	25%
Madison	28%	37%
Chisholm	28%	30%

Coke breeze had a negative effect on the strength; its additions caused the MSI to drop in all cases, as is shown in the following table:

	Reduction of the MSI	
Coal	Addition of 10%	Addition of 20%
Devco	19%	55%
Madison	29%	22%
Chisholm	22%	35%

Low temperature Devco coke-700°C had properties intermediate between the other two additives and behaved accordingly. The addition of 10% of this inert produced the following change in the MSI value: for Devco and Madison it was increased by 6% and 3.5% respectively, and for Chisholm it was reduced by 9%. The addition of 20% of the inert to Devco coal reduced the MSI value by 22%.

The results of the fluidity test using the Gieseler Plastometer were shown in Table 4.8. The blends prepared with Devco semicoke had higher fluidity than those of the other two inerts (comparing the same level of addition). Devco semicoke-500°C as well as low temperature Devco coke had some residual fluidity but the latter one to a lesser degree.

Two conditions can be identified as the main factors that influence the assimilation of the inert particle in the coke matrix: a) some properties of the inert, such as volatile matter, ash, true specific gravity and microhardness, and b) the fluidity of the blend. The relationship between the properties referred to in (a) on the microstrength index, are shown in Figures 5.1 to 5.6. Figure 5.1a,b shows the relationship between the MSI and the volatile matter of the inert; in Fig. 5.2 the volatile matter of the blends was plotted against the MSI. Devco semicoke-500°C particles have a higher volatile matter than coke breeze particles; when the temperature increases, the former will contract at a similar rate as the newly formed semicoke surrounding them. The coke breeze particles will contract at a lower rate producing a gap between this inert and the matrix.

Figure 5.3 shows the relationship between MSI and the true specific gravity of the inert. Devco semicoke-500°C has a lower density and a larger specific volume than coke breeze. Assuming uniformity in the particle size of the samples used for the determination of the true speci-

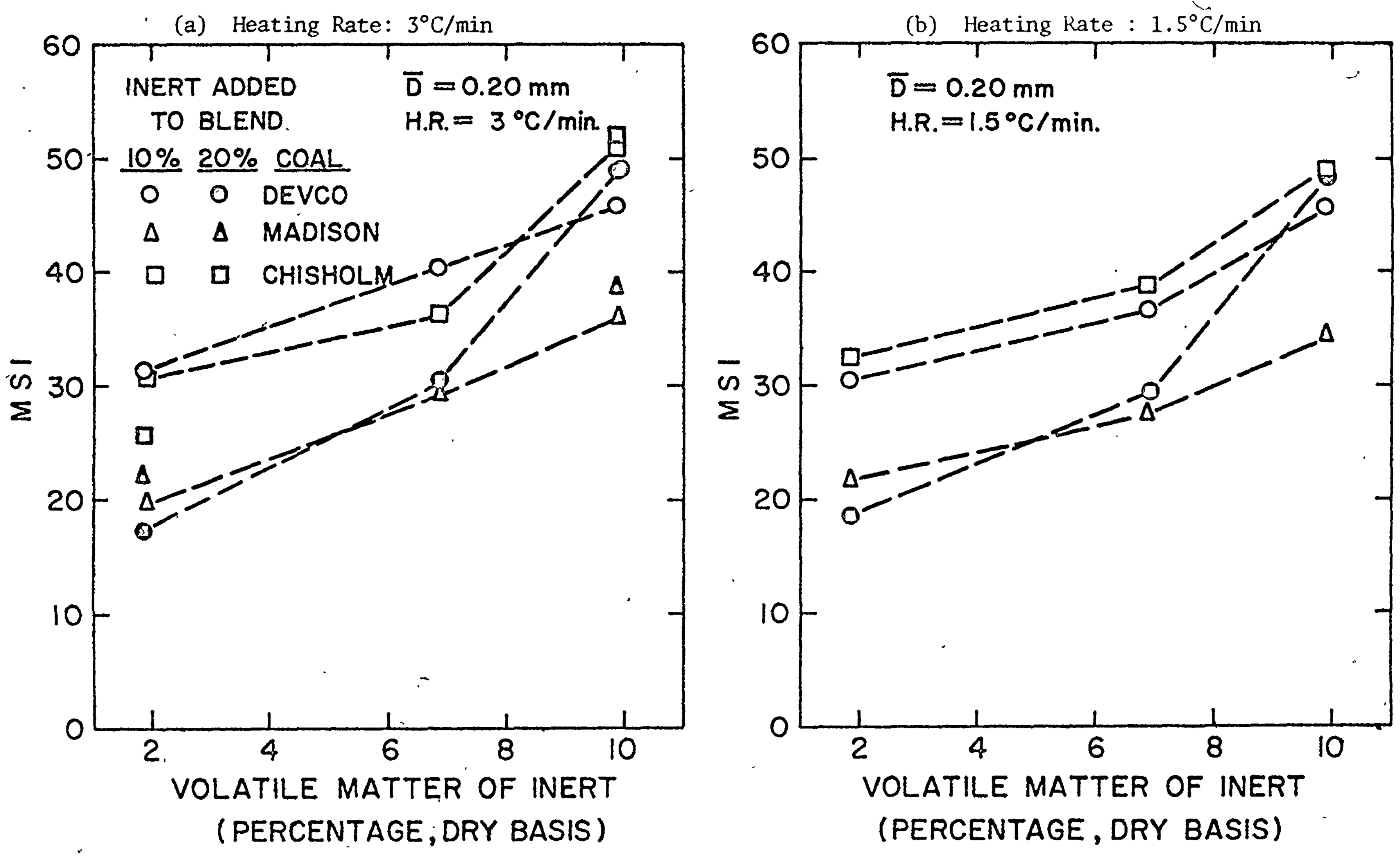


Figure 5.1: Relationship between MSI and volatile matter of the inert.

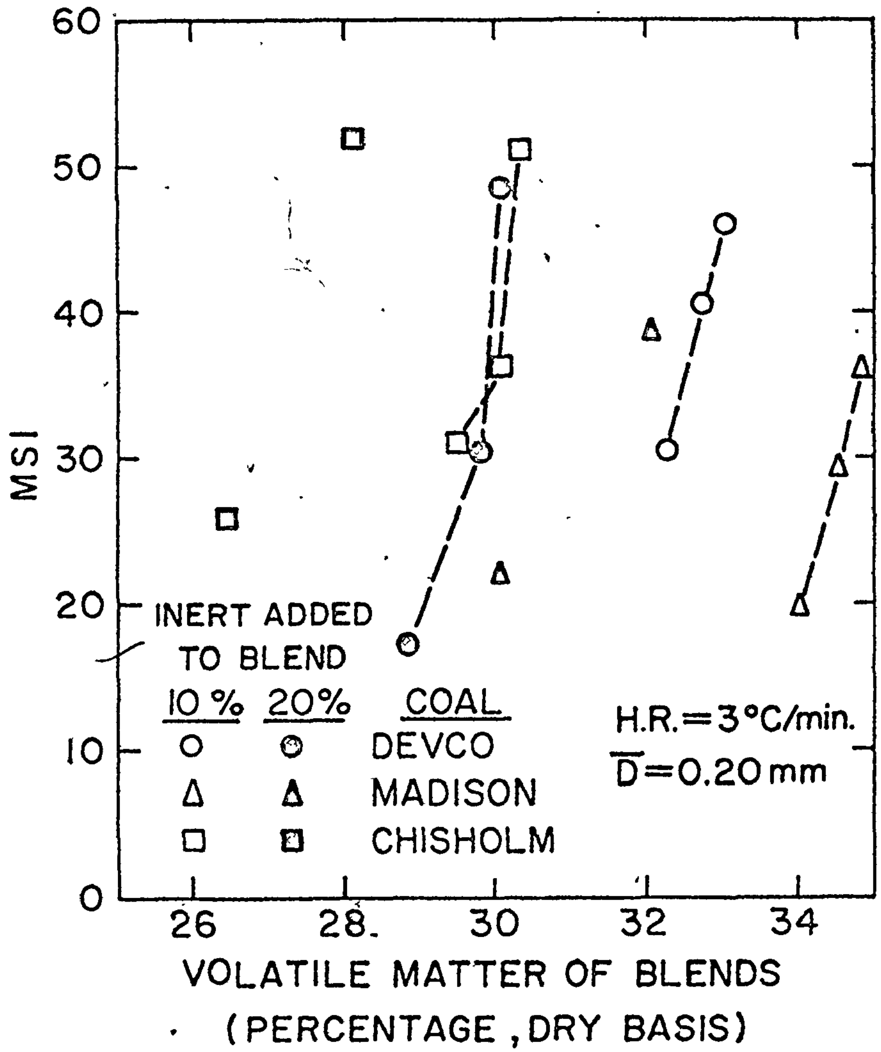


Figure 5.2: Relationship between MSI and volatile matter of the blends.

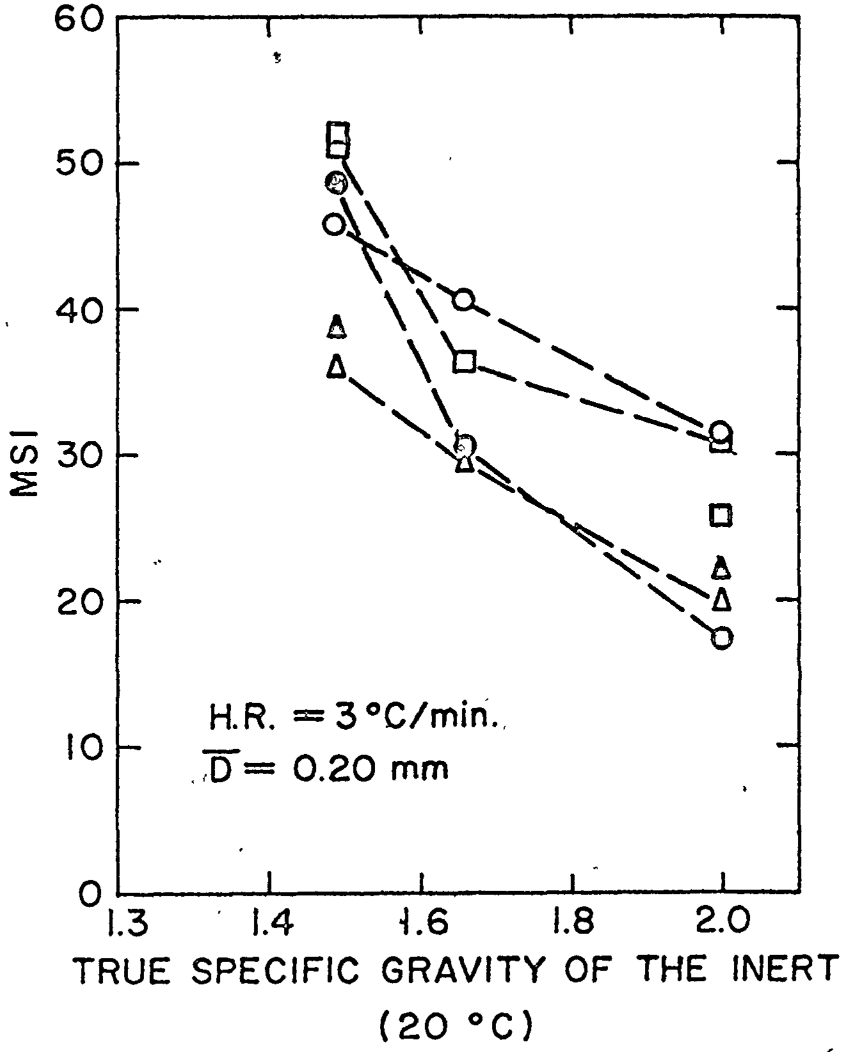


Figure 5.3: Relationship between MSI and the true specific gravity of the inert.

fic gravity (minus 200 mesh) the specific surface area will be also higher for Devco semicoke. A larger contact area between the inert particles and the plastic phase favours a strong wall structure.

Figure 5.4 shows the relationship between MSI and ash content of the inert, and Figure 5.5 represents the relationship between MSI and the microhardness number for the inert. In Fig. 5.6 the four properties of the inert are pooled in a function F which is plotted against MSI. Figures 5.7 a and b show particles of Devco semicoke 500°C (SC) well incorporated in the coke matrix; in (a) the particle has a higher anisotropic development than the structure surrounding it, but in (b) the opposite is true. The coke was produced from a blend of Devco coal and 10% of Devco semicoke-500°C and carbonized at 3°C/min until a final temperature of 1000°C was reached.

Figures 5.8 a and b, show the microphotograph of a sample of coke produced from a blend of Devco coal and 10% of low temperature Devco coke-700°C (3°C/min, 1000°C). In (a) the additive (LTC) is well incorporated in the structure; in (b) the shale (S) particle generates some gaps within the coke matrix.

Figures 5.9 a and b are microphotographs of coke produced from a blend of Devco coal and 10% coke breeze (3°C/min, 1000°C). The coke breeze particle (CB) is badly assimilated by the matrix in both photographs. Figure 5.10 shows a coke breeze particle (CB) in coke produced from a blend of Chisholm coal and 10% coke breeze (3°C/min, 1000°C). The photographs were taken using polarized light (crossed nicols) amd a green filter to increase the contrast; the magnification was 400 x. The main

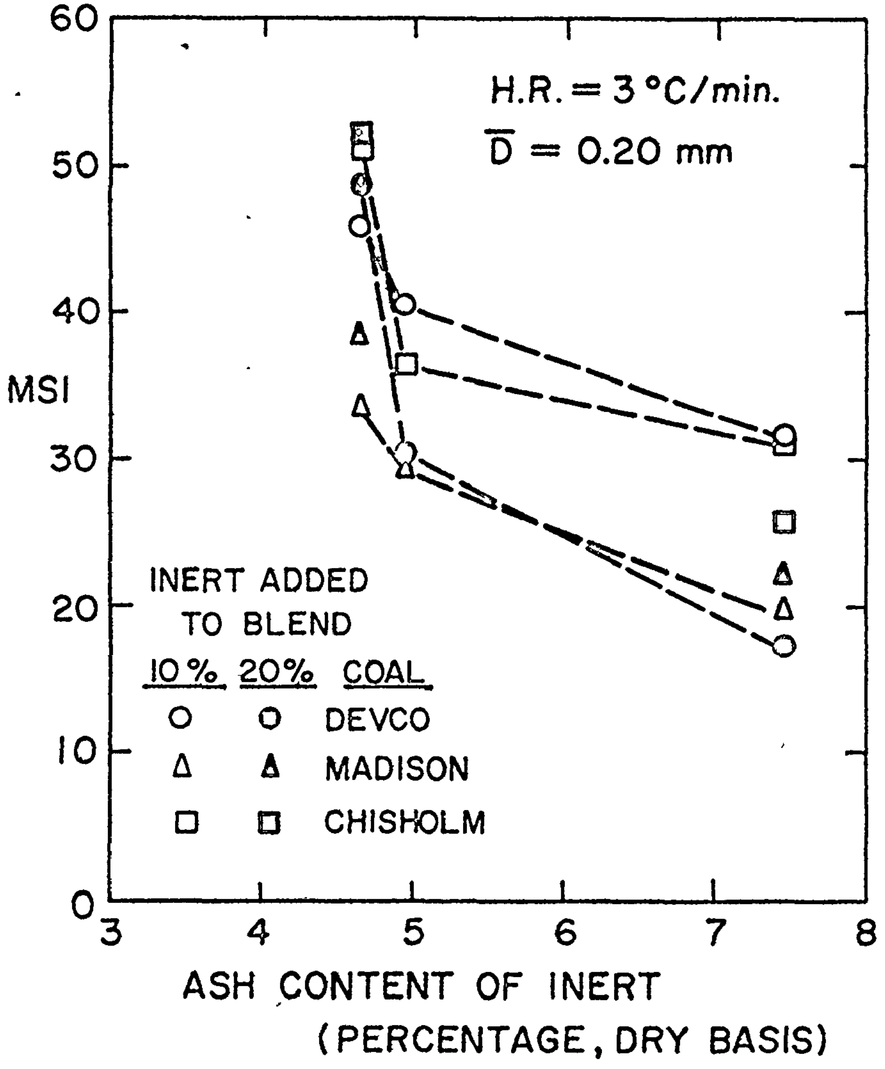


Figure 5.4: Relationship between MSI of the cokes and ash content of the inert.

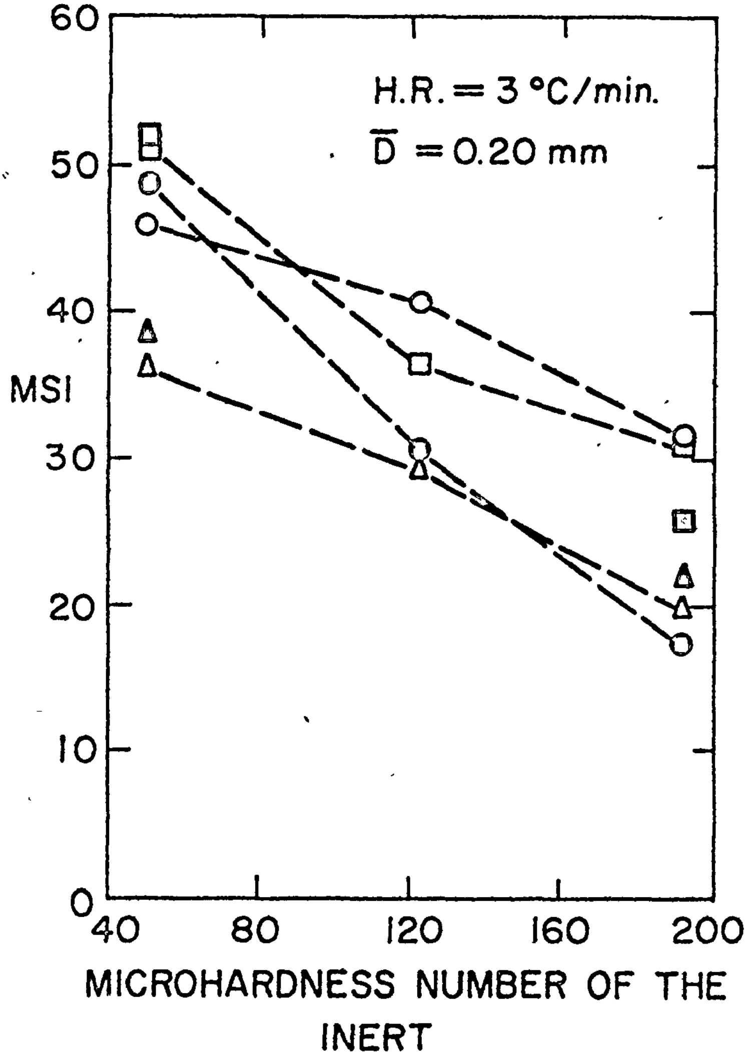


Figure 5.5: Relationship between MSI and microhardness of the inert.

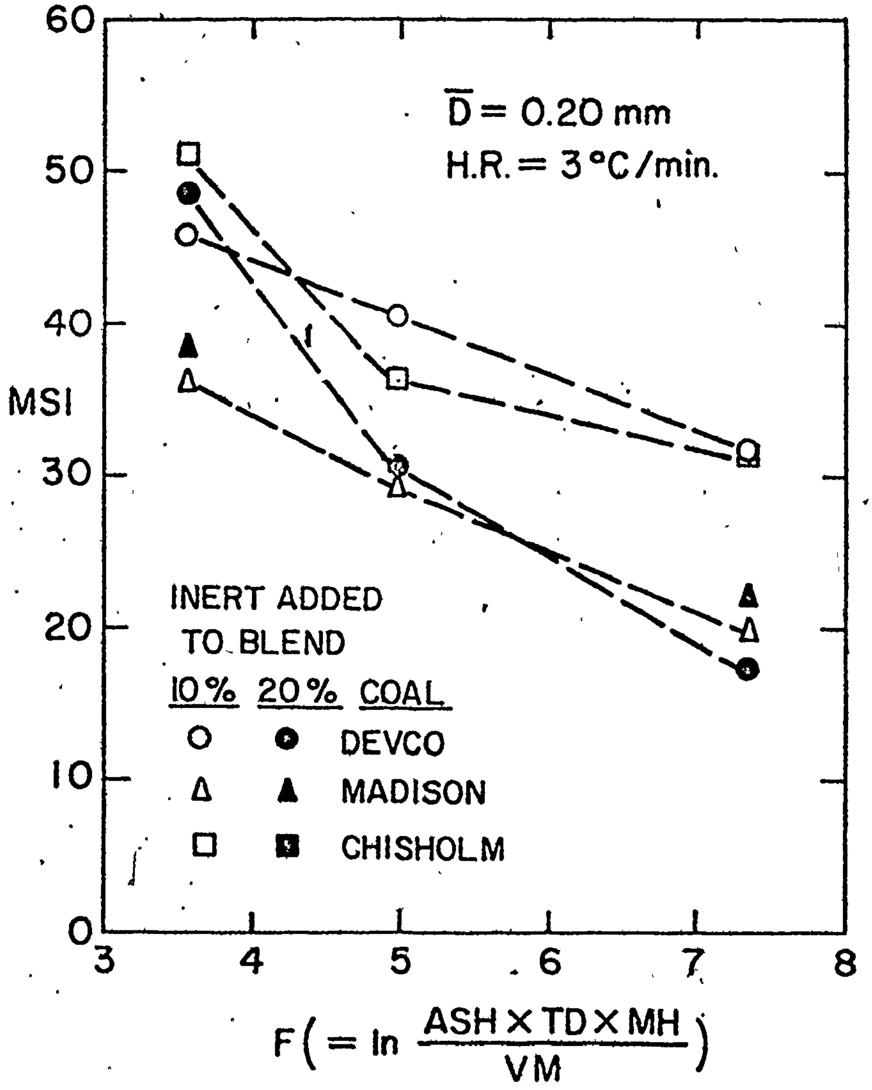
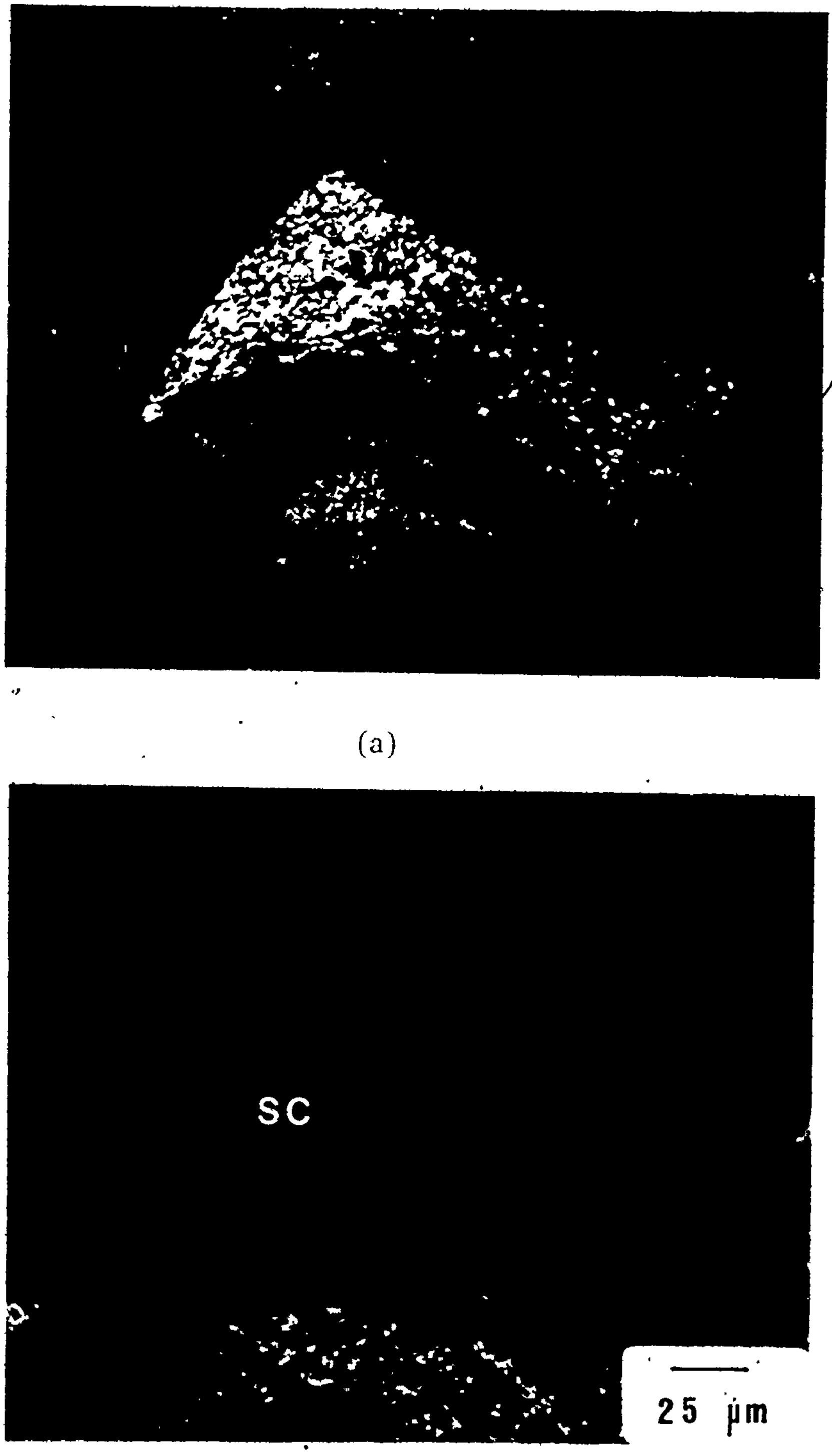


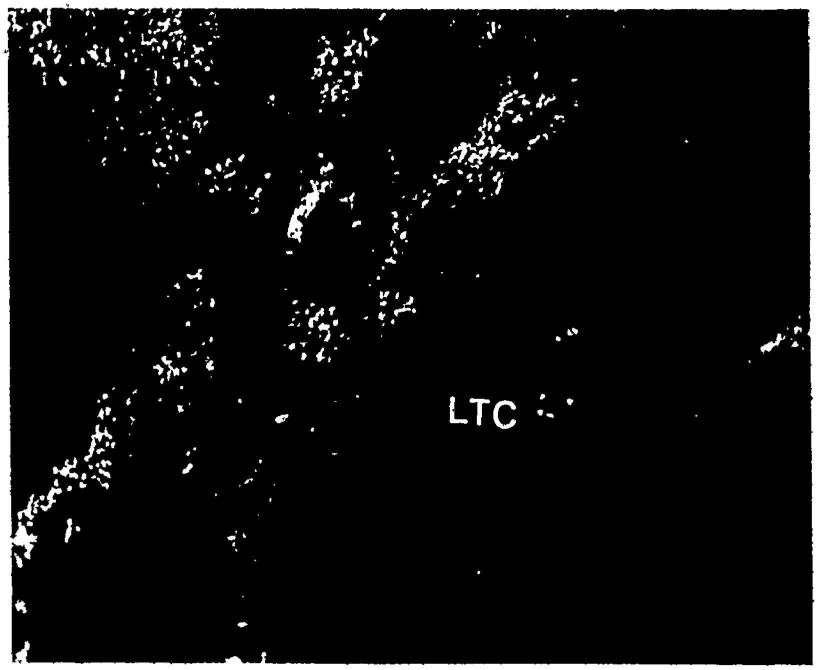
Figure 5.6: Relationship between MSI and F.



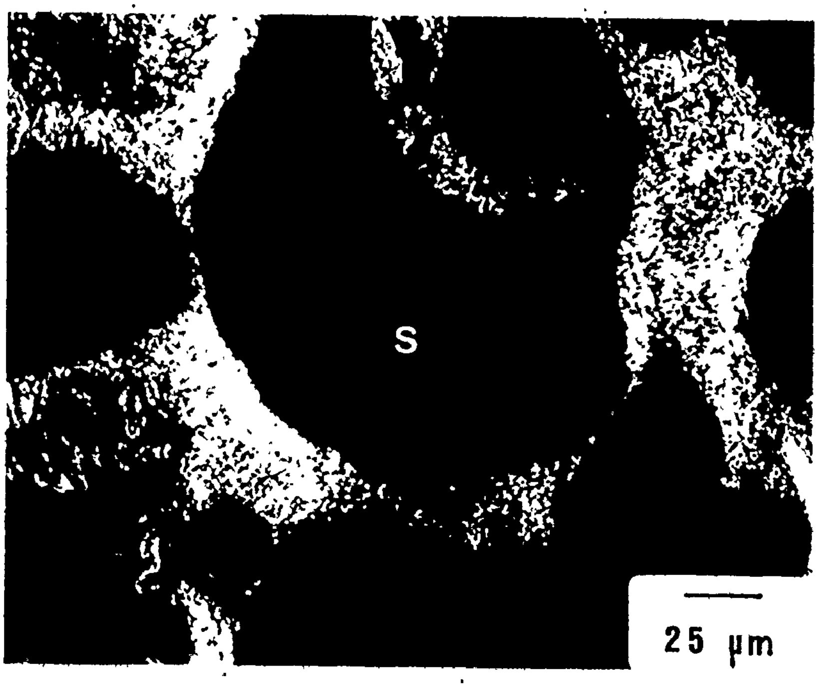
(a)

(b)

Figure 5.7 Devco semicoke particles in coke from blend of Devco coal and 10% Devco semicoke-500°C (3°C/min, 1000°C). Optical micrograph, crossed nicols, oil immersion, 400X.

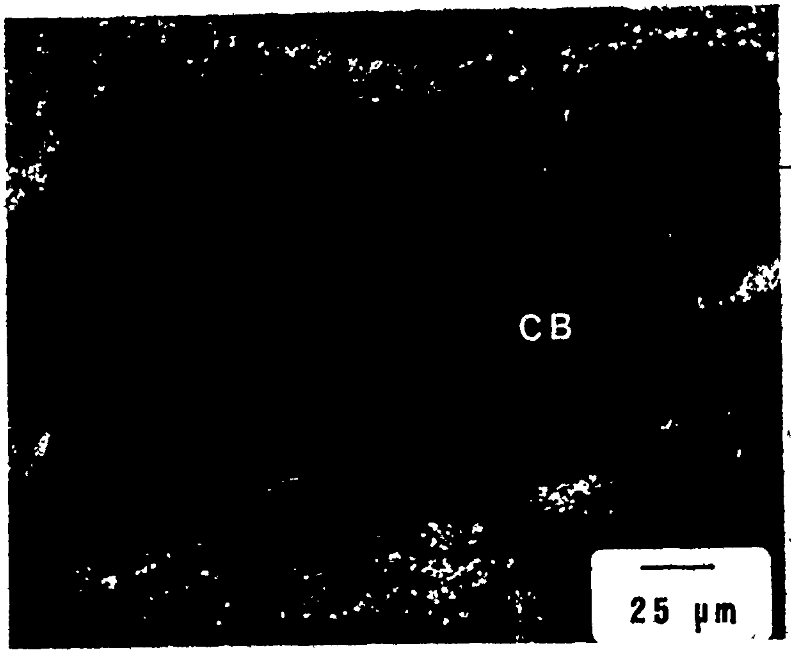


(a)
Low temperature coke particle (LTC) in coke

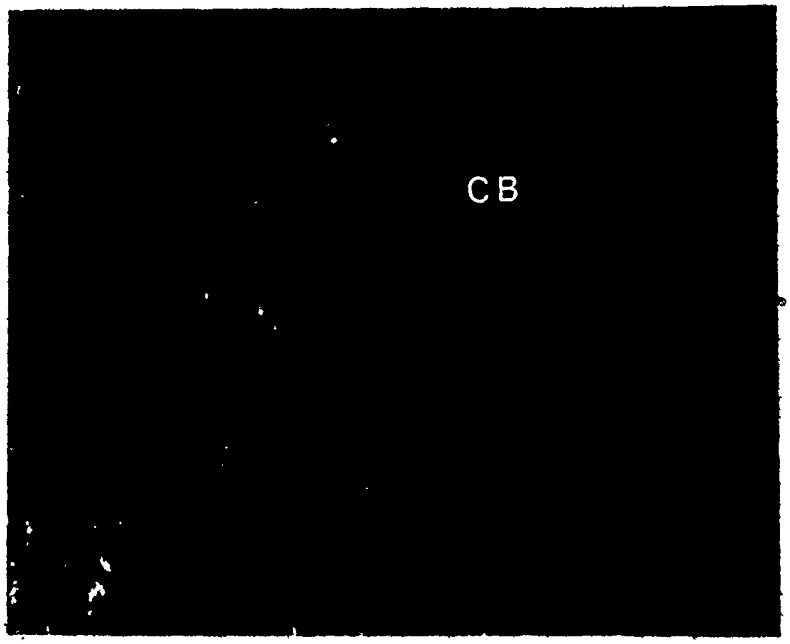


(b)
Shale particle (S) in coke

Figure 5.8 Coke from a blend of Devco coal and 10% low temperature Devco coke-700°C (3°C/min, 1000°C). Optical micrograph, crossed nicols, oil immersion, 400X.



(a)
Coke breeze particle (CB) almost separated from the coke matrix. Note the presence of fissures in the inert.



(b)
Coke breeze particle (CB) weakly bound to the coke matrix.

Figure 5.9 Coke breeze particles in coke from a blend of Devco coal and 10% of coke breeze (3°C/min, 1000°C). Optical micrograph, crossed nicols, oil immersion, 400X.

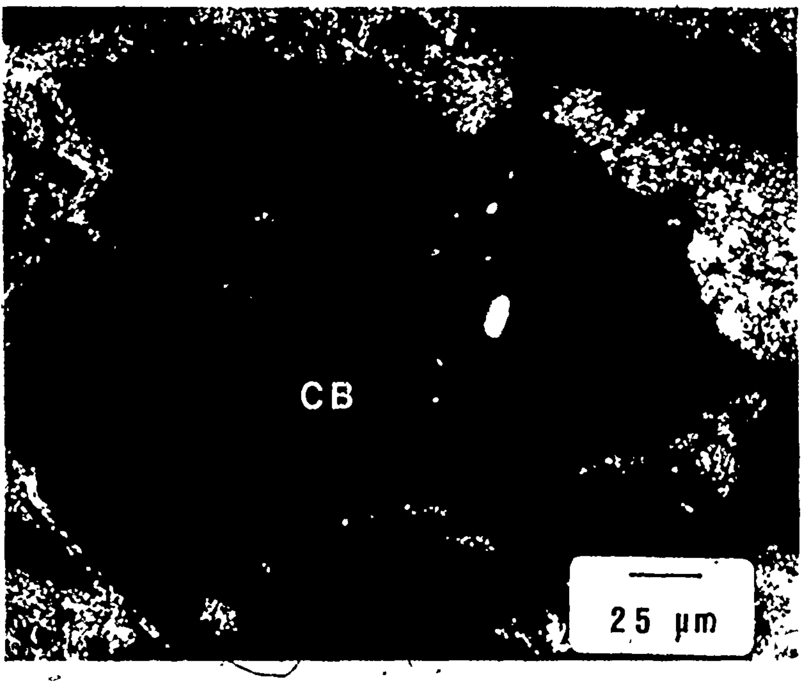


Figure 5.10 Coke breeze particle (CB) in coke from a blend of Chisholm coal and 10% coke breeze (3°C/min, 1000°C). Optical micrograph; crossed nicols, oil immersion, 400X.

conclusion drawn from these photographs is that Devco semicoke-500°C can be very well assimilated in the matrix. This is the most important factor in explaining the large increase of the microstrength index and tensile strength in some blends.

The effect of the maximum fluidity on MSI for blends of Devco coal and 10% and 20% of inert, is shown in Figures 5.11 a and b.

5.1.1 Correlations between strength indices

The variation in the tensile strength values followed almost the same trend as the microstrength index. The differences can be explained in terms of sampling. For the MSI test, the whole sample was used, but for the tensile strength test it was necessary to select the specimens.

The tensile strength was plotted against the microstrength index (Figures 5.12 a and b) for the blends prepared with Devco coal. It is apparent that there was a relation between MSI and the tensile strength for coke produced under the same carbonization conditions. In the blend containing 10% of inert ground at a particle size of 0.2 mm and carbonized at 3°C/min, and the one with the inert ground at 0.108 mm and carbonized at 1.5°C/min, the relation was not so definite as in the other cases; in these samples the large variations in the standard deviation of the tensile strength (Table 4.4) indicated that the correlation can be improved by testing a larger number of samples. The difficulty in obtaining a large number of suitable specimens was also the reason some blends of Madison and Chisholm had a low correlation (Fig.5.13). Figure

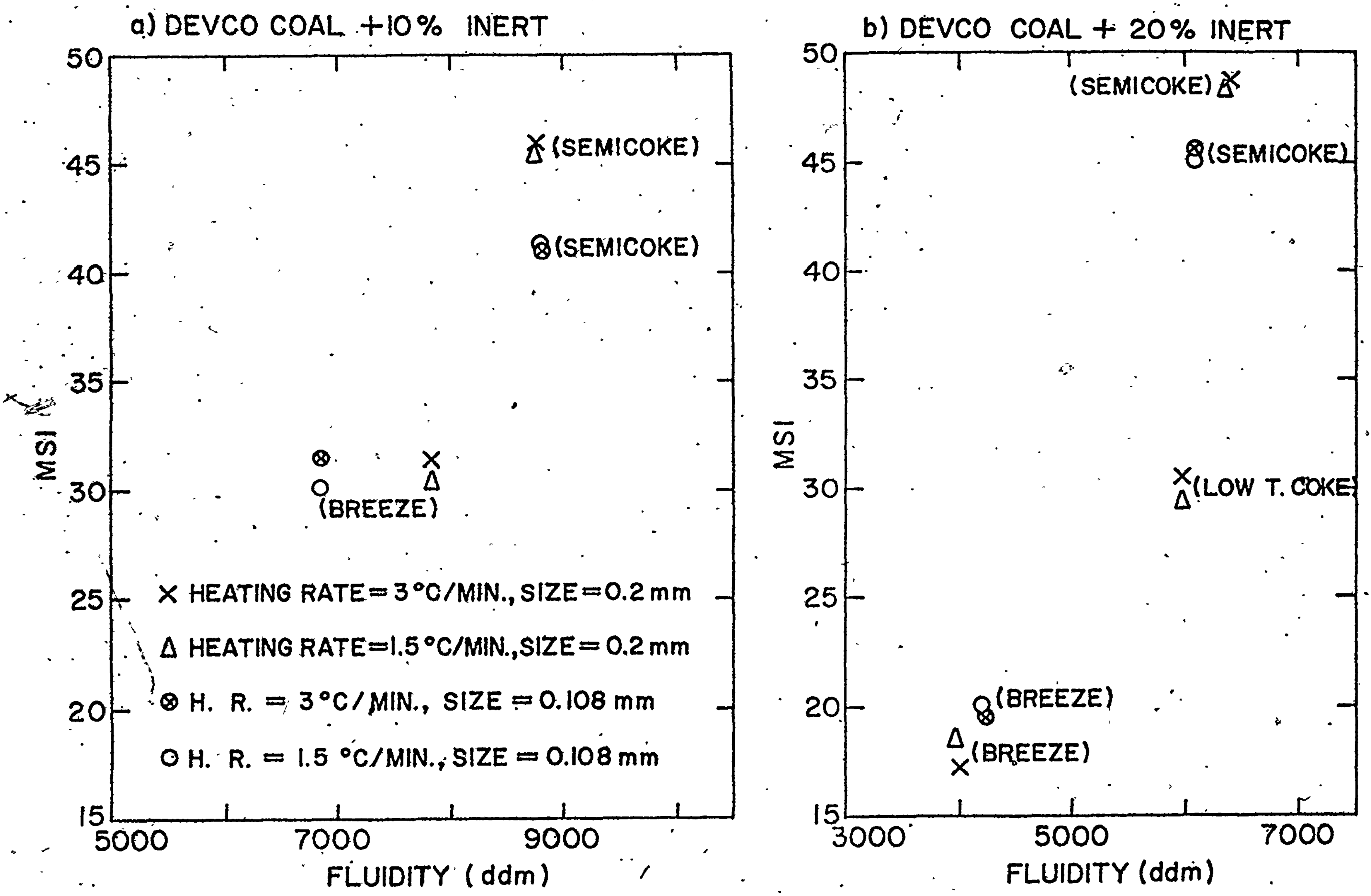
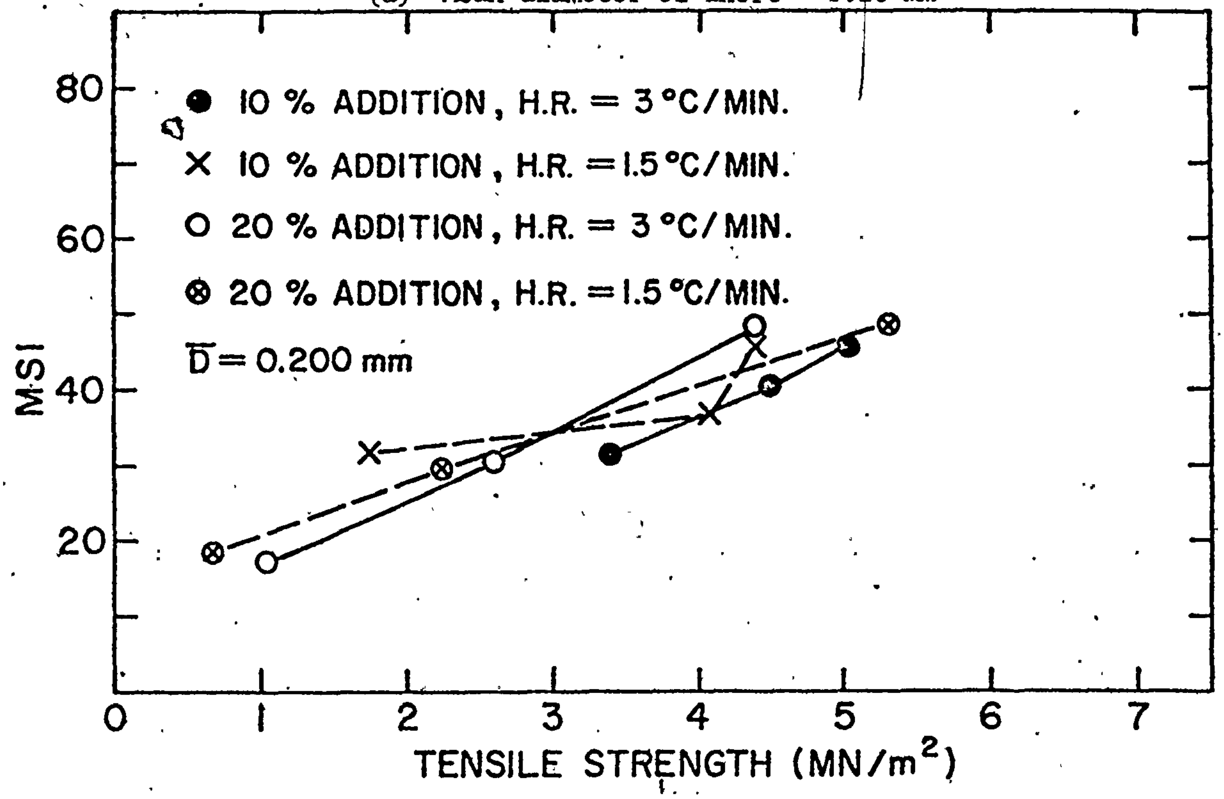


Figure 5.11: Relationship between maximum fluidity of blends and MSI

(a) Mean diameter of inert = 0.20 mm



(b) Mean diameter of inert = 0.108 mm

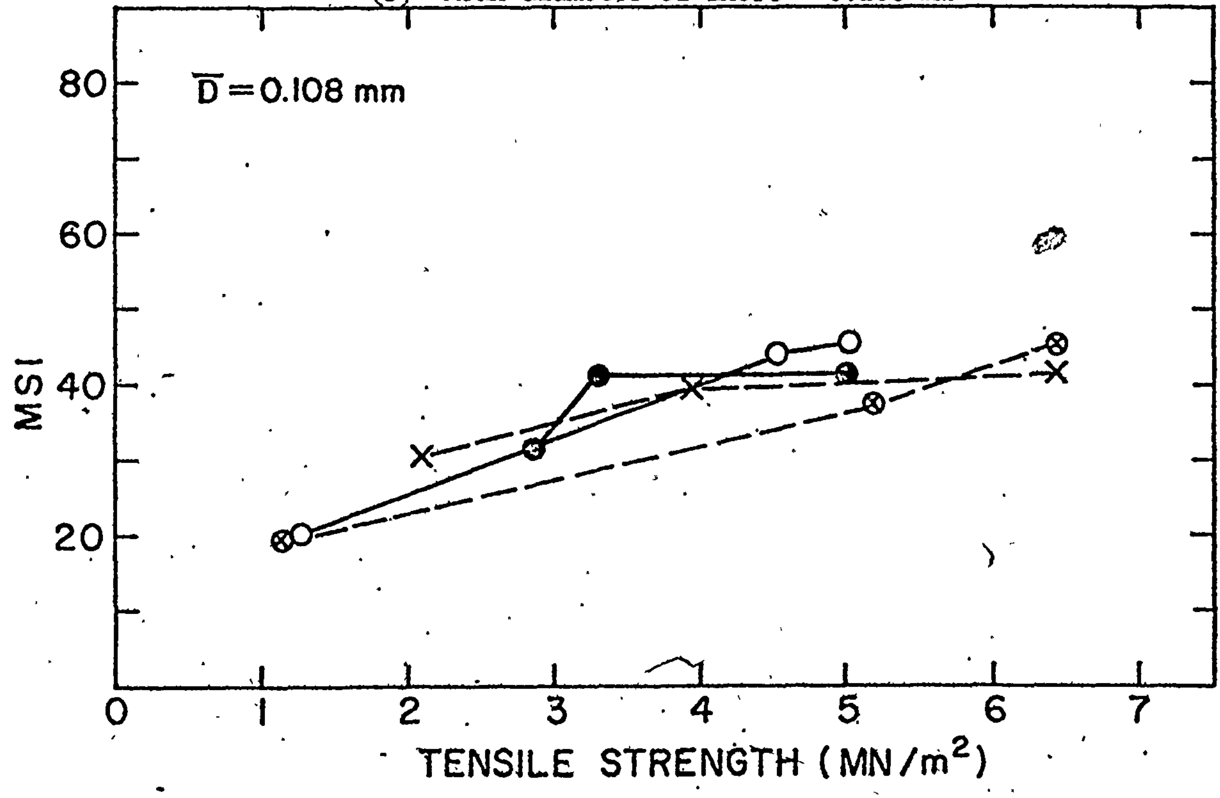


Figure 5.12: Relationship between tensile strength and MSI for cokes from blends of Devco coal.

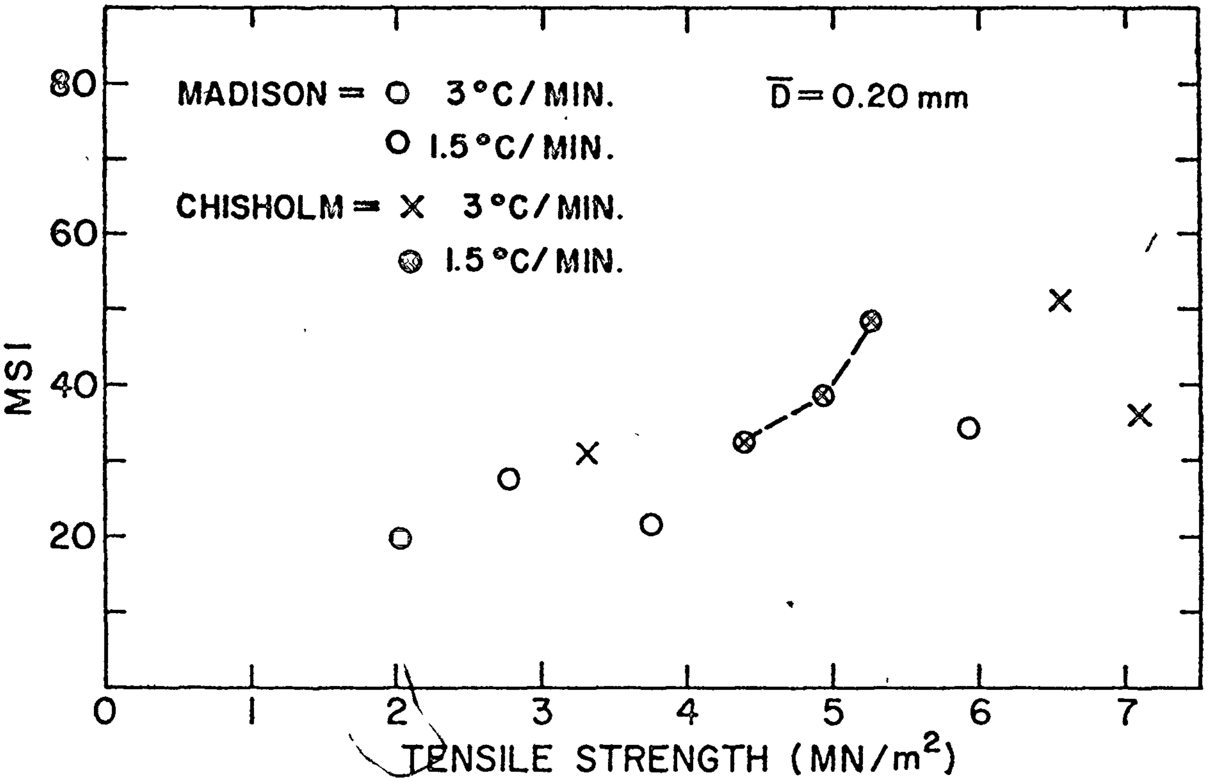


Figure 5.13: Relationship between tensile strength and MSI for cokes from blends of Madison and Chisholm coals.

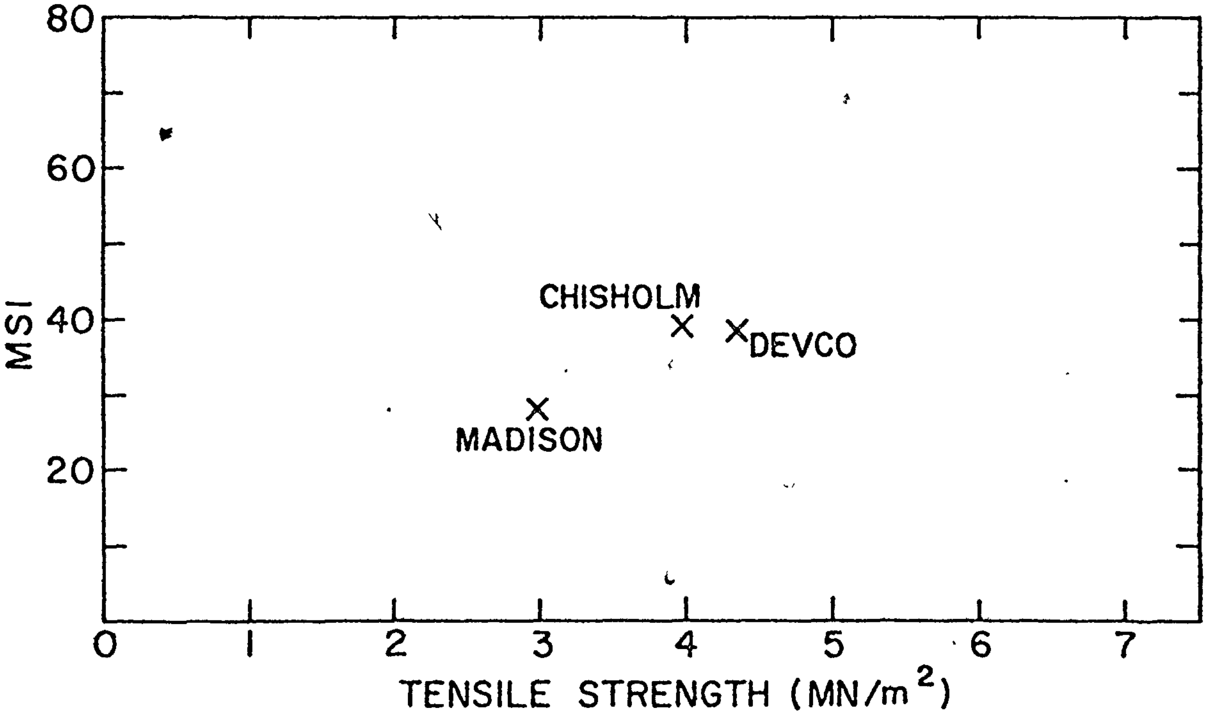


Figure 5.14: Relationship between tensile strength and MSI for cokes from single coals.

5.14 showed the relation for the cokes produced from single coals.

Patrick et al (67) found that the logarithm of the average tensile strength of foundry coke (carbonization temperature: 900°C) exhibited a linear correlation with the M10 index. In a later paper (68), they reported that it was not possible to find any correlation between the mean tensile strength and any of the micum indices (M40, M20, M10 or M0.5) for the blast furnace cokes studied.

In the present work it was found that for the same experimental conditions, there was a significant correlation between the microstrength index and the tensile strength. It is possible that a change in heating rate and size of the inert could have a different influence on the tensile strength that on the MSI. The large temperature gradient in an industrial oven could account in part for the lack of correlation between the indices for industrial blast furnace coke.

In the micum test the sample is taken after discarding the material which passes a 60 mm round-hole sieve and in the compressive test the specimens (15 mm in diameter) have to be free of visible cracks. Very small fissures will have a larger effect on the tensile strength than on the micum test M10, which is generally accepted as a measure of resistance to abrasion.

In the MSI test the particle is very small (1.18 - 0.6 mm) as compared with the sample for the other two tests, and the MSI value will be determined mainly by the strength of the pore wall and microfissures. In the microstrength test the coke will suffer two processes of size reduction: impact breakage and abrasion to a very low extent. A material subject to an impact usually breaks in tension. This is possibly the main reason the tensile strength correlates better with the MSI test than with any other mechanical test. Patrick (68) found that there is no correlation between M40 and M20 which are considered measures of impact breakage and the average tensile strength.

Correlations between the ASTM stability factor and the tensile strength have not been published. Probably the same type of problem can be found since Micum and ASTM tests are based on the same principle: degradation of the coke in a rotating drum. Nevertheless, the correlation between Micum and ASTM tests is very poor (70).

It is known that none of the empirical indices actually used describe thoroughly the fractural processes suffered by the coke pieces in the blast furnace. Nevertheless, the strength will depend to a large extent on the distribution of major cracks and fissures developed during the coking of the coal. The tensile strength of the coke obtained with the compressive test is a good measure of the capacity of the material to resist fissuring where there is stress concentration.

Since the MSI test seems to correlate with the tensile strength, it can be used in laboratory work instead of the compressive test, in order to compare different samples. This refers to coke produced under laboratory conditions and cannot be generalized to include industrial coke without a comprehensive study.

Correlations between the tensile strength and apparent density and porosity have been reported for British coals (34). In the present work, a reduction of the tensile strength was observed when the porosity increased, but in quite a number of cases there was lack of an acceptable correlation. It has been suggested that the type of carbon in the wall structure could have an influence on this behaviour (33).

5.1.2 Validity of the statistical models

The statistical analysis of the model found for Devco coal (Equation 4-1) showed that the "type of inert" had the greatest weight on the results. The content and mean particle size of the additive in the blend and their interactions with the type were also very important in determining the strength. The heating rate was not a significant variable under the experimental conditions. The critical importance of the type and amount of inert on the mechanical properties and the experimental error could mask the small changes produced by the levels of heating rate studied. Very large heating rates which might not have any practical significance were needed in order to produce an appreciable effect.

The statistical analysis of the mathematical model for the three-coal design (Equation 4-3) indicated that the type of coal is the variable with the greatest weight on the results. The type of inert could change drastically the mechanical properties. The effects of these two variables is so strong that the heating rate becomes insignificant.

The uncoded expressions (Equations 4-2 and 4-4) are equivalent to the coded ones (Equations 4-1 and 4-3, respectively). These correlations are valid for the coals studied, at the levels investigated, and can be applied when the blend has the following characteristics:

SI = 2.5 - 5 and CBI = 1 - 2. Equation (4-4) was tested with blends prepared by mixing the three coals in different ratios and the results were within the 95% confidence interval. The potential application of these equations to coals and inerts which were not used in the present work, needs further investigation, but it is clear that the effects of the inerts on the microstrength of the coke can be predicted following the procedure outlined here. Figs. 5.15 and 5.16 show the correlation between predicted and calculated values.

5.2 Optical Properties

The development of optical anisotropy of coke mainly depends on the type of coal used. It develops in the plastic phase and is directly related to the viscosity of this plastic phase and the amount of volatile matter evolved. It was observed that the addition of inert material reduced the amount of isotropic carbon in coke from 25% for Devco coal alone to 10% for Devco blended with 10% of semicoke or low temperature coke.

Marsh and other workers (49,53) have reported the effect of inert particles on the growth of the mesophase, which was liquid crystals that developed and grew in the plastic step of the carbonization process. Some authors accept the idea that small particles could act as nucleation points for the initial formation of the mesophase. The inert particles used as additives in the present work were relatively large (200 microns). Only four different cases were analyzed under the microscope for this part of the study, due to lack of time. It is apparent that the viscosity of the plastic phase played the most important role in the reduction of the amount of isotropic carbon.

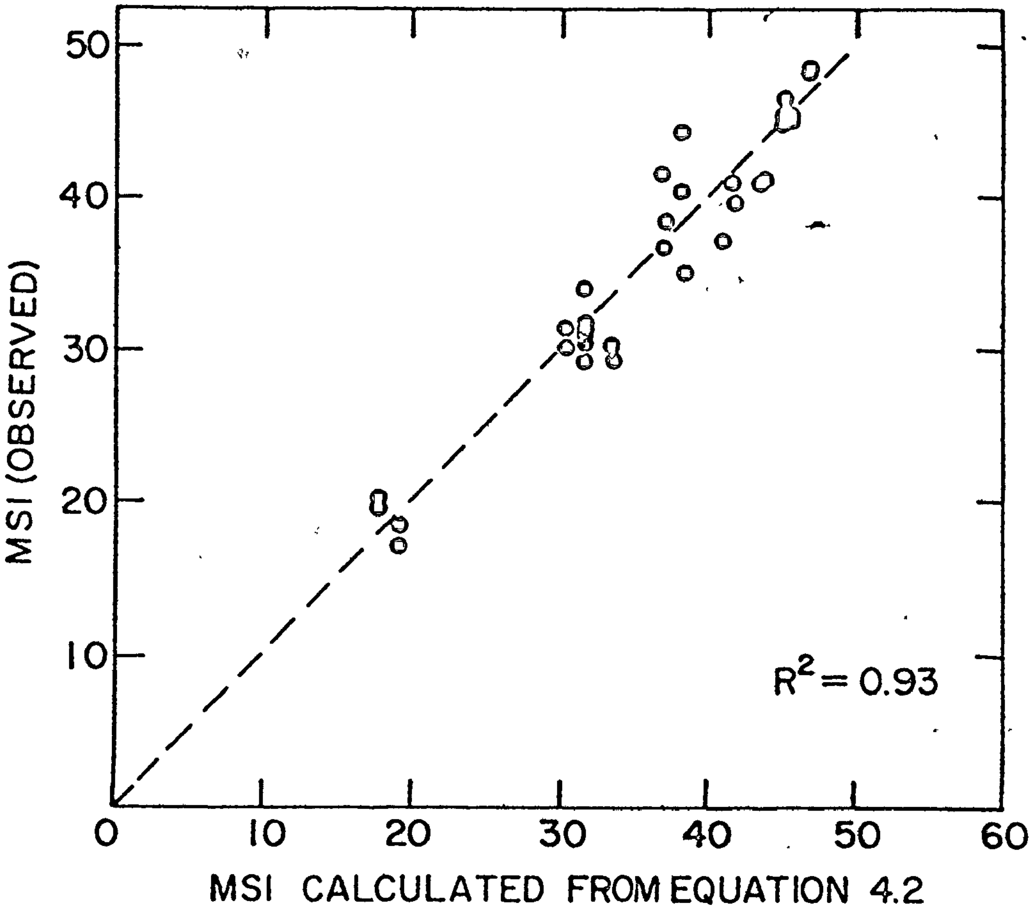


Figure 5.15: Correlation between observed and calculated MSI for blends of Devco coal.

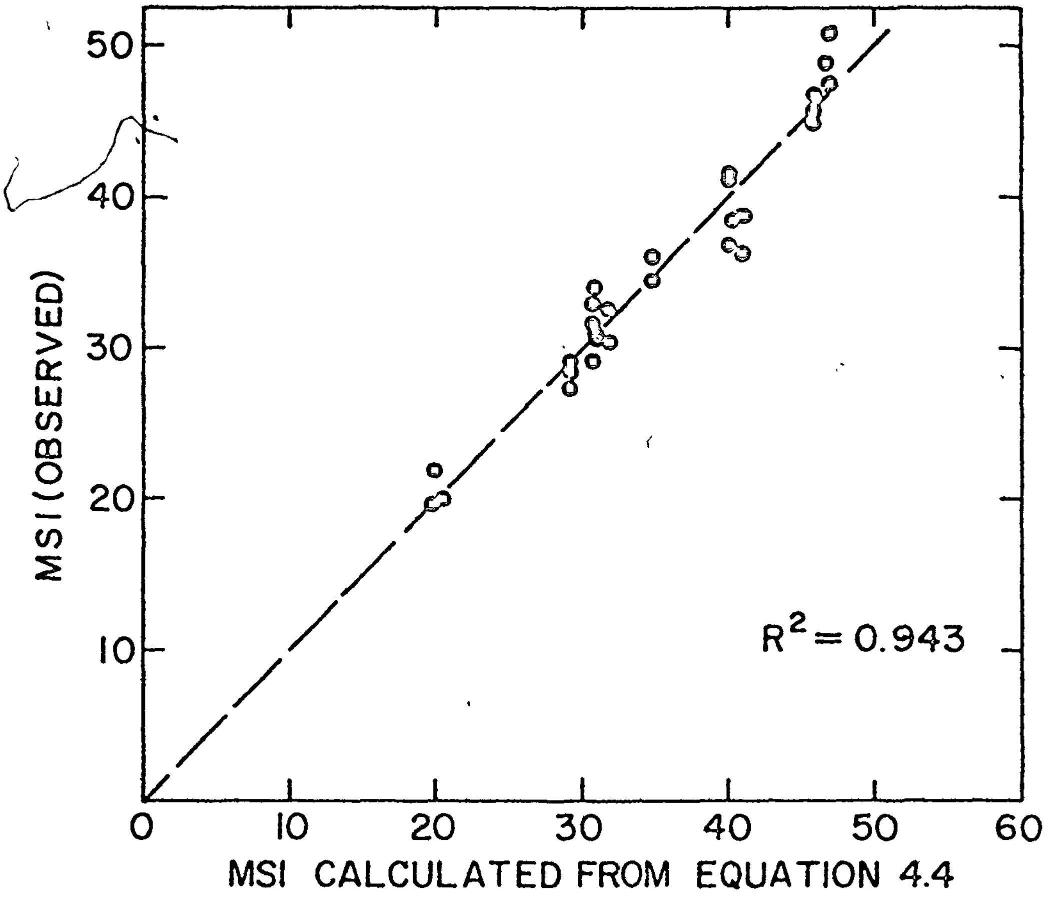


Figure 5.16: Correlation between observed and calculated MSI for blends of Madison, Chisholm and Devco coals and 10% of inert.

Probably there is an optimum ratio of the number of inert particles to the fluidity at which the nucleation of the mesophase is more favourable. One important feature observed under the microscope was that the intensity of the anisotropism of the majority of the particles of Devco semicoke-500°C was higher than that of the matrix. In Figures 5-7a, which are typical, the left hand side of the particle of Devco semicoke -500°C (SC) has a coarse grain mosaic structure while the matrix has a very fine granular mosaic and isotropic structure. The type of texture shown in Fig. 5.7b is less common for the Devco-semicoke-500°C particles.

The development of the anisotropism of coal is a matter of new interest since some authors believe that it does not follow the well known pattern observed in the carbonization of coal tar pitch and some pure compounds: formation of spherical bodies which grow and coalesce to produce the anisotropic mosaic structure.

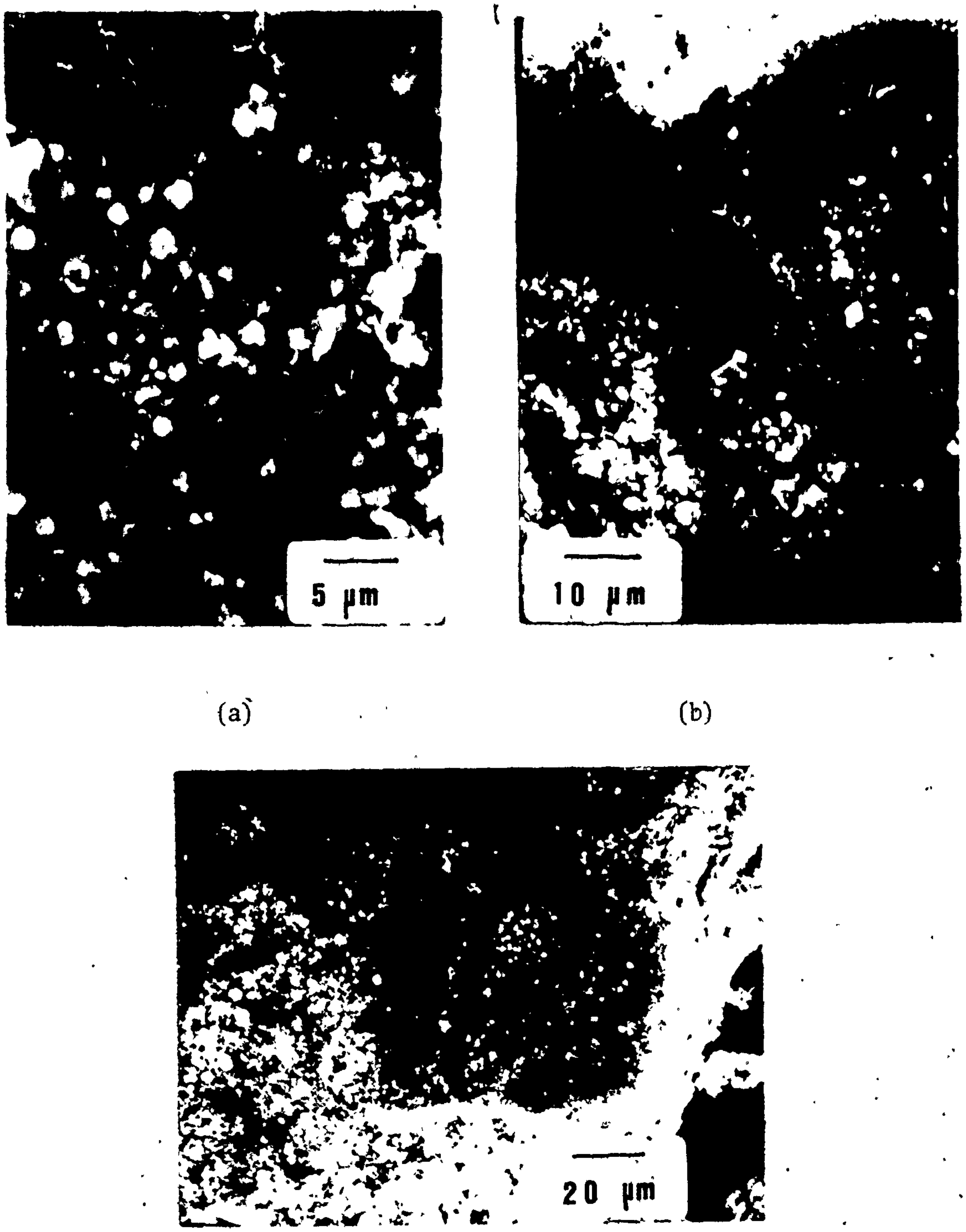
Taylor (53) and Ihnatowicz (71) observed the appearance of these spherical bodies or liquid crystals in Australian and French coals. Marsh et al. (48-51) conducted experiments in the carbonization under pressure of pure compounds and American and British coals. They reduced the growth and coalescence of the mesophase by slowing down the depolymerization reactions. Patrick (51) could not observe this growth and coalescence of the liquid crystals in experiments (under normal pressure) carefully designed for this observation. He and other investigators thought that coals could develop anisotropy without going through the step of spherical body formation, growth and coalescence.

Friel et al. (72) directly observed the development of the mesophase during the carbonization of four vitrinites of different rank by hot-stage transmission electron microscopy, using magnifications between 20000 and 100000 x. Two different forms of mesophase, related to coal type, were identified. Even a very poor coking vitrinite showed the formation of very small and isolated spherical bodies.

In the present work, it was found that in the sample prepared with Devco coal and 10% of low temperature coke, there were some spherical bodies (liquid crystals) that, for an unknown reason, did not coalesce (Figure 5.17); the final carbonization temperature was 1000°C. It may be that a combination of the effects of viscosity, time of formation of the mesophase, and absence of convective current in the plastic phase, was the reason for the structure observed and which is shown in Fig. 5.17a.

Figure 5.17b shows the same area of the sample but at lower magnification; at the upper left side of the micrograph there can be seen a higher degree of coalescence than that at the right side. The micrograph in Fig.5.17c shows a domain of small units with some degree of coalescence. Figures 5-18 a,b, show Devco coke structures, and Fig.5.19 corresponds to a micrograph of coke prepared with Devco coal and 20% coke breeze carbonized at 3°C/min up to 1000°C. In this case the mesophase grow as very rudimentary spheres.

The results of the MSI test and the microscopic examinations indicated that the blends with lower content of isotropic carbon were stronger. Heilpern and Wasilewski (67) published some relations for

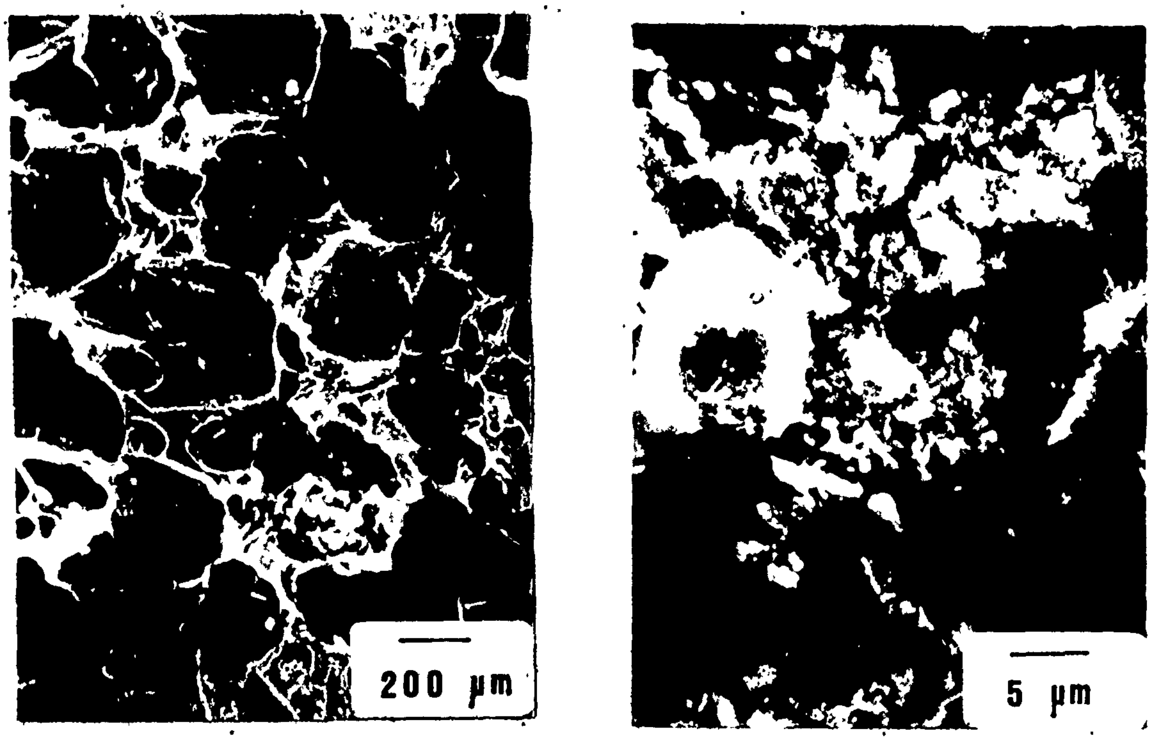


(a)

(b)

(c)

Figure 5.17. Stereoscan micrograph of surfaces of coke from a blend of Devco coal and 10% low temp. Devco coke -700°C. (Carbonization temperature 1000°C, Heating rate 3°C/min)



(a) (b)

Figure 5.18 Stereoscan micrograph of surfaces of Devco coke

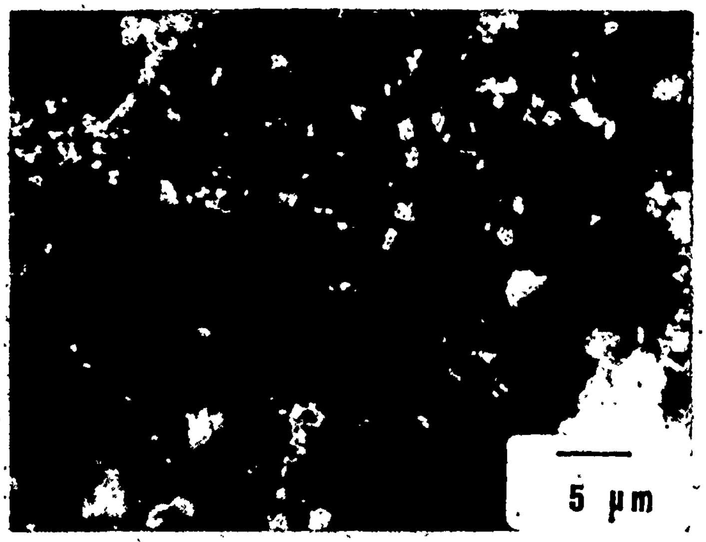


Figure 5.19 Stereoscan micrograph of surface of coke from a blend of Devco coal and 20% coke breeze.
(3°C/min, 1000°C)

Polish coals which are in agreement with this statement.

It is believed that the mosaic structure has better mechanical properties and resistance to thermal shock. There is evidence that the addition of inert to a coal affects the mechanical and optical properties of the coke. The knowledge on the control of the conditions of carbonization which would promote the anisotropic mosaic structure will be useful to the conventional coke oven process as well as to the formed coke processes.

CHAPTER 6

CONCLUSIONS

Mechanical Properties of Coke

The mechanical properties of coke can be improved with the addition of a carbonaceous inert additive to the coal blends provided that its coefficient of contraction is similar to the one for the matrix. The assimilation of the inert particle in the coke structure is favoured if there is some plasticity in the additive. The main conclusions of this work are the following:

1. In single coal experiments, the blending of Devco semicoke-500°C increased the mechanical properties of the coke.
2. The addition of coke breeze caused the microstrength index and the tensile strength to drop in all three coals investigated.
3. The effect of the low temperature Devco coke-700°C on the coke strength lies between the effects of Devco semicoke and coke breeze.
4. There is a direct relationship between the microstrength index and the tensile strength, based on data obtained from the present work.
5. For the blends containing additives, the microstrength index increases with the fluidity of the blend.

6. The effect of the heating rate on the coke strength is relatively small as compared to that of the additives.

Optical Properties of Coke

The analysis of cokes which were carbonized at a heating rate of 3°C/min and a final temperature 1000°C, showed that:

1. Additions of Devco semicoke-500°C and low temperature Devco coke-700°C reduced the amount of isotropic carbon present in the structure.
2. There was evidence that the anisotropic mosaic structure of coke from Devco coal passed through a prior stage of spherical liquid crystals.
3. The samples with a lower content of isotropic carbon had higher MSI values.

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APPENDIX 1

Classification of Coal

GROUPS (determined by coking properties)			CODE NUMBERS										SUBGROUPS (determined by coking properties)		
GROUP NUMBER	ALTERNATIVE GROUP PARAMETERS: Free swelling index (crucible-swelling number)	ALTERNATIVE GROUP PARAMETERS: Roga index	The first figure of the code number indicates the class of the coal, determined by volatile-matter content up to 33% V.M. and by calorific parameter above 33% V.M. The second figure indicates the group of coal, determined by caking properties. The third figure indicates the subgroup, determined by coking properties.										SUBGROUP NUMBER	ALTERNATIVE SUBGROUP PARAMETERS: Dilatometer	ALTERNATIVE SUBGROUP PARAMETERS: Gray-King
3	> 4	> 45					435	535	635 V_C				5	> 140	> G8
						334 V_A	434 V_B	534	634				4	> 50-140	G5-G8
						333	433	533	633	733 V_D			3	> 0-50	G1-G4
						332a 332b	432	532	632	732	832		2	≤ 0	E-G
2	2½-4	> 20-45				323	423	523	623 VI_A	723	823		3	> 0-50	G1-G4
						322 IV	422	522	622	722	822		2	≤ 0	E-G
						321	421	521	621 VI_B	721	821		1	Contraction only	B-D
1	1-2	> 5-20			212	312	412	512	612	712	812		2	≤ 0	E-G
					211	311 III	411	511	611 VII	711	811		1	Contraction only	B-D
0	0-½	0-5		100 I A B	200 II	300	400	500	600	700	800	900	0	Nonsoftening	A
CLASS NUMBER →			0	1	2	3	4	5	6	7	8	9	As an indication, the following classes have an approximate volatile matter content of: Class 6 33-41% volatile matter 7 33-44 " " 8 35-50% " " 9 42-50% " "		
CLASS PARAMETERS	Volatile matter (dry, ash-free) →		0-3	> 3-10 > 3-6.5 | > 6.5-10	> 10-14	> 14-20	> 20-28	> 28-33	> 33	> 33	> 33	> 33			
	Calorific parameter [a/] →		—	—	—	—	—	—	> 13,950	> 12,960-13,950	> 10,980-12,960	> 10,260-10,980			
			CLASSES (Determined by volatile matter up to 33% V.M. and by calorific parameter above 33% V.M.)												

Note: (1) Where the ash content of coal is too high to allow classification according to the present systems, it must be reduced by laboratory float-and-sink method (or any other appropriate means). The specific gravity selected for flotation should allow a maximum yield of coal with 5 to 10 percent of ash.
(a) 332a >14-16% V.M.
332b >16-20% V.M.

[a/] Gross calorific value on moist, ash-free basis (30° C, 96% relative humidity) B.t.u./lb.

International classification of hard coals by types with statistical groupings, shown bounded by heavier lines. The statistical groupings are designated by roman numerals. (Ref.80)

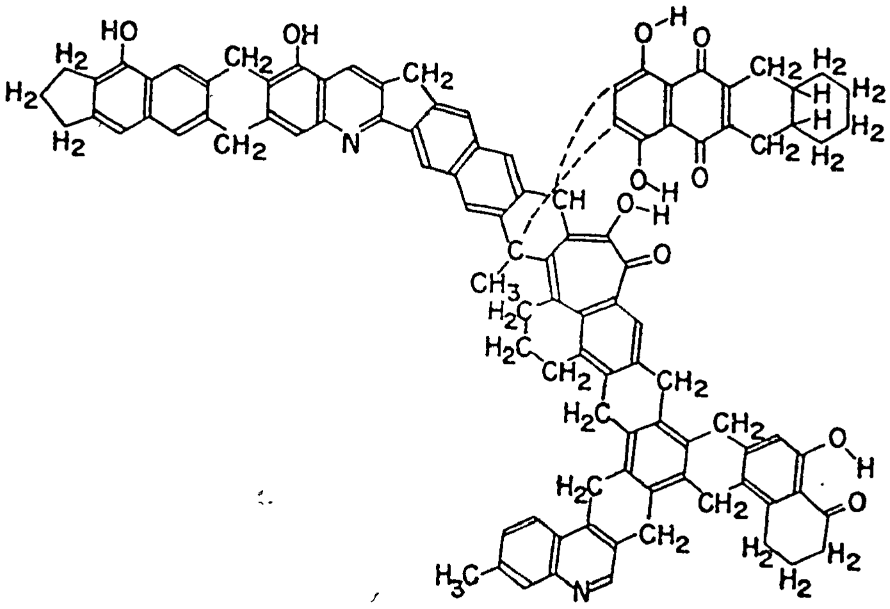

FIG. A.1: HYPOTHETICAL COAL MOLECULE WITH APPROXIMATELY 82 % CARBON (AFTER GIVEN) (74).

APPENDIX B

Properties of the Coals Used in the Present Work.

Chemical, Rheological and Screen Analysis Data

Coal:	Madison	Devco	Chisholm
ASTM Rank	hvAb	hvAb	hvAb
Proximate Analysis (db) %			
Ash	4.95	2.75	5.13
Volatile Matter	37.6	35.6	32.6
Fixed Carbon	57.5	61.6	62.3
Dry Ash-Free fixed carbon	60.38	63.34	65.67
Ultimate Analysis (db) %			
Only reported:			
Sulfur	0.95	1.15	0.63
Ash	4.95	2.75	5.13
Ash Analysis %			
Only reported:			
K_2O	1.70	1.30	2.4
Na_2O	0.52	0.75	0.71
Total alkali (in ash)	2.22	2.05	2.95
" " (in coal)	0.11	0.056	0.151
" " (in coke)	0.167	0.082	0.215
Gross calorific value			
Dry basis Btu/lb	14116	14929	14529
Dry Ash-free basis Btu/lb	15007	15626	15373
Free Swelling Index	4.1/2	8	8.1/2
Expansion/Contraction			
(Bulk dens. 52 $\mathrm{lb/ft^3}$, moisture $\leq 2\%$) %	-14.4	-18.1	-14.9

		Madison	Devco	Chisholm
Gieseler Plasticity				
Initial Softening point	°C	404	397	400
Fusion Temperature	°C	415	413	415
Maximum Fluid Temperature	°C	438	450	448
Final Fluid Temperature	°C	463	481	486
Solidification Temperature	°C	469	484	491
Maximum Fluidity	ddm	329	23670	15882
Melting Range	°C	59	84	86
Ruhr Dilatometer				
Ti Softening Temperature	°C	347	344	359
Tii Maximum Contraction Temp.	°C	413	401	410
Tiii Maximum Dilation Temp.	°C	440	455	452
Contraction, Maximum	%	24	26	24
Dilation, Maximum	%	27	208	146
Screen Analysis (as received) Cumulative	%			
2 in		5.4	-	-
1 in		8.0	2.7	4.4
3/4 in		18.6	4.3	8.6
1/2 in		29.0	12.3	16.7
1/4 in		50.7	34.3	39.1
6 mesh		63.7	50.1	54.8
10 mesh		75.6	65.9	69.4
20 mesh		83.8	76.5	79.0
35 mesh		88.2	83.9	85.6
65 mesh		91.4	89.3	90.5
100 mesh		92.8	91.4	92.5
- 100 mesh		7.2	8.6	7.5
Hardgrove Grindability Index		46.4	71.4	56

Petrographic Data

Coal:		Madison	Devco	Chisholm
Reactive Distribution:	%			
Type 2		7.4	4.6	5.4
" 3		3.1	1.5	1.5
" 4		-	-	-
" 5		-	-	-
" 6		5.1	1.4	-
" 7		17.2	10.8	0.6
" 8		37.5	28.0	11.9
" 9		3.2	29.4	38.3
" 10		0.2	3.7	12.6
" 11		0.3	-	0.6
" 12		0.8	0.2	0.2
" 13		0.2	0.6	0.5
" 14		0.3	0.2	0.8
" 15		0.4	0.4	0.3
" 16		0.2	0.7	0.6
" 17		0.5	0.2	0.6
" 18		0.3	0.3	0.3
" 19		0.7	0.2	0.3
Vitrinoids	%	63.0	73.1	63.4
Reactive Semifusinoids	%	3.9	3.0	4.2
Exinoids & Resinoids	%	10.5	6.1	6.9
Inert Semifusinoids	%	7.8	6.1	8.3
Micrinoids	%	9.3	8.2	10.9
Fusinoids	%	2.5	2.0	3.3
Mineral Matter	%	3.0	1.5	3.0
Total Reactives	%	77.4	82.2	74.5
Total Inerts	%	22.6	17.8	25.5
Mean Ro	%	0.81	0.88	0.95
Balance Index		0.92	0.63	0.96
Strength Index		2.98	3.21	3.56
Petrographic Stability		33.8	36.6	47.5

APPENDIX C

Calculation of the Composition Balance Index (CBI) and the Strength Index (SI)

This is one example to describe the method followed for calculating CBI and SI (See Section 2.3.2). The blend is prepared with Devco coal and 10% of inert. The columns of optimum ratio reactives/inerts and strength index, contain updated values (73).

Devco coal : Inerts = 17.8; Reactives: 82.2

Devco coal + 10% inert : Inerts = 26.0: Reactives= 74.0

Reactive distribution:	% of Reactives Devco Coal	 Devco coal +10% inert	Optimum Ratio Reacts/Inerts	Strength Index (K) of Type
Type 2	4.6	4.1	5.2	1.80
3	1.5	1.3	4.7	1.98
4	-	-	4.3	2.18
5	-	-	3.8	2.34
6	1.4	1.3	3.5	2.52
7	10.8	9.7	3.1	2.72
8	28.0	25.2	2.8	2.96
9	29.4	26.5	2.6	3.65
10	3.7	3.3	2.4	3.86
11	-	-	2.7	4.53
12	0.2	0.2	3.2	4.75
13	0.6	0.5	4.0	5.89
14	0.2	0.2	5.2	6.93
15	0.4	0.4	7.0	7.09
16	0.7	0.6	9.5	7.21
17	0.2	0.2	12.3	7.38
18	0.3	0.3	14.8	7.53
19	0.2	0.2	17.1	7.67

$$SI = \frac{\sum(\%\text{ of Type} \times K\text{ of Type})}{\%\text{ Reactives}} = \frac{231.93}{74} = 3.13$$

$$CBI = \frac{\%\text{ Inerts}}{\sum(\%\text{ of Type/Optimum ratio, Reactive:Inert})} = \frac{26}{24.03} = 1.08$$

CBI and SI for the Blends used

Coal	Amount of inert blended			
	10%		20%	
	SI	CBI	SI	CBI
Devco	3.13	1.08	3.10	1.44
Madison	3.52	1.11	3.49	1.28
Chisholm	3.14	1.53	3.11	1.77

APPENDIX D

Derivation of the Function G

The function G describes the dependence of coke strength on the petrographic composition of the coal or blend. It is used to give a numerical value to the variable "type of coal" included in the factorial design for the three-coal system.

The following values were taken from the isostability chart by Schapiro et al. (8,10).

SI:	2.5	3.0	3.5	4.0	4.5	5
CBI = 2; Petrographic Stability	0.5	19	32	42	48.5	53
CBI = 1.6 " "	7	27	38	47	54	58
CBI = 1.2 " "	15	32.5	44	53	60	62
CBI = 1.0 " "	17.5	34	46	55	61.5	63

Several empirical functions were tried; the best one is described here.

The stability could be expressed as a function of CBI if SI is kept constant. The values for stability (Stab.) were plotted against CBI. In the range studied (SI : 2.5 - 5 and CBI : 1 - 2) the relation can be expressed with a linear equation which was found by linear regression. The results are as follows:

SI	Equation	Correlation Coefficient
2.5	Stab = - 17.458 CBI + 35.314	- 0.998
3.0	Stab = - 15.127 CBI + 50.059	- 0.988
3.5	Stab = - 14.237 CBI + 60.644	- 0.998
4.0	Stab = - 13.305 CBI + 68.542	- 0.999
4.5	Stab = - 13.390 CBI + 75.415	- 0.997
5.0	Stab = - 10.169 CBI + 73.746	- 0.992

The slopes and intersections of the above equations can be expressed as a function of SI.

$$\text{General equation:}\quad \mathrm{Stab} = m(\mathrm{SI})\ \mathrm{CBI} + b(\mathrm{SI}) \tag{D-1}$$

It can be observed from a plot of m(SI) against ℓn SI that this relation can be approximated by a linear equation. Using linear regression the equation (D-2) was found:

$$m(\mathrm{SI}) = 8.774\ \ell n\ \mathrm{SI} - 25.306 \tag{D-2}$$

(correlation coefficient = 0.946, $R^2 = 0.895$)

The equation for the intersection was found in the same way:

$$b(\mathrm{SI}) = 58.563\ \ell n\ \mathrm{SI} - 15.194 \tag{D-3}$$

(correlation coefficient = 0.976, $R^2 = 0.953$)

The petrographic stability can be finally expressed as a function of the blend composition with the equation (D-4).

$$\mathrm{St} = (8.774\ \ell n\ \mathrm{SI} - 25.306)\mathrm{CBI} + 58.563\ \ell n\ \mathrm{SI} - 15.194 \tag{D-4}$$

$$G = (8.774\ \ell n\ \mathrm{SI} - 25.306)\mathrm{CBI} + 58.563\ \ell n\ \mathrm{SI} \tag{D-5}$$

The values of the function G for the blends of the three coals studied and 10% of inert are as follows:

Blend	SI	CBI	G
Madison + 10% Inert	3.52	1.11	57.87
Devco + 10% Inert	3.13	1.08	50.30
Chisholm + 10% Inert	3.14	1.53	43.65

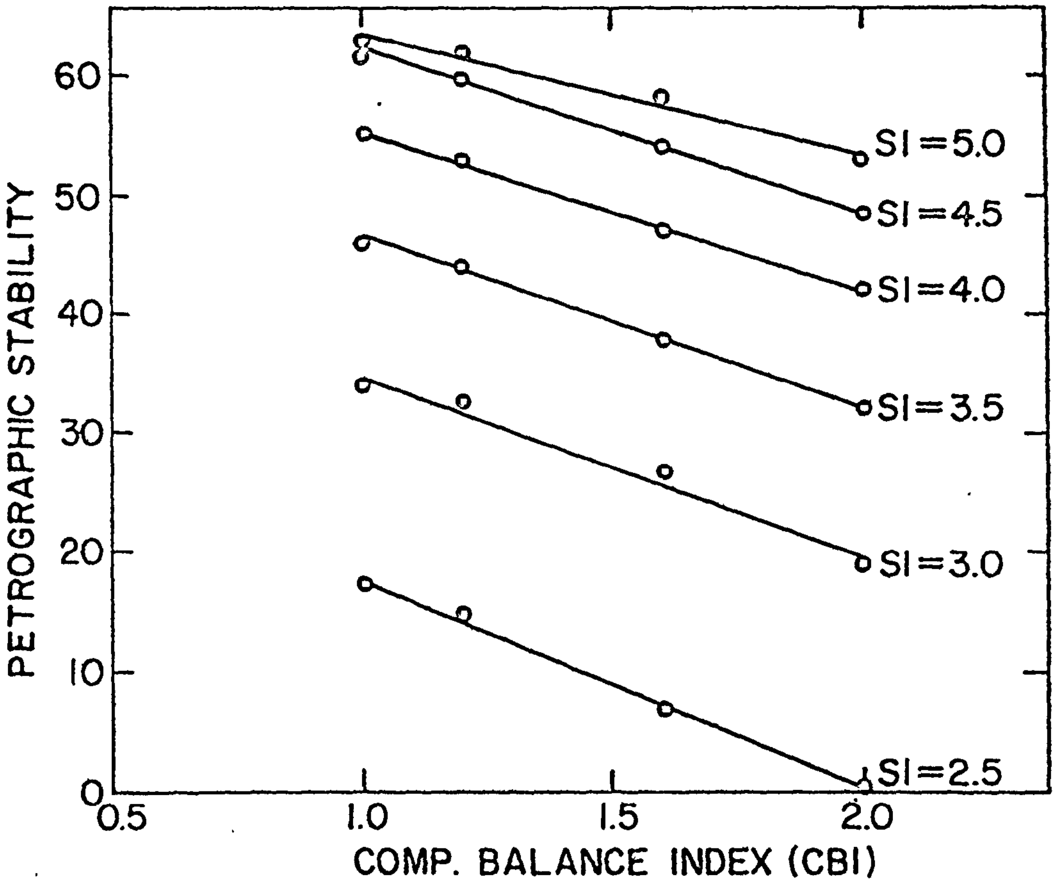

Figure D.1: Relationship among petrographic stability, SI and CBI.

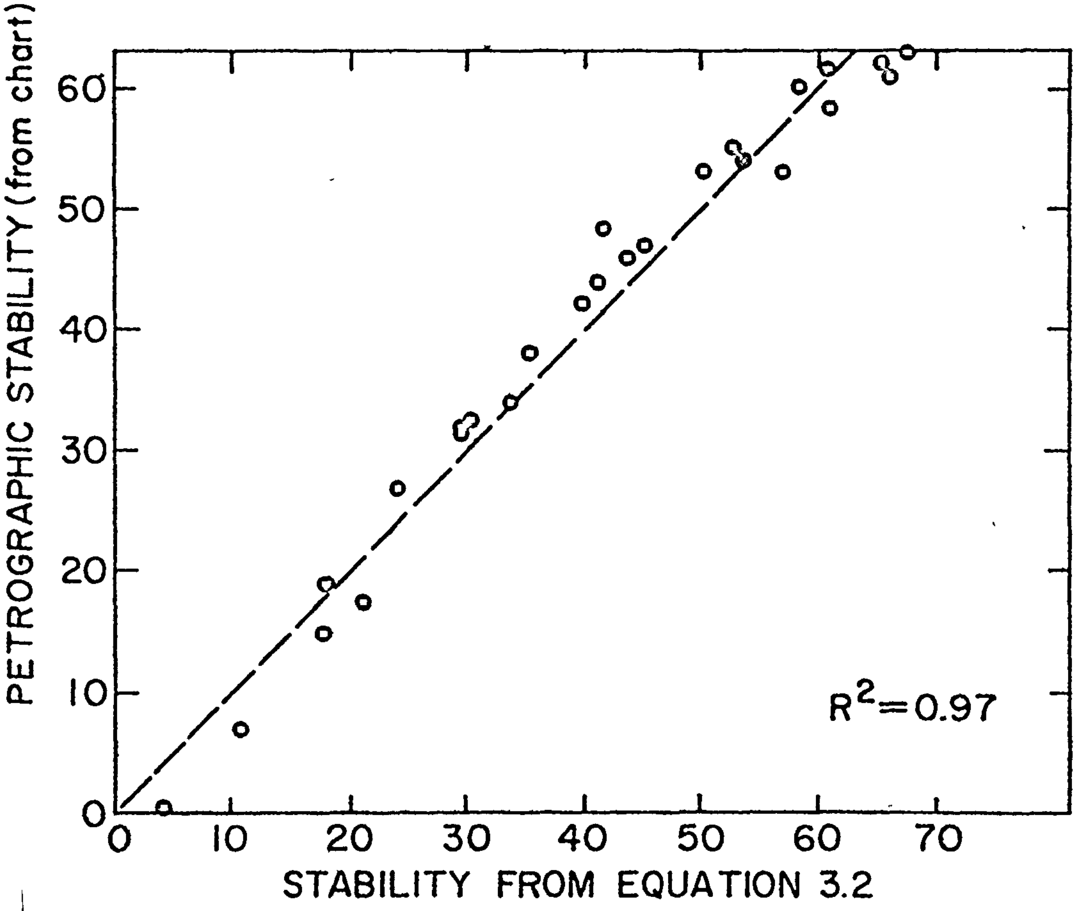

Figure D.2: Correlation between petrographic stability and stability calculated from equation 3-2 (or D-4).

APPENDIX E

Statistical analysis of the model - Devco coal

The following table shows the experimental design for the carbonization of blends of Devco coal and the results of the mechanical tests on the cokes produced. The coded variables are: (1) Heating Rate, (2) Mean Particle Size of the Inert, (3) Amount of Inert Added, and (4) Type of Inert (See Section 3.2.2.1).

Observation	Response (MSI)	Variable			
		(1)	(2)	(3)	(4)
1	41.3	-1	-1	-1	-1
2	31.6	1	-1	-1	1
3	30.6	-1	1	-1	1
4	44.9	1	1	-1	-1
5	19.6	-1	-1	1	1
6	45.5	1	-1	1	-1
7	48.3	-1	1	1	-1
8	17.3	1	1	1	1
9	39.9	-1	-1	-1	-0.251
10	44.5	1	-1	1	-0.251
11	29.4	-1	1	1	-0.251
12	41.7	1	1	-1	-0.251
13	35.1	-1	-1	1	-0.251
14	41.1	1	-1	-1	-0.251
15	36.8	-1	1	-1	-0.251
16	30.5	1	1	1	-0.251
17	30.2	-1	-1	-1	1
18	41.1	1	-1	-1	-1
19	45.7	-1	1	-1	-1
20	30.9	1	1	-1	1
21	45.1	-1	-1	1	-1
22	20.1	1	-1	1	1
23	18.6	-1	1	1	1
24	48.7	1	1	1	-1
25	46.8	1	1	-1	-1
26	38.5	1	1	-1	-0.251
27	41.2	1	1	-1	-0.251
28	40.5	-1	-1	1	-0.251
29	31.1	1	1	-1	1
30	31.7	1	1	-1	1
31	29.2	1	1	-1	1
32	34.2	1	1	-1	1

Observations 25-32 represent replicas of experiments.

The general statistical linear model for expressing the Micro Strength Index for coke produced from Devco coal is given by the equation (3-1).

$$\begin{aligned} MSI = {} & \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_1 x_2 + \beta_6 x_1 x_3 + \beta_7 x_1 x_4 \\ & + \beta_8 x_2 x_3 + \beta_9 x_2 x_4 + \beta_{10} x_3 x_4 + \beta_{11} x_1 x_2 x_3 + \beta_{12} x_1 x_2 x_4 + \beta_{13} x_1 x_3 x_4 \\ & + \beta_{14} x_2 x_3 x_4 + \beta_{15} x_4^2 + \beta_{16} x_1 x_4^2 + \beta_{17} x_2 x_4^2 + \beta_{18} x_3 x_4^2 + \beta_{19} x_1 x_2 x_4^2 \\ & + \beta_{20} x_1 x_3 x_4^2 + \beta_{21} x_2 x_3 x_4^2 + \beta_{22} x_1 x_2 x_3 x_4^2 + \beta_{23} x_1 x_2 x_3 x_4 + \varepsilon \end{aligned} \qquad \text{(E-1)}$$

The following values were taken from the print-out of the program:

Residual = SSE = 35.4197 DF = 8 S^2 = 4.4275 S = 2.1041

R^2 = 0.986

β_i and C_{ii} are listed below

<u>Confidence Intervals for the Parameters</u>

From statistical tables : $t_{0.975,8}$ = 2.306

Parameter (β_i)	C_{ii}	Confidence Interval $\beta_i \pm ts\sqrt{C_{ii}}$
β_0 = 35.6287	0.1268	35.6287 ± 1.7278 ←
β_1 = 1.0750	0.1308	1.0750 ± 1.7548
β_2 = -3.9509	0.1468	-3.9509 ± 1.8590 ←
β_3 = -2.9399	0.1512	-2.9399 ± 1.8867 ←
β_4 = -10.1331	0.0574	-10.1331 ± 1.1625 ←
β_5 = -0.3612	0.1354	-0.3612 ± 1.7854
β_6 = 0.2416	0.1354	0.2416 ± 1.7854
β_7 = 0.0419	0.0574	0.0419 ± 1.1625
β_8 = -3.0999	0.1515	-3.0999 ± 1.8896 ←
β_9 = -1.1956	0.0574	-1.1956 ± 1.1625 ←
β_{10} = -3.8669	0.0574	-3.8669 ± 1.1625 ←
β_{11} = -0.4672	0.1308	-0.4672 ± 1.7548
β_{12} = -0.1706	0.0574	-0.1706 ± 1.1625

Parameter (β_i)	C_{ii}	Confidence Interval $\beta_i \pm ts\sqrt{C_{ii}}$
$\beta_{13} = -0.2419$	0.0574	-0.2419 ± 1.1625
$\beta_{14} = -0.0794$	0.0574	-0.0794 ± 1.1625
$\beta_{15} = -0.5681$	0.1917	-0.5681 ± 2.1244
$\beta_{16} = -0.9394$	0.1974	-0.9394 ± 2.1558
$\beta_{17} = 4.699$	0.2207	4.699 ± 2.2794 ←
$\beta_{18} = 0.7793$	0.2270	0.7793 ± 2.3117
$\beta_{19} = 0.2343$	0.2040	0.2343 ± 2.1915
$\beta_{20} = -0.3773$	0.2040	-0.3773 ± 2.1915
$\beta_{2} = 2.6768$	0.2274	2.6768 ± 2.3138 ←
$\beta_{22} = 0.3691$	0.1974	0.3691 ± 2.1558
$\beta_{23} = -0.0544$	0.0574	-0.0544 ± 1.1625

The parameters β_0, β_2, β_3, β_4, β_8, β_9, β_{10}, β_{17} and β_{21} are significantly different from zero. Using these parameters it can be shown by an analysis of variance that several models fit the data. After several trials it was found that it is possible to reduce the model to the equation (E-2) which used only six parameters.

Parameter β_i	β_0	β_2	β_3	β_4	β_{10}	β_{17}
Variable associated with β_i		Size	Amount	Type	Interaction Amount-Type	Interaction Size-(Type)^2

The new reduced model is:

$$MSI = \beta_0' + \beta_1' x_1 + \beta_2' x_2 + \beta_3' x_1 x_2 + \beta_4' x_3 x_2^2 + \beta_5' x_3 + \varepsilon \qquad \text{(E-2)}$$

where x_1 = amount of inert; x_2 = type of inert and x_3 = mean size of inert

β_0', β_1',....,β_5' = new parameters

The values of the parameters were taken from the print-out of the program. The equation for predicting the MSI is as follows:

$$MSI_C = 35.228 - 2.662x_1 - 10.328x_2 - 3.588x_1x_2 + 3.258x_3x_2^2 - 2.578x_3 \quad \ldots \quad \text{(E-3)}$$

Uncoded equation:

$$MSI_C = 1.53\,AI + 33.35\,F - 0.38\,AI\times F + 19.71F^2MS - 215.04F\times MS + 530.34MS - 3.04F^2 - 39.73 \quad \text{(E-4)}$$

The next table shows the values of the MSI found in the laboratory and the one calculated using the expression (E-3); the last one was also taken from the print-out of the computer program.

Observation N	MSI (Observed)	MSI_C (Calculated)	Residual ($MSI-MSI_C$)
1	41.3	43.95	-2.65
2	31.6	30.47	1.13
3	30.6	31.83	-1.23
4	44.9	45.31	-0.41
5	19.6	17.97	1.63
6	45.5	45.80	-0.30
7	48.3	47.16	1.14
8	17.3	19.33	-2.03
9	39.9	41.96	-2.06
10	44.5	38.43	6.07
11	29.4	33.69	-4.29
12	41.7	37.21	4.49
13	35.1	38.43	-3.33
14	41.1	41.96	-0.86
15	36.8	37.21	-0.41
16	30.5	33.69	-3.19
17	30.2	30.47	-0.27
18	41.1	43.95	-2.85
19	45.7	45.31	0.39

Observation N	MSI (Observed)	MSI_c (Calculated)	Residual ($MSI-MSI_c$)
20	30.9	31.83	-0.93
21	45.1	45.80	-0.70
22	20.1	17.97	2.13
23	18.6	19.33	-0.73
24	48.7	47.16	1.54
25	46.8	45.31	1.49
26	38.5	37.21	1.29
27	41.2	37.21	3.99
28	40.5	38.43	2.07
29	31.1	31.83	-0.73
30	31.7	31.83	-0.13
31	29.2	31.83	-2.63
32	34.2	31.83	2.37

Observations 25-32 represent replicas of experiments.

Calculation of the Pure Error:

	Replicas (MSI)	$(MSI-\overline{MSI})^2$	D.F.	
(a)	44.9; 46.8	1.805	1	
(b)	41.7; 38.5; 41.2	5.927	2	
(c)	35.1; 40.5	14.58	1	
(d)	30.9; 31.1; 31.7; 29.2; 34.2	13.108	4	
		35.42	8	MSSPE = 4.428

ANOVA TABLE

Source	SS	D.F.	M.S.
Model	$\sum(MSI_c)^2$ = 43755.01	6	
Residual	$\sum(MSI-MSI_c)^2$ = 174.20	26	6.7
Pure error	SSPE = 35.42	8	4.428
Lack of fit	SSLOF = 138.78	18	7.71
Total	$\sum MSI^2$ = 43929.21	32	

$$\frac{MSLOF}{MSPE} = \frac{7.71}{4.428} = 1.74$$

$F_{0.95}(18,8)$ = 3.18 (From statistical tables)

Since $F_{0.95}(18,8) > \frac{MSLOF}{MSPE}$ the hypothesis that the parameters dropped from the general model are equal to zero is accepted.

APPENDIX F

Statistical analysis of the model - Three-coal design (Devco, Chisholm, Madison)

The following table shows the experimental design for the carbonization of blends from three coals and the results of the mechanical test on the cokes produced. The coded variables are: (1) Heating Rate, (2) Type of Coal, and (3) Type of Inert.

Observation	Response (MSI)	Variable		
		(1)	(2)	(3)
1	47.5	-1	-1	-1
2	51	1	-1	-1
3	34.3	-1	1	-1
4	36.1	1	1	-1
5	45.7	-1	-0.0647	-1
6	44.9	1	-0.0647	-1
7	38.9	-1	-1	-0.251
8	36.3	1	-1	-0.251
9	27.3	-1	1	-0.251
10	29.2	1	1	-0.251
11	36.8	-1	-0.0647	-0.251
12	41.7	1	-0.0647	-0.251
13	32.6	-1	-1	1
14	31.1	1	-1	1
15	21.9	-1	1	1
16	19.8	1	1	1
17	30.6	-1	-0.0647	1
18	30.9	1	-0.0647	1
19	49.0	-1	-1	-1
20	46.8	1	-0.0647	-1
21	28.5	-1	1	-0.251
22	38.5	1	-0.0647	-0.251
23	41.2	1	-0.0647	-0.251
24	31.3	1	-0.0647	1
25	31.7	1	-0.0647	1
26	29.2	1	-0.0647	1
27	34.2	1	-0.0647	1

The general statistical linear model to fit the data from the above experiments is given by equation (3-4).

$$\begin{aligned} MSI = {} & \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1 x_2 + \beta_5 x_1 x_3 + \beta_6 x_2 x_3 + \beta_7 x_1 x_2 x_3 \\ & + \beta_8 x_2^2 + \beta_9 x_3^2 + \beta_{10} x_1 x_2^2 + \beta_{11} x_1 x_3^2 + \beta_{12} x_2 x_3^2 + \beta_{13} x_2^2 x_3 + \beta_{14} x_2^2 x_3^2 \\ & + \beta_{15} x_1 x_2^2 x_3 + \beta_{16} x_1 x_2 x_3^2 + \beta_{17} x_1 x_2^2 x_3^2 + \varepsilon \end{aligned} \qquad \text{(F-1)}$$

The following values were taken from the print-out:

SSE = 22.5887 DF = 9 S^2 = 2.5099 S = 1.5843 R^2 = 0.987

Confidence Intervals for the Model Parameters

$t_{0.975,9} = 2.262$

Parameter (β_i)	C_{ii}	Confidence Interval $\beta_i \pm ts\sqrt{C_{ii}}$	
β_0 = 36.4558	0.3981	36.4558 ± 2.2611	←
β_1 = 2.0672	0.3976	2.0672 ± 2.2597	
β_2 = -4.1725	0.2578	-4.1725 ± 1.8196	←
β_3 = -7.1722	0.1725	-7.1722 ± 1.8196	←
β_4 = 1.0653	0.2578	1.0653 ± 1.4884	
β_5 = 0.1854	0.1707	0.1854 ± 1.4806	
β_6 = 0.8563	0.1172	0.8563 ± 1.2269	
β_7 = 0.0438	0.1172	0.0438 ± 1.2269	
β_8 = -5.6200	0.6634	-5.6200 ± 2.9189	←
β_9 = 1.6926	0.5997	1.6926 ± 2.7752	
β_{10} = -2.6950	0.6621	-2.6950 ± 2.9160	
β_{11} = -1.8268	0.6013	-1.8268 ± 2.7789	
β_{12} = -2.1837	0.3866	-2.1837 ± 2.2282	
β_{13} = -0.8590	0.2883	-0.8590 ± 1.9242	
β_{14} = 1.8529	0.9901	1.8529 ± 3.5659	
β_{15} = -1.2041	0.2878	-1.2041 ± 1.9225	
β_{16} = -1.2591	0.3866	-1.2591 ± 2.2282	
β_{17} = 2.5732	0.9939	2.5732 ± 3.5727	

The parameters $\beta_0, \beta_2, \beta_3$ and β_8 are significantly different from zero.

Hypothesis: $H_0 = \beta_k = 0$

for $k = 1, \ldots, 17$ but $k \neq 2, 3, 8$

Parameter β_i	β_0	β_2	β_3	β_8
Variable associated with β_i		Type of coal	Type of inert	(Type of coal)^2

The equation (F-2) represents the new reduced model:

$$MSI = \beta_0' + \beta_1' x_1 + \beta_2' x_2 + \beta_3' x_1^2 + \varepsilon \qquad \text{(F-2)}$$

where x_1 = type of coal; x_2 = type of inert

$\beta_0', \ldots \beta_3'$ = new parameters

Substituting the values of the parameters, the coded equation for predicting the microstrength becomes:

$$MSI_c = 37.973 - 5.979x_1 - 7.476x_2 - 4.641x_1^2 \qquad \text{(F-3)}$$

Uncoded equation:

$$MSI_c = 8.48G - 0.09181G^2 - 3.943F - 134.40 \qquad \text{(F-4)}$$

The next table is taken from the print-out of the program.

Observation N	MSI (Observed)	MSI_c (Calculated)	Residual ($MSI-MSI_c$)
1	47.5	46.79	0.71
2	51.0	46.79	4.21
3	34.3	34.83	-0.53
4	36.1	34.83	1.27
5	45.7	45.82	-0.12
6	44.9	45.82	-0.92
7	38.9	41.19	-2.29
8	36.3	41.19	-4.89
9	27.3	29.23	-1.93

Observation N	MSI (Observed)	MSI_C (Calculated)	Residual ($MSI-MSI_C$)
10	29.2	29.23	-0.03
11	36.8	40.22	-3.42
12	41.7	40.22	1.48
13	32.6	31.83	0.77
14	31.1	31.83	-0.73
15	21.9	19.88	2.02
16	19.8	19.88	-0.08
17	30.6	30.86	-0.26
18	30.9	30.86	0.04
19	49.0	46.79	2.21
20	46.8	45.82	0.98
21	28.5	29.23	-0.73
22	38.5	40.22	-1.72
23	41.2	40.22	0.98
24	31.3	30.86	0.44
25	31.7	30.86	0.84
26	29.2	30.86	-1.66
27	34.3	30.86	3.34

Observations 19-27 are replicas of some experiments.

Calculation of the Pure Error:

Replicas (MSI)	$(MSI-\overline{MSI})^2$	D.F.	
(a) 47.5; 49.0	1.125	1	
(b) 44.9; 46.8	1.805	1	
(c) 27.3; 28.5	0.720	1	
(d) 41.7; 38.5; 41.2	5.927	2	
(e) 30.9; 31.3; 31.7; 29.2; 34.2	13.108	4	
	22.685	9	MSSPE = 2.52

ANOVA TABLE

Source			D.F.	M.S.
Model	$\sum(MSI_c)^2$	= 36250.818	4	
Residual	$\sum(MSI-MSI_c)^2$	= 98.1154	23	4.27
Pure error	SSPE	= 22.685	9	2.52
Lack of fit	SSLOF	= 75.4304	14	5.39
Total	$\sum MSI^2$	= 36346.240	27	

$$\frac{MSLOF}{MSPE} = \frac{5.39}{2.52} = 2.14$$

$F_{0.95}\ (14,9) = 3.03$

Since $F_{0.95}(14,9) > \frac{MSLOF}{MSPE}$ the hypothesis that the parameters dropped from the general model are equal to zero is accepted.