THE FORMATION AND INFLUENCE OF THE SLAG PHASE
DURING THE REDUCTION OF SOME COMMERCIAL IRON ORE PELLETS

by

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ABSTRACT

An experimental investigation has been conducted to study the factors influencing the formation and behaviour of the primary slag phase formed in commercial iron ore pellets when reduced under conditions simulating those encountered in the iron blast furnace. Weight loss during reduction, metallographic and electron microprobe analysis techniques have been employed. Possible implications for blast furnace operation are discussed.
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CHAPTER 1
INTRODUCTION

A very large amount of research has been carried out on the reduction behaviour of iron ores. These studies have assisted greatly in the understanding of the blast furnace process.

Until recently, however, the great majority of studies have been made under isothermal conditions with gases of fixed compositions. Due to the proposition of a thermal reserve zone in the blast furnace, most frequently experiments were carried out at temperatures near and below 1000°C. Under these experimental conditions, which are not consistent with blast furnace operation, the interpretation of data became less difficult.

As burden materials descend in the blast furnace, they are continuously heated by the ascending gas flow. The composition of the gas phase, with which they are contacted, also changes continually due to gas/solid reactions. These dynamic conditions, combined with the forces of gravity and forces due to gaseous pressure gradients would influence physiochemical changes and make the behaviour of iron ore specimens quite dissimilar to that observed in laboratory testing under isothermal conditions with gas of constant composition.

During the past decade, a number of commercial blast furnaces have been quenched, so yielding valuable information about the internal state
of the operating blast furnace.

These studies have shown the existence and configuration of a softening-melting zone within the furnace to be of prime importance to consistent and efficient operation. The nature of this zone is determined by the raw materials and gas distributions, the physio-chemical behaviours of raw materials at various temperatures after certain extents of reaction, and of course, the operating practice. The importance of the primary slag phase has been recognized in these studies but little is known about the mechanism of its formation.

This study involves the reduction of a number of different commercial iron ore pellets under dynamic conditions which have been based upon quenched furnace data. By simulating the most realistic of reduction conditions, it is possible to more fully appreciate the behaviour of raw materials as they move through the blast furnace to the point of melting. In particular, attention has been paid to the development of and influences of the primary slag phase.

By varying the experimental temperature and gas composition as a function of time, some understanding of the influences of raw materials and raw material distribution at the blast furnace stockline can be gained.

Since the blast furnace process is complicated by many influences other than those investigated here, the results of this investigation are of limited significance. They do, however, illustrate the strong influence of reduction conditions upon raw material behaviour and indicate the possible influence of burden distribution upon blast furnace performance.
2.1 Introduction

In the 1950's and 1960's, very significant advances were made in blast furnace productivity and stability of operation. These advances were largely due to raw material beneficiation and preparation techniques, fuel injection and the development of improved control methods\(^{(1)}\).

While plant trials and plant developments allowed good control of furnace operation, the internal nature of the blast furnace remained largely a mystery due to the great difficulties associated with sampling by "through the wall techniques".

During the years 1965-75, Russian and Japanese investigators\(^{(2-6)}\), quenched and dissected a number of operating experimental and commercial blast furnaces in order to study the internal state of the blast furnace. These furnaces ranged in size from 0.5 m to 8.4 m in hearth diameter and were quenched with either water or nitrogen.

2.2 Quenched Furnace Observations

Experimental blast furnaces (hearth diameters 0.5' m to 0.8 m) proved to be too small in scale to clarify the blast furnace process sufficiently\(^{(3)}\) and the results so obtained will not be considered further.

Of the ten operational furnaces quenched, nine were quenched with water. The use of water as a quenching agent resulted in considerable
modification of the internal state of the furnace. These modifications included reoxidation of burden materials, leaching of some chemical species (e.g., alkali compounds), allutriation of some fine materials and other chemical and physical changes due to the modification of temperature distribution.

One furnace was completely quenched with nitrogen and even this costly process was unable to avoid all undesirable modifications to the operating state due to the extended period required for quenching.

Despite the great pains taken by investigators to develop correction factors for these changes \(^4,5\), it is difficult to give any great quantitative credence to many of the results reported. This is particularly true in the case of chemical distribution data, where for example, ferrous materials have been thought to exhibit reoxidation degrees as high as 30 - 40\% \(^5\).

Although the reported quantitative data from these experiments must be viewed cautiously, some very major advances in the qualitative understanding of the internal state of the blast furnace have been made.

In each of the furnaces investigated, three distinctly different yet intimately inter-related physical zones have been identified. These three zones may be described briefly as follows:

(a) **Lumpy zone**: the zone where ores descend as lumps in the furnace after charging.

(b) **Softening-melting zone**: the zone where ores soften and melt (down), commonly bounded by isotherms at approximately 1100°C and 1450°C.

(c) **Dripping zone**: the zone where molten metal and slag flow through a bed made up solely of coke prior to being cast from the furnace.
Considerable variations in the geometry of these zones has been observed but the investigators feel that they have been able to account for these variations in terms of furnace control parameters and raw material distribution regimes. Figure 2.1 shows two significantly different geometries.

The fundamental requirement of good blast furnace operation is efficient contact of solid and gaseous phases for heat and mass transfer. In this respect, most ironmaking researchers and operators now recognize the geometry and stability of the softening-melting zone to be of the greatest importance. Under normal conditions of operation, the softening-melting zone always consists of a number of approximately axially concentric yet vertically separated annuli of compressed and partly fused ferrous material as shown in Fig. 2.1. These slab-like portions consist of metallic iron, a primary slag phase rich in FeO and unreduced wustite. They are quite impermeable to furnace gases but are separated by layers of highly permeable coke. These "coke slits" in the softening-melting zone determine the zone's critical behaviour as distributor of furnace gases from the dripping zone to the lumpy zone where the majority of the reduction processes must occur.

Figure 2.2 allows the strong correlation between melting zone geometry and furnace temperature distribution to be clearly seen.

Figure 2.3 shows the observed correspondence between temperature and reduction state of ore materials.

Three major characteristics of any softening-melting zone can be identified: its stability, its shape, and its extent and the resistance which it offers to the flow of ascending furnace gases. These three factors are now discussed briefly:
Fig. 2.1 Distributions of softening-melting layers in the blast furnace. After Kanbara (4)

Fig. 2.2 Estimated temperature distributions in the blast furnace. After Kanbara (4)
Fig. 2.3 Distribution of reduction degree. After Shimomura (5). (See Figs. 2.1, 2.2 for comparison.)
(a) The stability of the zone depends on:
   i) the consistency of raw material chemistry and size distribution.
   ii) the consistency of raw material distribution at the furnace stockline.
   iii) the consistency of furnace control parameters such as wind rate, blast temperature, etc.
   iv) the thermal state of the furnace and the consistency of fuel rate.

(b) The shape of the zone depends on:
   i) the geometry of ore and coke layers in the lumpy zone. This results from the burden distribution technique, charging sequence and such charge parameters as ore/coke ratio and individual batch weights.
   ii) the furnace control parameters such as oil/total fuel ratio, wind rate and level of top pressure employed. Some investigators \(^{3,5}\) have pointed out that the shape of the zone may specifically reflect such things as total fuel rate (kg fuel used per ton of hot metal produced) and unit productivity (units of iron produced per unit of furnace volume day).
   iii) the size of the blast furnace. The presence of furnace walls (and furnace lines) are more important in small furnaces since the retention of layers near the furnace walls is often poor.

(c) The permeability of the zone:
   i) The nature and extent of the zone are dependent upon the
condition of material entering from the lumpy zone. This is strongly related to the reduction efficiency of the lumpy zone.

ii) The nature of materials in and leaving the softening-melting zone is also dependent on their chemical and physical behaviour at elevated temperatures (> 1100°C) and their melting properties.

iii) The resistance to gaseous flow offered by the zone is known to be substantial but few details are available. Figure 2.4 shows the pressure profile of Fukuyama No. 5 Blast Furnace (9). It will be noted that some 50% of the total pressure drop is ascribed to the softening-melting zone. This zone, therefore, provides a very significant limitation to the wind volume which can be satisfactorily blown through the furnace. Such a limitation also implies a significant limitation to furnace productivity.

Optimization of furnace operation is currently viewed by Japanese workers (3;8) (who have attained the world's lowest fuel rates and highest productivity at this time) as being consistent with the attainment of a stable softening-melting zone of the right shape and of the lowest possible resistance to gas flow.

While most of the factors influencing stability and to a lesser extent shape of the zone are well recognized and at least partially understood, the factors influencing the structure and extent of the softening-melting zone itself are only poorly understood.

This is largely due to the fact that prior to the observations made in quenched furnace investigations, by far the greatest volume of
Fig. 2.4 Pressure profile of Fukuyama No. 5 BF. (9)

Fig. 2.5 Phase diagram for the system $\text{Al}_2\text{O}_3$-$\text{SiO}_2$. After Meadowcroft (11).
research into the behaviour of ferrous burden materials were made at temperatures up to 1050°C and under conditions of constant temperature and gas composition. This poor state of affairs is well reflected by the range of standard testing techniques accepted by industry as reviewed by Kortman and Burghardt in 1977(10).

Several of the authors who have investigated quenched operating furnaces (3-7) have questioned the ability of existing standard testing techniques to satisfactorily simulate the behaviour of burden materials in the iron blast furnace. Shimomura et al. (5) have concluded that existing test methods should be modified to conform more closely to the dynamic thermal conditions prevailing within the furnace.

In all studies of the softening-melting zone of quenched furnaces, the investigators ascribe great importance to the presence and nature of a primary slag phase rich in FeO. Sasaki et al. (6) concluded from their study in 1973 that the formation of such a slag phase was not understood and recommended that researchers should in future extend the temperature ranges for research into iron ore reduction in order to observe and study the primary slag phase.

Subsequent sections of this review are devoted to the formation and influence of the slag phase during iron ore reduction.

2.3 Factors Influencing Slag Formation

2.3.1 Introduction

The gangue components in iron ores and coke ash are the most important contributors to blast furnace slag. Silica and alumina are usually the predominate constituents of both gangue and ash. Figure 2.5(11) shows the binary SiO$_2$-Al$_2$O$_3$ phase diagram. The line A indicates an average North American coke ash composition while the region B indicates
a typical range of ore-gangue compositions. [Note that the presence and influence of other constituents such as the oxides of calcium, magnesium and the alkali metals are ignored for the present.]

Combining these sources of silica and alumina in the ratio indicated by a "good" coke rate of 500 kg/thm* yields a product in the range indicated by C in Figure 2.5.

Such a composition is clearly not liquid at ironmaking temperatures and must be modified in order to be able to flush slag from the furnace. The fluxing agents lime and magnesia must be added to the furnace charge in order to obtain a slag that is fluid at ironmaking temperatures. The pseudo-ternary diagram SiO$_2$-CaO-MgO (at 10% Al$_2$O$_3$ level) is shown in Figure 2.6(12) to illustrate the significant reduction of liquidus temperature caused by CaO or MgO additions. These additions can also greatly reduce the viscosity and increase the desulphurizing capacity of the slag.

Two methods are available for flux addition; the first and simplest is by charging limestone and dolomite in lump form while the second involves grinding and mixing with iron-bearing materials prior to an agglomeration process. The second method is advantageous in that it avoids the generation of CO$_2$ gas by the calcination of limestone and dolomite (which are strongly endothermic reactions) in a critical region of the furnace. Other advantages claimed for this method will be mentioned in Section 2.4.

Silica and alumina are known as "acidic oxides" and so iron ores having gangue rich in these oxides are termed "acid ores" and slags rich

* 500 kg/thm = 500 kg of coke charged to the blast furnace per tonne of hot metal produced.
Fig. 2.6  Phase relations at liquidus temperatures in the 10% Al₂O₃ plane of the system CaO-MgO-Al₂O₃-SiO₂, after Osborn, DeVries, Gee, and Kraner. Abbreviations used have the following meanings: Mer = merwinite, Mon = monticellite.
in SiO₂ and Al₂O₃ are called "acid slags".

Lime and magnesia are known as basic oxides and so ore materials and slags rich in these oxides in relation to acid oxides are said to be "basic" or "fluxed".

Ironmakers have found the use of empirical compositional indices useful in simplifying the description of many aspects of slag behaviour.

Several indices exist, the simplest being the V ratio where \( V = \frac{\text{wt}\% \text{CaO}}{\text{wt}\% \text{SiO}_2} \).

The B ratio, where \( B = \frac{\text{wt}\% \text{CaO} + \text{wt}\% \text{MgO}}{\text{wt}\% \text{SiO}_2 + \text{wt}\% \text{Al}_2\text{O}_3} \), is however, generally more useful and will be used wherever possible in this work.

The B ratio for tapped blast furnace slag commonly falls in the range 0.95 to 1.25, the exact value depending upon individual plant practice.

The B ratio may also be used to describe the slag making oxides present in individual raw materials. Here the value of B may range from 0 to 4.0. Certain ranges of basicity are avoided because they are known to produce physically weak agglomerates which are unsuitable for blast furnace use. No precise value of B ratio can be given for such behaviour due to the behavioural variations which occur from ore to ore.

Since the primary slag phases produced in the upper levels of the blast furnace are the result of individual ore type compositions, and do not mix at this level, a fairly clear distinction between "acid" and "basic" raw materials can be made. It should, however, be noted that variations can occur within each of these groups - particularly at the basic end of the scale.

The development of primary acid and basic slags will now be considered separately for the case of pelletized material. The slag development may be different in the case of lump ores because of higher gangue levels.
and differing gangue distribution. Differences also arise in the case of sintered material due to larger particle size and also due to the presence of coke breeze in the sinter mix. This may cause some reduction to wustite followed by the formation of fayalite or ferrosilicate glass (14).

Lump ore and sinter, however, are not the subject of this work and so the following discussion will be restricted to pelletized materials.

Coke ash and lump charged limestone are mostly fused at lower levels of the blast furnace working volume than are ore-associated primary slag products (4,15) and so will not be considered further.

Some workers (6,32) have recently suggested that gaseous species such as H₂S, SO₂ and K may influence primary slag development but such influences are beyond the scope of this work and will not be considered here.

2.3.2 Acid Pellets

(a) Gangue Content and Distribution

The gangue content, its nature and distribution in any pelletized product are primarily determined by:

(i) the distribution and mineralogical nature of the gangue phase in the parent ore body and,

(ii) the extent to which the ore must be ground to effect sufficient liberation of the ore to allow beneficiation to the level required.

(b) Balling

To obtain satisfactory strength in pellets prior to firing, a bonding agent such as bentonite is normally added to the concentrate in proportions of up to approximately 10 kg per ton of pellet product.
A typical analysis of bentonite is given below:

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>59.90</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>19.80</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.90</td>
</tr>
<tr>
<td>MgO</td>
<td>1.30</td>
</tr>
<tr>
<td>CaO</td>
<td>0.60</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.40</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.20</td>
</tr>
<tr>
<td>H₂O</td>
<td>6.5 - 7.5</td>
</tr>
</tbody>
</table>

In view of this composition, bentonite must be considered a slag-making material but its level of usage is so low as to render it relatively unimportant.

(c) **Induration**

Induration of the pellets is required in order to obtain a product of sufficient strength to withstand the rigors of handling and the blast furnace environment.

Induration temperatures are commonly of the order of 1200 - 1300°C but the exact temperature, atmospheric conditions and residence time at peak temperature are determined by the nature of the particular ore and specifications of the pellets.

Figure 2.7(17) indicates the bonding regimes which are possible for acid pellets of magnetite concentrate and the conditions under which each type of bond can be obtained.

In practice, the superior strength and reducibility of haematite pellets demand that "green" magnetite pellets be indurated under quite oxidizing conditions in order to obtain a haematite product. For this
Fig. 2.7 Different bonds between single grains in a pellet made from magnetite concentrate, according to Tigerschiöld. (17)

Fig. 2.8 Phase diagrams for the system iron oxide-SiO$_2$ in contact (a) with metallic iron and (b) in air. Compositions of condensed phases have been projected onto the joins FeO-SiO$_2$ and FeO·Fe$_2$O$_3$-SiO$_2$, respectively.
reason, and thermal advantages (complete combustion of fuel and the exothermic oxidation of magnetite) haematite pellets are made from magnetite concentrates. It has been claimed that haematite plays an important role in the bonding of fired acid pellets.

By means of metallographic analysis, Cooke et al. (18, 19) have been able to demonstrate that recrystallization processes can contribute greatly to strengthening. Due to this effect, both firing temperature and duration of firing are of major importance to pellet properties, both in terms of recrystallization processes and the extent of sintering associated with interparticle bonding.

There are three major methods of pellet induration, the Shaft Furnace Process, the Straight Grate Process and the Grate Kiln Process. Since the thermal cycle associated with each is different, product properties also differ from process to process.

(d) Nature of Gangue in Acid Pellets

Under the thermal and atmospheric conditions employed during induration to produce haematite pellets, silica gangue particles remain essentially inert (20). Their size, distribution and composition therefore depend upon the characteristics of the parent ore body and the comminution and beneficiation processes employed during concentration.

2.3.3 The Formation of Fayalite

Figure 2.8 shows the pseudo-binary systems (a) "FeO"-SiO₂ and (b) FeO . Fe₂O₃ - SiO₂.

Fayalite, 2FeO . SiO₂, is shown as an intermediate compound in Figure 2.8a. No intermediate compound exists in the system FeO . Fe₂O₃ - SiO₂.

The formation of fayalite from pure ferrous oxide and silica powders
has been studied by Baldwin \(^{(21)}\). The mixtures used in his work were in the proportions of pure fayalite. The results of his work may be summarized as follows.

(a) **Grain size:** little formation of fayalite occurred in the solid state at 1100°C during a reaction time of one hour for particle mixtures of grain size greater than B.S. 200 mesh (i.e., > 0.076 mm).

(b) **Temperature:** using particles of less than 0.076 mm grain size, no fayalite formed at 700°C even after prolonged heating (24 hours), but at temperatures of 800°C and above, interaction did occur in the solid state.

(c) **The rate of fayalite formation was enhanced by the addition of 10% alumina.** At temperatures in excess of 1050°C hercynite (FeO·Al\(_2\)O\(_3\)) was formed.

(d) **At temperatures less than 1200°C,** the formation of fayalite was retarded by the addition of 10% magnesia which acted as an inert diluent. The addition of dolomite had a similar effect.

(e) **Upon the addition of 10% lime,** the formation of fayalite was completely suppressed at all temperatures. With lime/silica ratios \(\leq 1.0\), part of the ferrous oxide formed iron monticellite \((\text{CaO}·\text{FeO}·\text{SiO}_2)\). With lime/silica ratios in excess of 2.0, ferrous oxide was completely eliminated from silicate complexes.

(f) **Lime decomposed fayalite at temperatures in excess of 800°C.**

El-Geassy et al. \(^{(22)}\) have reported the formation of fayalite during the reduction of iron ore pellets in the temperature range 700 - 1100°C using CO, H\(_2\) and a 50/50 mixture of CO and H\(_2\) as reducing gases. Pellets made of pure Fe\(_2\)O\(_3\) (> .074 mm) and amorphous silica (> .074 mm) exhibited fayalite formation at temperatures in excess of 800°C. The formation of
Fayalite was always accompanied by a retarded reduction rate. When crystalline quartz was substituted for the amorphous silica, fayalite formation was not observed and the reduction rate was in fact enhanced. The authors report similar behaviour for each of the three reducing gases used.

The melting point of pure fayalite is 1205°C (12) (see Figure 2.8a). At temperatures in excess of 1200°C, many authors report the existence of iron silicate slag but the mechanism of formation has not been reported.

The properties of fayalite will be discussed further in Section 2.4.2.

2.3.4 Basic Pellets

The comminution and beneficiation steps involved in the production of basic pellets are generally similar to those for acid pellets with the exception that generally lower silica levels are required in order to avoid the generation of an excessive slag content with which are associated heavy energy and economic penalties.

The addition of bentonite as a bonding agent may not be required in some cases due to the acceptable bonding behaviour of lime (16).

The complex processes associated with the formation of the slag phase in basic pellets have been recently reviewed by Björkvall et al. (23). The following summary is based on their review of the literature.

(a) Magnetite ores: While variations occur from one magnetite ore type to another, the formation of a bonding phase usually starts with the exothermic oxidation of fine magnetite particles. The heat generated by this oxidation accelerates limestone calcination.

(b) Hematite ores: Since no exothermic oxidation reaction occurs, the
kinetics of limestone calcination are somewhat slower.

Following the calcination of limestone, the formation of calcium ferrite (CaO Fe2O3) is normally observed between contacting particles of lime and haematite for CaO/SiO2 ratios in excess of 0.5. This process is active at temperatures of up to about 1150 - 1200°C at which point calcium ferrite reacts with haematite to form calcium-diferrite (CaO . 2Fe2O3). The melting points of calcium-ferrite and of the calcium-ferrite-calcium-diferrite eutectic are 1216°C and 1185°C, respectively. The first liquid is generally formed at about this stage. With time and further increase in temperature, liquid ferrite reacts with silica particles to form a complex iron calcium silicate which thus constitutes the bonding phase.

When dolomite is added, calcination is followed by the formation of magnesio ferrite (MgO . Fe2O3) by solid state reaction in air at temperatures greater than 700°C. At temperatures in excess of 1100°C, and in the presence of MgO the formation of a spinel phase (Mg, Fe)O . Fe2O3 is observed.

Björkvall et al. (23) have noted that dolomite fluxed pellets from magnetite ores may display heterogeneities after induration. They propose that oxidation of magnetite to haematite in surface regions of the pellet occurs at low temperatures (< 1150°C) and that due to the limited mobility of oxygen ions and the high degree of stoichiometry of haematite, oxidation depends only upon the diffusion of Fe2+ and Fe3+ ions in the magnetite.

In central regions of the pellet, Björkvall et al. propose that the formation of liquid phase precedes oxidation and that in this region both Fe3+ and oxygen ions diffuse in the liquid slag phase to those
surfaces most suitable for haematite growth. The presence of a liquid/air interface is required for the transfer of oxygen to the condensed phases.

While a mineralogical study has been made by Murav'ev et al. (24) of basic slags found in a nitrogen quenched blast furnace, the literature contains little information regarding the development of liquid slag phase in basic pellets charged to the blast furnace.

2.4 Influences of the Slag Phase During Reduction

2.4.1 Degradation at Low Temperatures

During the early stages of reduction of haematite pellets, they swell by up to 20% of their initial volume. This increase in volume is inevitable and is associated with the haematite to magnetite phase transformation and is known as "normal swelling".

Depending upon composition and induration conditions, however, some pellets may suffer loss of coherency and strength in the 500 - 700°C temperature range. This phenomenon is known as low temperature breakdown or "LTB" and is thought (25,26) to be associated with internal stress and strains generated by anisotropic dimensional changes associated with the haematite to magnetite transformation.

Factors influencing resistance to low temperature breakdown are induration conditions, grain size, cooling rate, and the amount and distribution of gangue phases.

The exact influence of grain size is not clear, contradictory evidence having been reported by Stone and Daniell (27,28) and by Nabi (29).

The addition of both acidic and basic slagmaking materials have been shown to enhance reduction strength during the haematite to magnetite transformation. The mode of strengthening is, however, not known.
Björkvall et al. (23) have shown that in basic pellets, having a lime/silica ratio in excess of unity, recrystallization of the basic bonding slag phase can contribute to loss of strength and degradation during early stages of reduction.

Pellets showing volume changes in excess of + 20% are said to exhibit "abnormal swelling". This effect can be caused by improper firing of magnetite pellets, the presence of alkali metals or alkali metal compounds (carbonates or oxides) during reduction or the presence of impurities in the wustite lattice during reduction. Abnormal swelling is frequently associated with the formation of filamentary iron whiskers.

This subject has been reviewed in a recent work by El Kasabgy (30) and will not be pursued further here.

2.4.2 Retardation of Reduction by Slag Phase

This section reviews the influences of the slag phase observed to occur within the volume of a single pellet. The following sections (2.4.3 and 2.4.4) will examine slag influences with respect to the larger scale of the softening-melting zone of the blast furnace.

Several authors have recently reported that the reduction of iron ores is retarded at temperatures in excess of 1100°C in the presence of a slag phase (31-35). The mode of retardation is, however, not simple and can arise from any or a complex combination of the following factors depending upon the material and conditions of reduction in this complex heterogeneous system.

(a) Reduction of Porosity by Slag Phase

Continued reduction of a partially reduced pellet at an advanced stage of reduction requires the continued access of reducing gas to un-reduced central regions of the pellet. This requires diffusion of gases
through the pore network of the reduced portion of the pellet. Several authors have reported (1, 31-35) that the formation of large volumes of liquid slag phase during reduction can retard reduction rates by decreasing the effective porosity of the pellet. This effect has been reported for both acidic and basic pellets. Takahashi et al. (32) have reported that the effect is particularly pronounced when the melting point of the slag phase is lowered by the addition of sulphur.

Sasaki et al. (6) have observed that in some cases, the slag phase may migrate and accumulate in large volumes at levels near the surface of the pellet. Such a local concentration of slag can act as a very effective non-porous barrier to continued reduction.

It should be noted here that the quantity of gangue material present in the pellet can strongly influence the volume of slag available to retard reduction. The influence of gangue volume should also be borne in mind with respect to parts (b) and (c) of this section below.

(b) Reduction of Wustite Surface Area Available for Reduction

At temperatures in excess of 1200°C, unreduced wustite grains have frequently been observed to coarsen and recrystallize in the presence of a slag phase (1,32,35). Coarsening of the wustite grains reduces their surface area available for contact with reducing gas. In the presence of liquid slag, however, large surface areas of the wustite grains become covered with highly wetting slag. The presence of slag causes further very significant decrease in active wustite surface area available for gaseous reduction.

(c) The Reduction of Iron-Containing Slags

The formation of fayalite was introduced in Section 2.3.3. The kinetics of fayalite reduction by H₂, CO and CO + H₂ mixtures have been
investigated by Gaballah et al. (36). They found that fayalite could be rapidly reduced by H₂ at 1000°C but was practically un-reducible in pure CO. Mixtures of H₂ and CO produced intermediate results.

While the activity of FeO in the liquid FeO-SiO₂ and FeO-CaO-SiO₂ systems has been determined for a number of temperatures and over wide ranges of composition (37-39), the kinetics of gaseous iron reduction from such slags has not received attention.

Sasaki and Soma (40,41) have recently investigated reduction by solid carbon in the systems FeO-SiO₂ and FeO-CaO-SiO₂.

Their results indicate that for the system FeO-SiO₂:

(i) the rate of reaction is strongly temperature dependent in the range 1400-1600°C,

(ii) the reaction rate is strongly retarded by the addition of silica in the range 0-30% SiO₂.

In the system FeO-CaO-SiO₂:

(i) the rate of reaction is strongly temperature dependent in the range 1400-1600°C,

(ii) the rate of reaction increases with increased basicity (CaO/SiO₂) in the range 0.5-2.0 at 1400-1500°C.

(d) The Morphology of the Metal Phase

It has long been recognized (42) that the size and morphology of metal phase produced during reduction is strongly dependent upon temperature. Turkdogan (1), however, has recently pointed out that, in view of the relationships between pore structure and the diffusion rate of a gas, the temperature range of metallization can be of great importance to reduction kinetics.

While Turkdogan noted that subsequent rise in temperature did not
alone readily change an existing pore structure, he did note that significant changes to metal phase morphology could be caused by the presence of an acid slag phase. In experiments at 1300°C he reports the development of an almost continuous dense iron envelope at the surface of acidic pellets. Such a shell was not observed in the case of similarly reduced basic pellets. Turkdogan concluded that the formation of an iron shell was a function of slag phase basicity.

Similar observations have been made by several other authors\(^{(43,44)}\). In each case, the formation of a dense iron shell has been reported to have effectively terminated gaseous reduction.

2.4.3 Softening Behaviour

While softening behaviour is generally thought to be associated with the melting point of the slag phase, the high level of inconsistency evident in reported results stands testament to the complexity of the problem.

In a recent report, Barnaba\(^{(45)}\) reported that softening behaviour is strongly influenced by:

(a) the thickness of metallized layer formed during reduction,
(b) the basicity of the slag phase - he reported optimum behaviour in the range $\text{CaO}/\text{SiO}_2 = 1.65 - 1.80$, and
(c) the prior reduction history of the sample.

Several attempts have recently been made to substitute magnesia for lime in basic materials in order to increase the melting point of the slag and so improve softening behaviour without further increasing the basicity of the slag phase (recall that basicity is often defined as $B = \frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$). While the results of these attempts are not yet conclusive, several encouraging indications have been reported\(^{(31,45,46)}\).
In the blast furnace, softening has been observed to occur at temperatures in excess of approximately 1100°C (4-6). Quenched furnace observations and laboratory experiments now concur on the following points.

(a) Softening under load causes decrease in bed porosity and a resultant decrease in the rate of further reduction.
(b) When compressed, pellets containing liquid slag may rupture and expel FeO-rich slag into the pellet bed (45,47).
(c) Slag materials expelled by ruptured pellets come into contact with the CO-rich bulk furnace gas stream and may be rapidly reduced. The formation of solid reduction products in the inter-pellet spaces may further reduce the porosity of the bed (45).

The softening of burden materials is an extremely complex phenomenon, but the results of laboratory and quenched furnace investigations indicate that very significant productivity gains may be possible if the softening behaviour of raw materials can be confined to a narrow temperature range after a high degree of reduction has been attained. Such a temperature range should be as close to the temperature of the melting zone as possible in order to minimize the resistance to gas flow associated with the existence of a large, compacted softening zone.

2.4.4 Meltdown Behaviour

Sasaki et al. (6), after examining quenched blast furnaces and performing laboratory experiments, concluded that melting in the blast furnace was achieved by two methods:

(a) Reduced ore materials in contact with coke were carburized rapidly and became molten at temperatures as low as 1330°C.
(b) Ore materials remote from coke particles were carburized by the furnace gas stream at a lower rate and did not melt down until a tem-
perature of approximately 1500°C is attained.

Since these early observations, several laboratory investigations have been made in which the slag phase has been reported to play an important role.\(^{32,45,47,48}\)

Omori and Takahashi\(^{32}\) have tested a number of acid, basic and cold bond pellet types. They reported gangue melting point, basicity and previous reduction history to be the major factors influencing the temperature at which meltdown began. Temperatures in the range 1250 - 1485°C were reported for acid pellets and those for basic pellets lie between 1420 and 1470°C. (The variation in gangue melting point for these basic pellets was only 20°C.)

Basic sinters showed only 50°C variation in initial meltdown temperature over the basicity range 1.2 - 2.2 (CaO/SiO\(_2\)), with a maximum temperature of 1450°C at a basicity of between 1.5 and 1.8.

Barnaba\(^{45}\) has attempted to obtain a completely molten product at temperatures of up to 1400°C by contact of reduced and softened burden materials with coke. He was unable to obtain molten iron product and observed metallic carburization to no more than 0.2% C even in cases of closest coke/ore contact. Barnaba attributed this behaviour to the presence of the slag phase which had moved into the ore/coke interface after expulsion from pellet cores during softening.
CHAPTER 3
EXPERIMENTAL DESIGN AND EQUIPMENT

3.1 Experimental Design

3.1.1 Time-Temperature Conditions

During charging of the iron blast furnace, the principle burden components (ore and coke) are charged individually and so form separate layers at the furnace stockline. It was established in 1961 by Smolyak et al. that these layers are retained as the burden descends\(^{(49)}\). For each furnace radial position, the lower limit of layered structure is determined by the form of the melting zone.

As mentioned in Section 2.2, Japanese investigators have been able to identify several forms of the melting zone, but the most common and seemingly the most efficient\(^{(3)}\) is that having the geometry of Hirohata No. 1 BF. This investigation has been made for a melting zone having such an arched geometry (see Figure 2.1).

Experimenting with iron ore pellets doped with radioactive isotopes\(^{(8)}\), Japanese investigators have been able to determine the residence times prior to melting for ferrous materials charged to different radial positions at the furnace stockline.

When this information is combined with in-burden temperature distributions obtained from quenched furnace data and known top gas radial temperature profiles\(^{(4)}\), the thermal history of an ore particle prior
to melting can be estimated with considerable confidence.

In Figure 3.1 a schematic representation of the blast furnace is given. The figure indicates the form of the melting zone under consideration and stockline gas temperature profile most commonly associated with it (3). The melting zone is assumed to be approximately isothermal but considerable radial temperature variation is known to occur at the stockline. The usual form of this variation is also shown in the diagram along with arrows indicating two different burden trajectories.

Shinomura et al. (5) have used quenched furnace data to plot time-temperature conditions within the blast furnace as shown in Figure 3.2. It will be noted that the curves in Figure 3.2 have their origin at 0°C. In this investigation, the influence of top gas temperature distribution has been taken into account and the resulting time-temperature plots are shown in Figure 3.3. These curves are felt to be more realistic than those shown in Figure 3.2. The arrows in Figure 3.1 correspond to the centre and wallside terminology of Figures 3.2 and 3.3.

The time-temperature conditions shown in Figure 3.3 are those used in this work to investigate the influence of radial position upon reduction behaviour.

Infra-red cameras mounted at stockline level have established that burden materials attain temperatures approaching that of the gas phase within a very few minutes of introduction to the furnace (8).

3.1.2 Time-Gas Composition Conditions

The gas compositions to which ferrous burden components are subject during transit through the blast furnace shaft are far more difficult to estimate than are the thermal conditions. While quenched furnaces can yield data about temperature distribution, they offer no information.
Fig. 3.1 Schematic cross section of the blast furnace.
Comparison of raw material testing conditions and practical time temperature conditions in the blast furnace. After Shimomura (5).
Fig. 3.3 Experimental temperature profiles.
about local gas compositions.

Radial variations in top gas analysis, usually expressed in the form $\eta_{CO} = \frac{CO_2}{CO + CO_2}$, are readily accessible by above-burden probing techniques. Radial variation of the $\eta_{CO}$ parameter is known to be closely related to the top gas temperature profile as exemplified by Figure 3.4. Both temperature and composition profiles of top gas are essentially constant with time for stable blast furnace operation. Only minor, short term fluctuations are caused by the intermittent introduction of raw material batches.

The Boudouard Reaction,

$$CO_2 + C \rightarrow 2CO$$

$\Delta G^\circ = 40800 - 41.7$ Tcal/mole

is of prime importance when considering gas compositions encountered within the blast furnace.

The Boudouard Equilibrium or equilibrium between $CO_2$ and $CO$ in contact with solid carbon as a function of temperature is shown in Figure 3.5.

Figure 3.5 is drawn for the condition $P_{CO} + P_{CO_2} = 1$ atm. Conditions within the blast furnace are such that $P_{CO} + P_{CO_2}$ is usually less than one atmosphere and is not constant throughout the furnace volume. These departures from the idealized conditions of Figure 3.5 cause equilibrium conditions within the blast furnace to be slightly modified from those of Figure 3.5. The modifications caused are, however, only slight and the curve shown in Figure 3.5 is considered to be sufficient for the following discussion of gas compositional changes during its passage through the furnace. This discussion is made with reference to Figure 3.6 in which the shaded band represents the range of oxygen
Fig. 3.4 Top gas temperature and composition profiles for a number of furnace operating conditions. After Wakayama et al. (8).
Fig. 3.5 Variation with temperature of the concentration of carbon monoxide in equilibrium with carbon dioxide and solid carbon at one atmosphere pressure.
Fig. 3.6 Changes in the composition of a small volume of gas during its ascent through a blast furnace. After Richardson and Jeffes (53).
potentials which are found by taking simultaneous gas samples and temperature measurements at various levels in the furnace stack.

Blast air enters the blast furnace at a preheat temperature of approximately 1000°C and the initial oxygen potential is atmospheric \( P_{O_2} = 0.21 \text{ atm. unless artifically enriched} \). These conditions set the starting point (A) of the compositional changes which are marked on the diagram by the heavy line. Immediately in front of the tuyeres, the oxygen in the blast reacts with coke, the temperature rises to about 2000°C and the oxygen potential is lowered towards the C-CO equilibrium line. This is the lowest attainable oxygen potential under these conditions. Before this limit is reached, the gas will probably come into contact with and react with unreduced iron oxides; this reaction raises the oxygen potential of the gas towards the appropriate iron-oxygen line. At temperatures in excess of 900°C, this is assumed to be the Fe-FeO line. Alternate contact with ore and coke layers causes the gas composition to cycle between these limits (C-CO, Fe-FeO lines) as the gas rises up the furnace and its temperature falls by thermal transfer to the burden. The magnitudes of the composition fluctuations diminish progressively as the two limiting lines converge with decreasing temperature. Since there is insufficient time at lower temperatures for the attainment of equilibrium, the band is situated at oxygen potentials lower than those for the CO-CO₂ equilibrium (see Figure 3.5). With further decrease in temperature the speed of the reactions diminishes rapidly and the limits of the band converge towards the point (B) where the gas leaves the stockline (average composition over entire stockline area).

Figure 3.6 is drawn for the "average" furnace top gas analysis.
The variation in gas composition at the stockline which have previously been discussed are due to the relationship between gas composition and gas temperature. The non-uniformity of gas phase velocity and residence time across the furnace are also important in determining the top gas composition profile.

Reference to Figure 3.6 allows appreciation of the differences in gas composition to which individual ore particles are subjected during their passage through the furnace shaft.

Those particles at the bottom of any layer experience a gas composition given by a line joining the sequence of minimum values of the solid line in Figure 6.4. Particles at the top of a layer experience a composition given by the join of maximum values for the solid line. Here again, it should be remembered that Figure 6.4 is a generalization and that radial variations (particularly in ore layer depth) will cause modifications to the local gas composition experienced by different ore particles within the blast furnace.

By considering Figures 3.5 and 3.6 in conjunction with Figure 3.3 it is now possible to estimate gas composition vs. time conditions suitable for experiments simulating blast furnace conditions. This determination is quite simple for particles at the bottom of an ore layer, and the time-gas composition curves utilized in this study for this condition are shown in Figure 3.7a. Curves are shown for central and wallside conditions, these correspond to the temperature-time conditions shown in Figure 3.3. The "Boudouard Line" from Figure 3.5 is also included along with lines indicating equilibrium phase fields in the system Fe-C-O.

Figure 3.6 clearly indicates the direction of the deviation, which
Fig. 3.7a Experimental gas composition profile.
Fig. 3.7b Experimental gas composition profile.

\[ \frac{p_{\text{CO}}}{p_{\text{CO}} + p_{\text{CO}_2}} \]

- CENTRE PROFILE
- UPPER BED LEVEL
- BOUDDOUARD REACTION

TEMPERATURE (°C)
the gas composition-time curve must take as the ore particle being considered assumes positions higher in the ore layer bed.

For any particular radial position, there are two ways in which modifications to the gas composition-time curve can be achieved in the laboratory in order to simulate ore particles not adjacent to the ore/coke interface.

The first method involves the use of a bulk inlet gas (having supercritical velocity) of a different composition with time. The curve marked "upper bed level" in Figure 3.7b is an example and corresponds to the furnace centre position.

The alternative method by which the local gas composition can be modified in the laboratory is by conducting experiments at "subcritical" gas velocities.

The "critical" gas velocity is that velocity above which the gas phase flow rate ceases to exercise control over the rate of the reduction reactions. At velocities below the critical velocity, a "boundary layer" or surface film of relatively stagnant gas may be assumed in order to explain the retardation of reaction kinetics accompanying the lower flow rate.

Such a layer can be represented as in Figure 3.8a. When such a layer exists, the reagent gaseous species (here CO) must diffuse across the "boundary layer" before reaching the surface of an iron ore pellet. Similarly the product gaseous species (here CO₂) must diffuse away from the pellet surface. The form of concentration profiles for CO and CO₂ across the boundary layer are shown in Figure 3.8b. The net result of such events is that the surface of the pellet experiences a gas composition of ratio \( \frac{\text{CO}}{\text{CO} + \text{CO}_2} \) somewhat less than the bulk.
a)

![Diagram of a porous solid with boundary layer](image)

**BOUNDARY LAYER**

**BULK GAS FLOW**

b)

![Diagram of a porous solid with CO and CO2](image)

**POROUS SOLID**

**CO2**

**CO**

**BULK GAS PHASE**

**Variation of CO & CO2 concentrations in the boundary layer.**

*Fig. 3.8* The gaseous boundary layer.
At "supercritical" velocities, the influence of a gas film is negligible and the surface of the pellet experiences the bulk or inlet gas composition.

In this study, a supercritical gas velocity ($\approx 30$ cm/sec) has been used to simulate material at the bottom of an ore layer and a subcritical velocity of $\approx 3$ cm/sec has been used to simulate material at some higher level in the ore layer. The same bulk inlet gas-composition-time relationship has been maintained with each flow rate for both central and wallside simulations.

In order to verify experimentally that similar trends could be generated by changing the bulk inlet gas composition (retaining supercritical velocity) or lowering the gas velocity to subcritical levels while maintaining the same bulk inlet gas composition, some experimental runs were conducted along the gas profile marked "upper bed level" in Figure 3.7a and at the supercritical gas velocity of $\approx 30$ cm/sec.

Gas velocities within the blast furnace shaft are of the order of 3 m/s and so subcritical velocities are not in general encountered (except in areas of particularly low active voidage)\(^{(4)}\). Within a given ferrous layer, the reaction rate of those particles at upper levels within a given layer is retarded by the CO$_2$ produced by their neighbours below (but in the same layer). In a laboratory experiment at a subcritical gas velocity, the individual iron ore particle retards its own reaction rate by virtue of its own CO$_2$ reaction product.

Carbon monoxide is not the only reducing agent present in the blast furnace. Steam, which is always present in the blast air, and auxilliary fuel injection at the tuyeres act as sources of hydrogen. Comparison of figures 3.9a and 3.9b shows that the locations of equili-
Fig. 3.9a The Fe-C-O system showing the fields of stability of iron and various iron oxides (54).

Fig. 3.9b The Fe-H-O system showing the fields of stability of iron and various iron oxides (54).
brium phase fields for iron and its oxides differ substantially for
the two systems Fe-C-O and Fe-H-O (54).

In order to avoid excessive complication, the present work has
been restricted to the use of gas streams containing only carbon mon-
oxide, carbon dioxide and argon.

Reduction rates obtained with hydrogen are usually considerably
in excess of those obtained with carbon monoxide (55) and this should
be kept in mind when assessing the significance of the experimental
results obtained in this investigation.

Nitrogen accounts for some 78% of the blast volume to the blast
furnace and represents about 55% of the top gas volume. Nitrogen has
been replaced in this work by argon. This substitution was made in
order to remove the possibility of cyanide formation. Cyanides can
result if hydrogen or alkalis are introduced into the furnace gas
stream.

Argon content of all experimental gas streams was maintained con-
stant at 56% by volume at all times. Strictly speaking, such constancy
is analogous to a blast furnace process in which "direct reduction" or
reduction of FeO at temperatures in excess of 1000°C does not occur.

The "direct reduction" or "solution loss" reaction may be written:

\[
\text{FeO} (s) + C (s) \rightarrow \text{Fe} (s) + \text{CO} (g)
\]
\[
\Delta G^\circ = 35,350 - 35.9T \text{ cal/mole} (51)
\]

but is more properly presented as the result of two subreactions:

\[
\text{FeO} (s) + \text{CO} (g) \rightarrow \text{CO}_2 (g) + \text{Fe} (s)
\]
\[
\Delta G^\circ = -5,450 + 5.8T \text{ cal/mole}
\]

and

\[
\text{CO}_2 (g) + C (s) \rightarrow 2\text{CO} (g)
\]
\[
\Delta G^\circ = 40,800 - 41.7T \text{ cal/mole}
\]
Direct reduction cannot be avoided in an efficient blast furnace operation and can be seen to dilute the nitrogen content of the furnace gas stream. No attempt has been made to allow for the site of such a dilution in this work since such a compensation requires prior knowledge or an assumption about the extent and more particularly, the location of the solution loss reaction in the blast furnace.

This lack of compensation for direct reduction is not felt to be a serious experimental shortcoming in this work because, for temperatures greater than 1000°C it is the ratio \( \frac{P_{CO}}{P_{CO} + P_{CO2}} \) rather than the absolute value of \( P_{CO} \) which is of primary significance.

The pressure drop across a commercial blast furnace is generally 1.5-1.7 atmospheres and the absolute pressure depends upon the pressure maintained at the furnace top. This "in-furnace" pressure gradient is not linear and only a minor portion occurs in the upper levels of the furnace \(^{(9)}\) (see Fig. 2.4). No attempt has been made to allow for this effect in this work. The resultant modifications to \( P_{CO} \) and \( P_{CO2} \) are, in any event, not expected to be of primary significance.

3.2 Experimental Apparatus

3.2.1 Lindberg Furnace

The furnace employed in this investigation was a Lindberg Heavy Duty Model 54253 silicon carbide resistance furnace. The furnace was coupled with a Lindberg Heavy Duty Model 59545 controller. The silicon carbide elements were supplied in matched sets of 16 elements. The control thermocouple was a Pt-Pt 13% Rh thermocouple. Maximum furnace load rating was 6.5 KW, operating at a line voltage of 230 V.

The manufacturer's rated maximum temperature for this furnace is 1482°C, but temperatures in excess of 1400°C were found to be unattain-
able. Temperatures above 1380°C were attainable, but control and response rate were found to deteriorate in the range 1380°C to 1400°C. A very few early experiments were carried out to 1400°C, but when the effects mentioned above were recognized, a limit of 1380°C was adopted for all further work.

The furnace temperature profile for set point values of 1000°C and 1200°C are shown in Figure 3.10. Due to the mode of experimental control which was employed, the disparities between hot zone temperature and set point temperature apparent from Figure 3.10 were not a problem.

The furnace was operated in the horizontal position.

3.2.2 Furnace Tube and Extension

The entire furnace tube assembly is shown schematically in Figure 3.11.

The furnace tube was of high purity recrystallized alumina and was 110 cm. long with an inside diameter of 3.7 cm. and an outside diameter of 4.5 cm. Alumina was selected on the basis of its high temperature capabilities and its greater resistance to alkali attack when compared with mullite. The use of alumina did present a minor restriction with respect to sample quenching; this will be discussed in a later section.

At each end of the furnace tube, a water-cooled brass fitting, equipped with rubber "O" rings, provided a gas-tight connection to a silica extension piece of 12 cm. length and 4.1 cm. outside diameter. On the downstream end of the furnace, this extension piece was joined by a ground glass fitting to a glass end piece. This end piece was equipped with an optical glass plate, so allowing direct observation.
Fig. 3.10  Furnace temperature profiles.

Setpoint = 1200°C

Setpoint = 1000°C

Sample position at T > 1000°C

"hot zone"
Furnace Tube Assembly:

1. Furnace chamber
2. Alumina furnace tube
3. Silica joining tube
4. Glass extension tube
5. Optical viewing plate
6. Sample
7. Graphite dish
8. Sample push rod
9. Steel weight
10. Magnet
11. Thermocouple & sheath
12. Thermocouple wires
13. Bituminous seal
14. Three-piece brass joint
15. Threaded joint
16. Rubber "O" Ring
17. Copper cooling coil

**Fig. 3.11** Furnace tube assembly.
of the sample at all times.

On the upstream side of the furnace, the silica section was joined by a ground glass fitting to a glass extension tube of 66 cm. length and 50 cm. outside diameter. This extension tube served to house the sample carrier push rod assembly and the flexible thermocouple extension wiring. The thermocouple extension wiring passed from the furnace atmosphere to the laboratory atmosphere by means of a T-piece on the gas inlet tubing. A gas-tight seal between laboratory and furnace atmospheres was obtained by solidifying a bituminous mixture within an arm of the T-piece through which the wiring passed. The thermocouple wires then passed directly to a Honeywell Electronik 19 recorder having 0 - 10 mV and 0 - 20 mV scales suitable for use with the Pt-Pt, 13% Rh thermocouple over the temperature range of the investigation.

3.2.3 Sample Holder

The sample holder assembly is shown schematically in Figure 3.12.

Two pellets could be tested in each experimental run and were positioned side by side on the sample carrier. The sample carrier was machined from a graphite block and had the form of a hollow dish, some 2.5 cm. in diameter and approximately 1.0 cm. in depth. In experiments to study melting phenomena, the graphite dish was filled with sized coke particles and the pellets were allowed to rest directly upon the coke bed.

In experiments to study the reduction behaviour of pellets prior to melting, a shallow alumina liner was inserted into the graphite dish and the sample pellets suspended on two mullite rods above the alumina dish. These rods were positioned approximately 0.8 cm. apart and held in position by small grooves in the side of the graphite dish and a
Sample Holder Assembly:

1. Graphite boat
2. Alumina dish
3. Alumina push rod
4. Mullite locking pin
5. Mullite supporting rods
6. Sample
7. Thermocouple bead
8. Thermocouple sheath

Fig. 3.12 Sample holder assembly.
small amount of ALUNUMCement.

The mullite rods served to support the samples and elevate them into the gas stream, so minimizing the influence of sample holder geometry upon gas flow.

The graphite dish was connected to an alumina push rod of approximately 0.6 cm. diameter by means of a small mullite locking pin. The push rod length was 75 cm. and at the opposite end to the sample carrier, a steel weight was attached. The presence of this weight allowed the use of a magnet to move the entire sample carrier into and out of the furnace hot zone during an experiment with safety.

The Pt-Pt 13% Rh thermocouple was enclosed in a mullite sheath of approximately 0.5 cm. outside diameter and 53 cm. length and tied to the alumina push rod. The bead of the thermocouple was positioned some 0.6 cm. from the hindmost mullite support rod and considerable care was taken to keep the position of the bead constant with respect to that of the samples for all experimental runs.

The connections between the Pt and Pt 13% Rh thermocouple wires and the thermocouple extension wires were at all times well away from the furnace.

3.2.4 Experimental Gas Train

The experimental gas train is shown in Figure 3.13 in simplified schematic form. For simplicity the furnace tube detail has been omitted from this figure.

Following the determination of the gas composition-time conditions desired for each of the experimental conditions, rotameters having suitable ranges of sensitivity were calibrated for each gas used, using a bubble flow meter and stop watch.
Fig. 3.13 Experimental gas train.

1. Control Valve
2. Drying Tubes
3. Rotameter
4. Mixing Chamber
5. Bubbler
6. Bubble Flowmeter
Argon partial pressure remained constant in all experiments and so no adjustment to argon flow rate was necessary during an experiment. For carbon monoxide and carbon dioxide however, the required partial pressures changed with time for a substantial period during each experiment. With the known calibration curves and the use of micro-needle valves in conjunction with rotameter indications, the flow setting of each gas could be individually controlled throughout the experiment. Such non-automated control cannot be continuous, and small adjustments were made at regular intervals; three, five or ten minutes apart. The most frequent adjustments were made during periods of greatest compositional change. Using this technique, the experimental curves shown in Figure 3.7 would be closely followed. An estimation of errors is best made in terms of the ratio $\frac{P_{CO}}{P_{CO} + P_{CO_2}}$ since this is the ratio which best represents the reducing potential of the gas. For the periods of most rapid compositional change (around 700°C) an error calculation based on a 5-minute interval between adjustments yields a maximum error of ± 0.10 (± 12%) in this very sensitive parameter. Fortunately, the time periods, during which changes in gas composition were most rapid, were confined to periods of about 20 minutes and so represent a relatively small proportion of most elapsed experimental times. At all times when the sample temperature exceeded 1000°C, only carbon monoxide and argon flowed and the flow rate of each remained constant. Hence, during these (often very substantial periods) a maximum error of only ± 3% for carbon monoxide needs to be considered. Argon flow rates, being always constant are considered to be within ± 3% of the required volume at all times.

Obviously the maximum error level of the ratio $\frac{P_{CO}}{P_{CO} + P_{CO_2}}$ is far
from desirable and this represents an obvious point for improvement in any future work of this kind.

3.2.5 Temperature Control

Owing to the wide temperature range investigated (100 - 1380°C), two modes of temperature control modes had to be employed. For temperatures less than 1000°C, the furnace controller was set at 1000°C and the sample holder moved slowly (by means of the magnet) along furnace tube through the furnace's natural temperature profile (at the 1000°C set point) until the hot zone was reached. For temperatures greater than 1000°C, the furnace controller was used to increase the hot zone temperature of the furnace without further change to the sample position. At all times, the thermocouple output could be checked against the desired time-temperature profile so allowing adequate control to be maintained.

The most rapid changes in temperature occurred in the 800 - 900°C temperature range and here the errors are expected to be greatest, owing to the lack of a continuous, automatic control system. The thermocouple outputs indicate that maximum deviation from the desired temperature profile was about ± 10°C. At temperatures less than 700°C and greater than 1000°C, deviations were considerably less, owing to the less rapid rise in required temperature.

The use of the furnace temperature profile implies some non-uniformity of temperature across the samples for temperatures less than 1000°C. This effect is not considered to be of great significance due to the influence of conductive heat transfer within the pellet and the presence of this effect in all experimental runs.

It will be noted that control of temperature and gas flow were
independent. Such independence is desirable, particularly when experiments involving different gas flow rates are undertaken.

3.3 Materials Investigated

Three commercial pellets have been used in this investigation and have been designated A, B and C.

**Pellet A** is a North American acid pellet of specular haematite origin and is notable for its high manganese content. This ore is easily liberated from the gangue and requires grinding to only 75% + 100 mesh (.147 mm) for concentration. Further grinding to 63% - 325 mesh (45 μm) is however required for satisfactory balling. The ore has a surface area of 1700 cm²/g.

Induration of this product is performed on a straight grate-type machine.

**Pellet B** is a second North American acid pellet but is of magnetitic origin. Liberation of this ore from the silica-rich gangue is not easy and grinding is required to the level of ~93% - 325 mesh (45 μm) and ~69% - 500 mesh (30 μm).

This ore has a specific surface area of 1565 cm²/g.

The pellets are produced in a grate kiln-type furnace.

**Pellet C** is a European basic pellet of magnetitic origin. The ore is ground to 90% - 325 mesh for concentration and balling and has a surface area of approximately 1700 cm²/g. Both limestone and dolomite are used as fluxing agents in the production of this pellet. The pellet is produced in a grate kiln-type machine.

Owing to the fluctuations which occur in the operation and control of a pelletizing plant, it was not possible to obtain precise information regarding the induration conditions which were experienced by the
pellets tested in this work. Figure 3.14, however, serves to illustrate the very significant differences which exist between the firing cycles of straight grate and grate kiln processes.

The chemical analyses of the three pellet types are listed in Table 3.1.

Physical properties of the pellets are presented in Table 3.2. Results for "Sizing", "Tumble Test" and "Compressive Strength" are based on ASTM techniques (56-58). Results reported for "Swelling" and "Degree of Reduction" are based on an I.S.O. test in which a bed of pellets is reduced for one hour at 900°C with pure carbon monoxide gas flowing at 20 N.l/min through a vertical tube of 57 mm inside diameter (59). "Low Temperature Breakdown" results are based on an I.S.O. method of evaluation (60).
Fig. 3.14 Heating cycles in straight grate and grate-kiln pelletizing processes.
<table>
<thead>
<tr>
<th></th>
<th>Pellet A (%)</th>
<th>Pellet B (%)</th>
<th>Pellet C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>65.61</td>
<td>65.27</td>
<td>64.0</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3.01</td>
<td>5.42</td>
<td>2.74</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.25</td>
<td>0.25</td>
<td>0.70</td>
</tr>
<tr>
<td>CaO</td>
<td>0.12</td>
<td>0.07</td>
<td>3.30</td>
</tr>
<tr>
<td>MgO</td>
<td>0.02</td>
<td>0.29</td>
<td>1.20</td>
</tr>
<tr>
<td>Mn</td>
<td>2.05</td>
<td>0.05</td>
<td>0.73</td>
</tr>
<tr>
<td>P</td>
<td>0.009</td>
<td>0.021</td>
<td>0.035</td>
</tr>
<tr>
<td>S</td>
<td>0.006</td>
<td>0.004</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.11</td>
<td>0.017</td>
<td>0.025</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.030</td>
<td>0.017</td>
<td>0.052</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.023</td>
<td>0.009</td>
<td>0.070</td>
</tr>
<tr>
<td>CaO + MgO</td>
<td>0.042</td>
<td>0.063</td>
<td>1.31</td>
</tr>
<tr>
<td>SiO₂ + Al₂O₃</td>
<td>0.063</td>
<td>1.31</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.2  Physical Properties

<table>
<thead>
<tr>
<th></th>
<th>Pellet A</th>
<th>Pellet B</th>
<th>Pellet C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sizing:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ 5/8&quot;</td>
<td>1.71</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>+ 1/2&quot;</td>
<td>20.94</td>
<td>16.88</td>
<td>44.6</td>
</tr>
<tr>
<td>+ 3/8&quot;</td>
<td>85.40</td>
<td>90.85</td>
<td>92.8</td>
</tr>
<tr>
<td>+ 1/4&quot;</td>
<td>97.35</td>
<td>98.49</td>
<td>98.2</td>
</tr>
<tr>
<td>- 1/4&quot;</td>
<td>2.65</td>
<td>1.51</td>
<td></td>
</tr>
<tr>
<td><strong>Tumble Test:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ 1/4&quot;</td>
<td>93.32</td>
<td>97.00</td>
<td>96.00</td>
</tr>
<tr>
<td>- 28 mesh</td>
<td>6.22</td>
<td>1.96</td>
<td></td>
</tr>
<tr>
<td><strong>% Reduction</strong></td>
<td>24.8</td>
<td>19.25</td>
<td>25.0</td>
</tr>
<tr>
<td><strong>% Swelling</strong></td>
<td>9.76</td>
<td>25.45</td>
<td>15.0</td>
</tr>
<tr>
<td><strong>Compressive Strength - Lbs.</strong></td>
<td>584</td>
<td>648</td>
<td>850</td>
</tr>
<tr>
<td><strong>Low Temp. Breakdown + 1/4&quot;</strong></td>
<td>97.4</td>
<td>91.5</td>
<td>93.6</td>
</tr>
</tbody>
</table>
CHAPTER 4
EXPERIMENTAL PROCEDURE

4.1 Sample Selection and Preparations

Samples were received in batches of approximately 10 kg. Upon receipt each sample batch was dried at 150°C for 48 hours and weighed.

Because commercial iron ore pellets are known to show significant variations in such important physical properties as size, mass, density and porosity, several steps were taken to standardize the pellets actually used for experimental investigation.

Firstly, the entire as-received, dried sample was sized, using screens ranging from 0.0328" (20 mesh) up to a 3/4" mesh opening. Such an analysis provides some indication of the uniformity of the sample but is unfortunately the only indication available.

Following the screen analysis, the size range + 7/8", - 1/2" was removed and dried for a further period of 24 hours to ensure constant weight.

Individual pellets were selected from this size fraction on the basis of weight and physical appearance. Pellets were weighed individually on a laboratory balance, and all pellets selected for testing (with a few exceptions in the case of Type C pellets due to a shortage of suitably sized pellets at later stages of testing) had a weight of 3.5 ± 0.1 g. Pellets with obvious physical flaws, surface irregular-
ities or poor sphericity were not considered for selection.

The dry weight of each selected pellet was recorded along with its volume as determined by a mercury displacement technique. The volumenometer employed has been previously described by ElKasabgy (36) and a description will not be given here, although an error analysis is included in Appendix 1.

4.2 Reduction

At the start of each experimental run, the two pellets to be tested were placed on the sample holder and the sample holder was introduced to the furnace tube and positioned at the point coincident with the starting temperature for the experiment to be undertaken. With the sample inserted, the system was sealed and argon introduced to purge the system at the flow rate required for the experiment.

A purging period of at least ten minutes was allowed prior to all experiments to allow the pellet sufficient time to attain constant temperature at the required starting value.

At the completion of the experimental run, all gases except argon were turned off. Argon flow was maintained for ten minutes to purge the system. The sample was quenched from its final reduction temperature by rapid removal away from the furnace hot zone. This removal was done using the magnet device and had to be done in several steps in order to avoid thermal shock and damage to the furnace tube.

Consistency of quenching was poor and this led to some minor initial difficulty in microstructural analysis.

The optical plate at the end of the reaction tube made it possible to observe pellets during reduction and quenching. In this manner a check could be made as to whether pellets cracked during reduction or
as a result of quenching.

Once the pellets had been cooled, they could be removed from the furnace.

Following reduction each sample was reweighed to determine its degree of reduction and its final volume measured to determine its swelling index.

The methods of calculation for degree of reduction and swelling index are given below.

(a) Degree of Reduction:

\[ R = \frac{\text{Weight of oxygen removed} \times 100}{\text{Weight of oxygen originally combined with Fe}} \]

where \[ W_o \] = initial pellet weight

\[ W_f \] = final pellet weight

\( k \) = constant determined by pellet analysis

Pellet A - \( k \) = 0.2819
Pellet B - \( k \) = 0.2805
Pellet C - \( k \) = 0.2766

(b) Swelling Index:

\[ \Delta \left( \frac{V}{V_o} \right) = \frac{\text{Change in volume} \times 100}{\text{Initial volume}} \]

4.3 Metallographic Preparation

Samples for metallographic examination were vacuum mounted in epoxy resin and sectioned with a jeweler's saw. Silicon carbide papers were used for primary grinding followed by an emery paper prior to final polishing on 6µ and 1µ diamond pads. Odourless kerosene was used as the lubricant during all stages of preparation to avoid the possibility of
leaching from the slag phase.

Due to the number of phases present in impregnated samples and their varying hardnesses, a good polish was difficult to obtain. Polishing to less than 1μ was attempted, but was found to result in problems associated with depth of field at higher magnifications and so was abandoned.

To check for carburization, a 2% Nital etchant was used. This etchant was also found to etch grain boundaries in some highly reduced basic slags which crystallized during quenching.

4.4 The Observation of Melting Behaviour

Runs to study the melting behaviour of the pellets were conducted following the central temperature profile with the high gas flow rate of 50 cc/sec (STP). In these runs, the alumina dish and mullite supporting rods were removed and a bed of fine coke (100% - 20 mesh, 30% - 80 mesh) was placed in the graphite boat. Pellets were placed on the bed of coke and were observed during reduction by means of the optical plate on the end of the reaction tube. Carburized, partially melted and fully melted products from these runs were examined metallographically and some melt products (slag and metal) were chemically analyzed.

To investigate the influence of the melting point of the gangue material, differential thermal analysis was performed on samples prepared according to the analyses given in Table 3.1.

4.5 Microprobe Analysis

4.5.1 The Cameca Microprobe

Microprobe analyses were performed on selected specimens using an Acton (CAMECA NS-64) microprobe. This instrument has four spectrometers (Quartz 1010, Quartz 1011, Mica and R.A.P.) and a take-off angle
of 18°. The original high voltage supply unit has recently been replaced with a C.P.S. Model 6001 unit. With this instrument, a beam voltage of 20 kV and sample currents of approximately 0.05 μA were found to be suitable for specimens coated with a conducting film of carbon. Counting periods of 20 and 40 seconds were found to generate sufficient counts for statistical analysis.

4.5.2 Microprobe Standards

While some suitable standard materials were readily available in pure form, others had to be prepared from laboratory grade materials. These standards were prepared under suitable atmospheric conditions and where necessary the identity of phases obtained were confirmed using the X-ray powder diffraction technique.

4.5.3 Corrections to the Microprobe Data

A computer programme, the MAGIC IV, developed by Colby (61) for microprobe data correction was used for reducing the raw microprobe data to concentrations. The MAGIC IV, developed mainly for oxides and silicates, is based on the correction procedure recommended by Philibert and Texier (62).

Microprobe data for peak and background counts of standards and specimens are supplied to the programme in the same order that they are generated from the microprobe readout and the programme corrects for Atomic Number Factor, Absorption Factor and Characteristic Fluorescence Factor. Details of the MAGIC IV and the correction procedure can be found in the literature (61,62). The basic equation for data correction is:

\[ W = \frac{U \ln x}{F_0} \left( \frac{R_0}{R_1} \right)^{S_1} \left( \frac{f(x)_0}{f(x)_1} \right)^{1 + \gamma_0} \left( \frac{1 + \gamma_1}{1 + \gamma_1} \right) \]
where \( W = \) True concentration

\[ U_{IN} = \text{Measured concentration, after correction for} \]
\[ \text{counter dead time and background intensity} \]

\[ \frac{R}{S} = \text{Atomic Number Factor} \]

\[ f(x) = \text{Absorption Factor} \]

\[ 1 + \gamma = \text{Characteristic Fluorescence} \]

The subscripts 0 and 1 refer to the standard and sample respectively; \( R \) and \( S \) refer to background loss factor and stopping power for electrons, respectively.

Concentrations in wt. % are printed out for the elements analyzed and were then converted to the appropriate oxides.

Only the principal slagmaking elements were analyzed for each system investigated.
CHAPTER 5

EXPERIMENTAL RESULTS

5.1 Introduction

In Sections 5.2 - 5.6 of this chapter, experimental observations of reducibility and swelling and cracking behaviour are presented graphically. Sections 5.7 - 5.9 report metallographic observations and electron microprobe analyses from partially reduced specimens and melting experiments which are then summarized in Section 5.11. Computer outputs for microprobe analyses reported in this chapter are to be found in Appendix 4.

5.2 Size Distribution of As-Received Samples

The results of screen analyses are shown in Figure 5.1 and listed in Appendix 2A.

5.3 Reducibility

The reducibility results, based on weight loss data and confirmed by chemical analysis are plotted against experiment finishing temperature in Figures 5.2 to 5.9 and are listed in Appendix 2B.

5.4 Swelling Behaviour

The Swelling Index, \( \frac{AV}{V_0} \times 100, \% \), computed from volume measurements made before and after reduction are plotted against finishing temperature for the various experimental conditions in Figures 5.10 to 5.17 and are listed in Appendix 2B.
Fig. 5.1 Size distributions of the as-received samples.
Reduction of Pellet A along centre temperature profile at a gas flow rate of 5 cc/sec.

Fig. 5.2
Fig. 5.3 Reduction of Pellet A at a gas flow rate of 50 cc/sec. (centre and wall temperature profiles).
Fig. 5.4  Reduction of Pellet A along wall temperature profile at a gas flow rate of 5 cc/sec.
Fig. 5.5 Reduction of Pellet B at a gas flow rate of 5 cc/sec. (centre and wall temperature profiles).
Fig. 5.6 Reduction of Pellet B at a gas flow rate of 50 cc/sec. (centre and wall temperature profiles).
Fig. 5.7 Reduction of Pellet C along centre temperature profile at a gas flow rate of 5 cc/sec.
Fig. 5.8 Reduction of Pellet C at a gas flow rate of 50 cc/sec. (centre and wall temperature profiles).
Fig. 5.9 Reduction of Pellet C along wall temperature profile at a gas flow rate of 5 cc/sec.
Fig. 5.10  Swelling behaviour of Pellet A reacted along centre temperature profile at a gas flow rate of 5 cc/sec.
Fig. 5.11 Swelling behaviour of Pellet A reacted with a gas flow rate of 50 cc/sec. (centre and wall temperature profiles).
Fig. 5.12 Swelling behaviour of Pellet A reacted along wall temperature profile at a gas flow rate of 5 cc/sec.
Fig. 51‡ Swelling behaviour of Pellet B reacted with a gas flow rate of 5 cc/sec.
(centre and wall temperature profiles).
Fig. 5.14 Swelling behaviour of Pellet B reacted with a gas flow rate of 50 cc/sec.
(centre and wall temperature profiles).
Fig. 5.15  Swelling behaviour of Pellet C reacted along the centre temperature profile with a gas flow rate of 5 cc/sec.
Fig. 5.16 Swelling behaviour of Pellet C reacted with a gas flow rate of 50 cc/sec. (centre and wall temperature profiles).
Fig. 5.17  Swelling behaviour of Pellet C reacted along the wall temperature profile with a gas flow rate of 5 cc/sec.
5.5 Cracking Behaviour

With the optical viewing plate, pellet cracking could be observed during reduction. The temperature ranges most frequently observed for cracking are listed below:

- Pallet A: 720 - 770°C
- Pallet B: 700 - 750°C
- Pallet C: 730 - 780°C

In Table 5.1, cracking behaviour is presented as a function of reduction conditions for each pellet type. Pellets were considered to be "cracked" if any crack opening could be optically detected at the surface. Although considerable variations in cracking severity were observed, no effort has been made to include any qualitative information in Table 5.1. In view of the temperature ranges observed to be associated with cracking, only the results of runs terminated at temperatures of 900°C and greater have been used in compiling Table 5.1.

5.6 The Influence of Gas Flow Rate

To investigate the influence of gas flow rate upon reduction behaviour, a number of runs (using pellet types A and C) were performed using the centre temperature profile. These runs were terminated at 1000°C. The results are listed in Appendix 2C and are plotted in Figures 5.18 and 5.19.

A few experiments were also performed (using pellet types A and C) with the "upper bed level" gas composition profile shown in Figure 3.7b. These experiments were terminated at 1000°C and 1200°C, following the centre profile, and served to confirm that the use of a subcritical gas flow rate influences reduction behaviour in a manner similar to the use of a less powerful reducing gas flowing at supercritical velocity.
Fig. 5.18 Reduction behaviour of Pellet A with variation of gas flow rate (centre temperature profile).
Fig. 5.19 Reduction behaviour of Pellet C with variation of gas flow rate (centre temperature profile).
Table 5.1  Cracking Frequency at T ≥ 900°C.

a)  Gas Flow Rate = 5 cc/sec.

<table>
<thead>
<tr>
<th>Profile</th>
<th>Pallet A</th>
<th>Pallet B</th>
<th>Pallet C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centre</td>
<td>3/16 = 18.6%</td>
<td>12/12 = 100%</td>
<td>14/16 = 87.5%</td>
</tr>
<tr>
<td>Wall</td>
<td>5/12 = 41.7%</td>
<td>4/4 = 100%</td>
<td>11/12 = 92.3%</td>
</tr>
</tbody>
</table>

b)  Gas Flow Rate = 50 cc/sec.

<table>
<thead>
<tr>
<th>Profile</th>
<th>Pallet A</th>
<th>Pallet B</th>
<th>Pallet C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centre</td>
<td>0/12 = 0%</td>
<td>12/12 = 100%</td>
<td>6/12 = 50%</td>
</tr>
<tr>
<td>Wall</td>
<td>0/4 = 0%</td>
<td>4/4 = 100%</td>
<td>0/8 = 0%</td>
</tr>
</tbody>
</table>
These results are also included in Appendix 2C.

5.7 Metallographic Observations

For each of the three pellet types investigated and for each of the two gas flow rate conditions, the microstructural features of pellets reduced along the wall profile of temperature and gas composition showed marked similarities to those of their centre profile counterparts. In view of these similarities, only samples reacted on the centre profile are considered in this section.

In order that the reader may develop an appreciation for the scale of morphological features observed for the various reduction conditions employed, the majority of photographs in this section are presented at a constant magnification of 400 times. Photographs taken at lower magnifications are clearly labelled.

5.7.1 Pallet A; As-Received Condition

Figure 5.20 shows the microstructure of the as-received material. Liberation of ore and gangue particles is virtually complete. The bonding phase is recrystallized haematite. Gangue particles exist as discrete entities and do not contribute to bonding. A few very small areas of magnetite were detected.

Electron microprobe analysis showed the manganese content of these pellets to be very inhomogeneously distributed in the as-received condition. Large grains returned an analysis of 97.8 ± 0.4 % Fe₂O₃ and 0.9 ± 0.7 % Mn₂O₃ while many smaller grains (diameter < 10 μm) returned an analysis much higher in manganese, viz. 65.6 ± 6.3 % Fe₂O₃ and 32.1 ± 1.7 % Mn₂O₃. Microprobe analysis of gangue particles indicated their composition to be essentially pure silica (100.0 ± 0.8 % SiO₂).
Fig. 5.20 Pellet A. As-received condition: light particles are haematite, grey particles are gangue and dark areas are pores (filled with resin).
Magnification 400 x or — 25 μm.
5.7.2 Pallet A: Reduced With a Gas Flow Rate of 5 cc/sec.

After reduction to 700°C, reduction to wustite was found to be virtually complete but only a very few iron nuclei were observed near the surface of the pellets. Gangue particles showed some minor modification of internal structure but remained as inert entities. Figure 5.21a shows the microstructure of a surface area. The transformations from haematite to wustite are seen to have caused considerable change to the iron oxide particles.

Samples reduced to 900°C exhibited metal nucleation at depths of up to about 3 mm (i.e., 50% of the pellet radius). The inner boundary of this zone was not however, well defined. While most gangue particles still remained inert, the formation of small areas of a new phase was detected at points of closest contact with wustite. A surface microstructure is shown in Figure 5.21b.

In samples quenched from 1000°C, metal nuclei were found at all depths. Gangue particles near the pellet surface remained inert but most gangue particles in inner regions (of lower metallization) showed some signs of interaction with adjacent wustite grains.

Pallets quenched from 1100°C showed metallization to be continuing at all depths. While gangue particles near the pellet surface remained inert most of those in inner regions were observed to have been consumed by reaction with adjacent wustite grains. Figure 5.21c shows a central region in which the fayalite product of wustite-gangue interaction can be seen. The wustite and fayalite phases were analyzed with the electron microprobe and the following results were obtained:

Wustite: $97.7 \pm 0.5 \% \text{ FeO, } 3.8 \pm 0.4 \% \text{ MnO}$

Fayalite: $64.5 \pm 1.4 \% \text{ FeO, } 7.1 \pm 0.8 \% \text{ MnO, } 30.0 \pm 0.7 \% \text{ SiO}_2$
Fig. 5.21a  Surface of pellet A, quenched from 750°C. Light material is wustite, grey material is gangue and the outlined matrix is mounting resin.
Magnification 400x or ______ = 25 μm.

Fig. 5.21b  Surface of Pellet A, quenched from 900°C. The white phase is iron and light grey material is wustite. An inert gangue particle is seen to be surrounded by highly metallized material.
Magnification 400x or ______ = 25 μm.
Fig. 5.21c  Pellet A, quenched from 1100°C. Significant quantities of (mid-grey) fayalite are seen to be associated with light grey wustite and small remnants of gangue particles (dark grey). A few metal particles (white) can also be seen. Magnification 400x or _____ = 25 µm.

Fig. 5.21d  Pellet A, quenched from 1200°C (centre). Rounded particles of wustite and metal are wetted by fayalite slag containing some secondary wustite precipitates. Magnification 400x or _____ = 25 µm.
Fig. 5.21e  Pellet A, quenched from 1300°C (surface view). A two-phase slag is associated with large, rounded metal particles. Magnification 400x or _____ = 25 μm.

Fig. 5.21f  Pellet A, quenched from 1400°C. Large quantities of wustite precipitate are observed in the slag phase. Magnification 400x or _____ = 25 μm.
Fig. 5.21g  Surface structure of Pellet A quenched from 1400°C. A dense surface layer of iron is clearly seen. Magnification 40x or —— = 250 μm.
Pellets quenched from 1200°C showed remarkably heterogeneous structure, three distinct zones being readily identifiable as shown schematically in Figure 5.22.

The structure of zone A is shown in Figure 5.21d. The wustite and metal particles are seen to be coarse and rounded and are surrounded by considerable quantities of slag which has precipitated some wustite on cooling. The gas/solid contact area is seen to have been significantly reduced.

Zone B was found to be highly metallized but almost devoid of slag.

The metal phase in zone C was found to be coarse, highly rounded and associated with significant quantities of liquid slag. Precipitation of secondary wustite from the slag phase (during quenching) was also frequently observed in zone C.

Metallization was observed to be most active at the boundary between zones A and B.

The pellets quenched from 1300°C also showed a zoned structure, similar to the above with the following changes:

(a) Zone B had grown at the expense of zone A.
(b) Metal and wustite particles in zone A were larger and greater quantities of secondary wustite were observed.
(c) Slag in zone C did not contain secondary wustite but frequently showed separation into two phases as seen in Figure 5.21e. The lighter phase was analyzed in the electron microprobe and found to contain 42.8 ± 0.6% FeO, 24.3 ± 0.9% MnO and 33.4 ± 0.8% SiO₂. Qualitative analysis indicated the darker phase to contain more silica and less FeO and MnO than the lighter coloured fayalite-like phase.
Fig. 5.22 Schematic representation of heterogeneous ("cored") pellet structure.
Samples reacted to 1380°C and 1400°C prior to quenching contained central cavities in place of zone A. The metal phase in zones A and B exhibited large rounded morphology and wustite precipitates were observed in the slag phase at most locations as shown in Figure 5.21f. Figure 5.21g shows the surface structure at a lower magnification (40x). The formation of a dense surface layer of iron can be clearly seen. The slag phases seen in Figures 5.21f and g were analyzed in the electron microprobe and the following analyses were obtained:

(a) light phase (manganowustite):
\[ 87.0 \pm 1.6 \text{ FeO}, 14.1 \pm 0.7 \text{ MnO} \]

(b) dark phase (manganous fayalite)
\[ 41.7 \pm 0.9 \text{ FeO}, 23.5 \pm 0.5 \text{ MnO}, 29.0 \pm 0.9 \text{ SiO}_2 \]

5.7.3 Pellet A: Reduced With Gas Flow Rate of 50 cc/sec.

Reduction to wustite was complete in pellets quenched from 750°C and metallization at surface areas was quite high as shown in Figure 5.23a. While metal nuclei were found at all depths, the extent of metallization in central areas was much lower than at the surface. Gangue particles behaved inertly at all locations.

The structures of samples quenched from 900°C and 1000°C were similar to the above with the exception that the degree of metallization was higher at all locations. Figure 5.23b shows partial metallization at the centre of a pellet quenched from 1000°C.

Metallization was almost complete in samples reacted to 1100°C. Gangue particles were observed to behave inertly in almost all cases with only very small quantities of fayalite formation being detected in some central regions. A typical structure is shown in Figure 5.23c.

Pellets reduced to 1200°C showed a structure very similar to that
Fig. 5.23a  Surface area of Pellet A, quenched from 750°C showing a high degree of metallization. Magnification 400x or ______ = 25 μm.

Fig. 5.23b  Metallization in the central region of Pellet A at a temperature of 1000°C. A large gangue particle is seen at top left. Magnification 400x or ______ = 25 μm.
Fig. 5.23c  
Pellet A, quenched from 1100°C. Metallization is almost complete and some gangue particles can be identified.  
Magnification 400x or ______ = 25 µm.

Fig. 5.23d  
Pellet A, quenched from 1300°C. This structure indicates some coarsening of the metal phase and shows both an inert gangue particle and the slag phase.  
Magnification 400x or ______ = 25 µm.
at 1100°C with the exception that the formation of minor quantities of liquid slag was indicated in central regions.

Samples quenched from 1300°C contained significant quantities of single-phased slag which appeared to have been liquid at 1300°C. Figure 5.23d is typical of the observed structure and shows slag, an inert gangue particle and metal phase which shows some signs of minor coarsening. The coarsening is much less marked than that shown in Figure 5.21b. Central regions showed a relatively higher porosity than surface regions which showed some accumulation of slag phase. Inert gangue particles were observed to be most populous in surface areas but a significant number were still observed in the pellet centre.

Samples reacted to 1380°C showed structures very similar to those observed for 1300°C with only a slightly higher degree of metal phase consolidation at surface areas. Inertly behaving gangue particles could still be seen at all radii. The single-phased slag was examined with the electron microprobe and a qualitative analysis suggesting high proportions of MnO (\(\sim 50\%\)) and SiO\(_2\) (\(\sim 30\%\)) and very low FeO concentration was obtained.

5.7.4 Pellet B: As-Received Condition

The fine grain size of the concentrate can be clearly seen in Figure 5.24 which should be compared with Figure 5.20 (Pellet A). The bonding phase in this pellet is also haematite. The liberation of ore particles from gangue is considerably poorer than in the case of Pellet A and is clearly shown by the high proportion of gangue particles which contain occluded fine ore particles. A few small areas of residual magnetite were observed in central regions.
Fig. 5.24 Pellet B. As-received condition; dark gangue particles containing occluded ore particles and some small areas of residual magnetite (slightly darker than haematite) are seen in this centrally located field. Magnification 400x or ____ = 25 µm.
Pellet B: Reduced with a Gas Flow Rate of 5 cc/sec.

Samples quenched from 750°C exhibited almost complete reduction to wustite and the formation of a very small number of iron nuclei at the pellet surface. Gangue particles were observed to behave inoffily with respect to both occluded and liberated portion of ore.

Samples reduced to 900°C contained metal nuclei at all depths but exhibited significant metallization only at the surface as shown in Figure 5.25a. Gangue particles showed little sign of interaction with surrounding wustite grains but some interaction with occluded wustite particles to form fayalite was observed as seen in Figure 5.25a.

Pellets reacted to 1000°C showed significant fayalite formation in subsurface areas as the result of silica reaction with both internal and external wustite as seen in Figure 5.25b. Fayalite formation was not as extensive in surface areas where many gangue particles continued to behave inoffily.

While surface regions of pellets reached to 1100°C were similar to those observed above (1000°C) central regions contained large quantities of fayalite and only small amounts of uncombined gangue. Metallization was almost complete at original and crack surface areas but very minor in internal areas. The wustite, gangue and fayalite phases observed in this condition were analyzed with the electron microprobe, yielding the following results:

Wustite: 98.5 ± .4% FeO
Gangue: 99.2 ± 1.52% SiO₂
Fayalite: 71.2 ± 1.2% FeO, 28.7 ± 6% SiO₂

Samples reduced to 1200°C showed features similar to the three-zone structure of Pellet A under similar conditions. In this case,
Fig. 5.25a Pellet B, quenched from 900°C. Metallization at the surface of the specimen and the formation of fayalite from ore particles occluded by gangue. Magnification 400x or ____ = 25 μm.

Fig. 5.25b Pellet B, quenched from 1000°C. Wustite and gangue particles are seen with fayalite formation. Magnification 400x or ____ = 25 μm.
Fig. 5.25c  Pellet B, quenched from 1200°C. Central region shows coarsening of the wustite phase and the precipitation of secondary wustite from the slag phase during cooling. Magnification 400x or \( \frac{1}{25} = 25 \mu m \).

Fig. 5.25d  Pellet B, quenched from 1200°C. Surface area shows coarsened metal and slag which has precipitated wustite during quenching. Magnification 400x or \( \frac{1}{25} = 25 \mu m \).
Fig. 5.25e  Pellet B, quenched from 1300°C. The formation of an iron shell and the presence of two-phased slag at the pellet surface. Magnification 400x or ______ = 25 μm.

Fig. 5.25f  Pellet B, quenched from 1380°C shows coarse metal phase and a three-phase slag mixture. Magnification 400x or ______ = 25 μm.
however, zone A existed as a number of areas owing to the extensive cracking of the pellet and subsequent rapid metallization of crack surfaces. The structure of one of these areas is shown in Figure 5.25c, where secondary wustite precipitation can be seen. Areas adjacent to these "cored" central regions were observed to be slag deficient but surface areas contained significant quantities of slag in which secondary wustite precipitation was frequently observed. Very few uncombined gangue particles were observed even at surface locations for this condition. A surface area is shown in Figure 5.25d and considerable coarsening of the metal phase can be observed.

The microstructure associated with reduction to 1300°C before quenching was similar to that for the 1200°C condition in central regions where the unreduced wustite "cores" were slightly smaller. In surface areas, however, wustite precipitation from the slag phase during cooling was in most places replaced by a separation into two phases as shown in Figure 5.25e. The light phase in this figure was analyzed in the electron microprobe and found to be fayalite containing $76.2 \pm .6\% \text{FeO}$ and $27.4 \pm .4\% \text{SiO}_2$. A qualitative indication that the dark phase was rich in silica and relatively deficient in iron was also obtained. The formation of an iron shell at the pellet surface can be seen in Figure 5.25e.

Samples reduced to 1380°C prior to quenching showed very extensive coarsening of the metal phase and the formation of a thick iron shell (similar to Pellet A for equivalent conditions). Significant volumes of pellet slag contained precipitated wustite particles as shown in Figure 5.25f. Minor volumes of a third slag phase can also be seen in this figure. These particles were too small for analysis with the
electron microprobe but X-ray mapping with the scanning electron microscope indicated them to be relatively deficient in iron and rich in silica.

5.7.6 Pellet B: Reduced at a Gas Flow Rate of 50 cc/sec.

The structure observed after quenching from 750°C showed almost complete reduction to wustite and some minor metallization at the pellet surface. Gangue material behaviour was inert with respect to both occluded and surrounding wustite.

Samples quenched from 900°C showed significant metallization at the pellet surface and the formation of metal nuclei to a depth of approximately 3 mm. A surface view is shown in Figure 5.26a where the ore particles occluded by a silica grain have reacted to form fayalite. The formation of fayalite from liberated ore particles was not observed at any depth.

The microstructure observed upon reaction to 1000°C before quenching showed extensive areas of metallization in which fayalite formation occurred only from occluded wustite. Central regions, which were not highly metallized, showed some fayalite formation between adjacent grains of gangue and wustite, similar to that shown in Figure 5.25b.

Samples quenched from 1100°C showed higher metallization than those from 1000°C but were otherwise similar with extensive fayalite formation being confined to small internal regions (of low metallization). Gangue particles in extensively metallized regions remained intact despite the presence of internal fayalite phase in many cases.

After reduction to 1200°C some very small areas of coarsened wustite (similar to Figure 5.25c) could be observed. Metallized regions adjacent to these wustite "cores" were slag deficient but a
Fig. 5.26a  Pellet B, quenched from 900°C showing surface metalization and fayalite formation from wustite occluded by a gangue particle. Magnification 400x or \( \frac{1}{25} \) in. = 25 \( \mu \text{m} \).

Fig. 5.26b  Pellet B, quenched from 1300°C showing a subsurface region exhibiting slight coarsening of the metal and showing gangue particles at right and two-phased slag at left. Magnification 400x or \( \frac{1}{25} \) in. = 25 \( \mu \text{m} \).
considerable concentration of slag was observed near but not at the pellet surfaces. The metal phase showed some minor evidence of coarsening in these areas and some gangue particles appeared to be being dissolved by the liquid slag. Gangue particles at surface locations mostly remained inert.

Samples quenched from 1300°C did not exhibit areas of unreduced wustite and showed only minor coarsening of the metal phase compared to the structure observed for the 1200°C finishing temperature. Figure 5.26b shows an area just below the pellet surface where some minor metal coarsening can be seen. Both uncombined gangue and two-phased slag can be seen in this figure. The darker slag phase was analyzed with the electron microprobe and found to contain 98.0 ± 1.0% SiO₂ and only 0.1 ± 0.3% FeO. The lighter phase could not be analyzed quantitatively but a qualitative analysis suggested a silica content of approximately 50% and an FeO content of less than 10%.

The structure observed after quenching from 1380°C was very similar to that obtained after reaction to 1300°C. No formation of an iron shell was suggested.

5.7.7 Pellet C: As-Received Condition

Figure 5.27 shows the as-received structure of this pellet type. Slag materials provide the bonding phase in this case. Three phases can be identified in Figure 5.27, the light haematite, the darker bonding phase and a third (light grey) phase which is always surrounded by the bonding phase. Björkvall et al. (23) have investigated pellets of very similar composition in the as-indurated condition and report the third phase to be a magnesio ferrite containing approximately 80% Fe₂O₃ and 15% MgO. They also report the darker bonding phase to contain
Fig. 5.27 Pellet C, as-received condition. The white material is haematite and is bonded by a darker slag phase. Light grey areas of magnesio-ferrite can be seen and are always surrounded by slag. The dark mottled material is mounting plastic.

Magnification 400x or \[ \text{---} = 25 \mu\text{m} \].
approximately 20% Fe₂O₃, 30% CaO, 40% SiO₂, 2.5% Al₂O₃ and 2.5% MgO.

5.7.8 Pellet C: Reduced With a Gas Flow Rate of 5 cc/sec.

Magnetite cores could be detected with the naked eye in samples reduced to 750°C. A few tiny metal nuclei could also be detected at the surface of the sample. In regions reduced to wustite, the magnesio ferrite phase could no longer be discerned.

Samples reduced to 900°C showed no residual magnetite. Metallization was observed to be confined to a narrow (approximately 0.5 mm deep) well defined zone at the pellet surface. The structure at the pellet surface is shown in Figure 5.28a.

Samples quenched from 1000°C and 1100°C showed structures similar to that at 900°C with the exception that the well defined limit of metallization was more advanced at each higher temperature. The slag phase showed no sign of change in wustite-rich areas and could be discerned in highly metallized areas only with great difficulty. Figure 5.28b shows the surface structure at 1100°C which is typical of most metallized areas.

The central areas of pellets quenched from 1200°C had the structure shown in Figure 5.28c. Wustite grains in these areas had become quite rounded. This structure shows some similarity to the central regions of acid pellets reduced under the same conditions to the same finishing temperature. Metallization was observed to be most active at the well defined limits of the wustite core. The structure of highly metallized zone was similar to that seen at 1100°C and no sign of slag melting could be seen.

Electron microprobe analysis of the slag phase near the pellet surface gave the following results:
Fig. 5.28a  Pellet C, quenched from 900°C, showing mettallization at the sample surface. Magnification 400x or \( \frac{1}{25} \) = 25 \( \mu m \).

Fig. 5.28b  Pellet C, quenched from 1100°C showing a surface region. Metallization is typical of most metallized areas. Magnification 400x or \( \frac{1}{25} \) = 25 \( \mu m \).
Fig. 5.28c Pellet C, quenched from 1200°C. Central region showing modified wustite structure wetted by slag. Some metal particles can also be seen. Magnification 400x or \( \frac{2}{25} \) = 25 \( \mu \text{m} \).

Fig. 5.28d Pellet C, quenched from 1300°C. Central region showing considerable coarsening of the wustite grain size. Magnification 400x or \( \frac{2}{25} \) = 25 \( \mu \text{m} \).
Fig. 5.28e  Pellet C, quenched from 1300°C. Surface structure showing considerable coarsening of the metal phase in association with liquid slag.
Magnification 400x or ______ = 25 µm.

Fig. 5.28f  Pellet C, quenched from 1380°C. Significant coarsening of the metal phase has occurred, but no iron shell formation can be seen.
Magnification 40x or ______ = 250 µm.
<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>3.3 ± .7%</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>31.7 ± 1.7%</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7.2 ± 2.3%</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>38.7 ± .5%</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>10.5 ± 1.1%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>91.4%</td>
<td></td>
</tr>
</tbody>
</table>

A qualitative analysis of slag associated with wustite in central regions suggested an FeO content of approximately 20%.

Samples quenched from 1300°C still showed central cores of wustite but the size of wustite grains had increased dramatically as shown in Figure 5.28d. Metallization was observed to be still most active at the edges of the wustite core, but the adjacent (most recently formed) metal was of much larger morphology than that formed at lower temperatures. Figure 5.28e shows the surface structure where considerable coarsening of the metal phase can be seen in association with an apparently liquid slag phase.

Samples quenched from 1380°C and 1400°C contained central cavities. The slag in regions adjacent to the central cavity contained considerable quantities of precipitated wustite while slag in areas removed from the cavity was generally single phased and glassy. Figure 5.28f shows the surface structure at a reduced magnification of 40X. Considerable metal coarsening occurred between 1300°C and 1400°C but the final structure is still finer than that shown for Pellet A under similar circumstances (Figure 5.21f). The formation of an iron shell was not observed.

5.7.9 Pellet C: Reduced With a Gas Flow Rate of 50 cc/sec.

Pellets quenched from 750°C showed very little residual magnetite
and significant metallization at the surface.

Samples quenched from 900°C, 1000°C and 1100°C showed progressively higher degrees of metallization, the process being almost complete at 1100°C. Slag materials showed no physical signs of change during the reduction process and appeared to behave inertly after metallization. Figure 5.29a shows a central area at 1000°C and Figure 5.29b shows a similar area at 1100°C.

Samples quenched from 1200°C and 1300°C showed iron morphologies, very similar to that shown in Figure 5.29b. Coalescence of the slag phase indicated its melting point to be approximately 1300°C.

Figure 5.29c shows the structure observed after quenching from 1380°C. Coarsening of the iron phase in the temperature range 1300-1380°C has caused dramatic changes to pellet structure. An exuded droplet of slag can be seen at the pellet surface in Figure 5.29c which is taken at a reduced magnification.

5.8 Gaseous Carburization

In order to avoid confusion, micrographs in Section 5.7 were presented in the unetched condition. The extent of gaseous carburization which had occurred was estimated from metallographic examination after etching with 2% Nital (2% HNO₃ in methanol) solution. The observations made for samples reacted to 1380°C on the centre profile of temperature and gas composition are presented in Table 5.2. (The value < 0.02% has been inserted wherever no iron carbide particles were observed after etching.)

The highly carburized state of Pallet C at 1380°C after reduction with the gas flow rate of 50 cc/sec. is shown in Figure 5.30. It should be noted that a carbon content of < .02% was always recorded
Fig. 5.29a  Pellet C, quenched from 1000°C showing a partially metallized central region. Magnification 400x or \( \frac{\text{area}}{25 \, \mu \text{m}} \).

Fig. 5.29b  Pellet C, quenched from 1200°C showing typical metallized morphology. Magnification 400x or \( \frac{\text{area}}{25 \, \mu \text{m}} \).
Fig. 5.29c  Pellet C, quenched from 1380°C: The structure shows massive iron phase morphology and significant coalescence of slag phase. Some slag has been exuded as a droplet on the metal surface (top centre).
Magnification 40x or — = 250 μm.
for Pellets A and B after reaction to temperatures of .1300°C and less. Pellet C showed < .02% carbon for reduction to 1300°C with a gas flow rate of 5 cc/sec. and only ~ .04% carbon for reduction to 1300°C with a gas flow rate of 50 cc/sec.

Table 5.2

Estimated Extent of Metallic Carburization from the Gas Phase

(Samples quenched from 1380°C using central gas-temperature profile.)

<table>
<thead>
<tr>
<th>Gas Flow Rate</th>
<th>Pellet A</th>
<th>Pellet B</th>
<th>Pellet C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 cc/sec.</td>
<td>&lt; .02% C</td>
<td>&lt; .02% C</td>
<td>.02% C</td>
</tr>
<tr>
<td>50 cc/sec.</td>
<td>0.02% C</td>
<td>&lt; .02% C</td>
<td>0.65% C</td>
</tr>
</tbody>
</table>

5.9 Melting Behaviour

Experiments to examine the carburization and melting behaviour of pellets in contact with coke were performed on the centre gas-temperature profile with a gas flow rate of 50 cc/sec.

5.9.1 Pellet A

A run terminated at 1300°C showed a small region of heavily sintered iron where the pellet had contacted the coke bed. The etched structure of this area is shown in Figure 5.31a. A large gradient of carbon concentration can be seen (< .02% to ~ .07%). Although the slag phase had obviously been liquid, no melting of the iron had occurred.

The slag materials in contact with the carburized area were analyzed with the electron microprobe. The slag associated with metal containing approximately 0.6% carbon returned the following analysis:
Fig. 5.30 Pellet C, quenched from 1380°C, etched with 2% Nital and showing carbon content of approximately 0.65%. Some grain boundaries are also seen in the slag phase. Magnification 200x or \( \frac{\text{\_\_\_\_\_}}{50 \mu\text{m}} \).
The slag adjacent to metal containing approximately 0.02% carbon was found to contain two phases, the first representing approximately 30% of the slag volume, returned the following analysis:

<p>| | | |</p>
<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>0.3 ± 0.1%</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>43.5 ± 0.9%</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>46.4 ± 1.1%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90.2%</td>
<td></td>
</tr>
</tbody>
</table>

A quantitative analysis of the second phase could not be obtained but a qualitative analysis suggesting a higher FeO level of approximately 10% was obtained.

In an attempt to obtain a molten iron product, two pellets were reacted to 1380°C and maintained at that temperature (with the CO/Ar gas mixture flowing) for 21 minutes until the pellets were observed to collapse. Upon quenching the pellets were found to have partially melted. Figure 5.31b shows the appearance of the sample obtained. Portions of the sample were submitted for wet analysis. The results are shown below:

<table>
<thead>
<tr>
<th>Metal</th>
<th>C 2.59%</th>
<th>Slag</th>
<th>SiO₂ 55.66%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si 0.28%</td>
<td>FeO 0.22%</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>1.01%</td>
<td>MnO 30.81%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al₂O₃ 6.36%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaO 2.99%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MgO 2.06%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>K₂O 0.51%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na₂O 2.04%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100.65%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FeO 0.3 ± 0.1%
MnO 43.5 ± 0.9%
SiO₂ 46.4 ± 1.1%

The slag adjacent to metal containing approximately 0.02% carbon was found to contain two phases, the first representing approximately 30% of the slag volume, returned the following analysis:

FeO 3.3 ± 0.6%
MnO 14.6 ± 0.9%
SiO₂ 74.8 ± 1.1%

92.7%

A quantitative analysis of the second phase could not be obtained but a qualitative analysis suggesting a higher FeO level of approximately 10% was obtained.

In an attempt to obtain a molten iron product, two pellets were reacted to 1380°C and maintained at that temperature (with the CO/Ar gas mixture flowing) for 21 minutes until the pellets were observed to collapse. Upon quenching the pellets were found to have partially melted. Figure 5.31b shows the appearance of the sample obtained. Portions of the sample were submitted for wet analysis. The results are shown below:

<table>
<thead>
<tr>
<th>Metal</th>
<th>C 2.59%</th>
<th>Slag</th>
<th>SiO₂ 55.66%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si 0.28%</td>
<td>FeO 0.22%</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>1.01%</td>
<td>MnO 30.81%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al₂O₃ 6.36%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaO 2.99%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MgO 2.06%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>K₂O 0.51%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na₂O 2.04%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100.65%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 5.31a  Pellet A. Carburized area of pellet quenched from 1300°C following reduction in contact with a coke bed. Etched with 2% Nital solution. Magnification 50x or \[ \frac{1}{200} \] = 200 μm.

Fig. 5.31b  Pellet A: Partially molten products obtained from melting experiment.
Fig. 5.31c  Pellet A. Section of previously solid and liquid products from a melting experiment. Etched with a 2% Nital solution. Magnification 40x or $\frac{1}{\mu m} = 250 \mu m$. 
The results for the metal phase refer to the previously liquid portion as seen in Figure 5.31c. Solid metal at the solid liquid interface is estimated to contain 0.75% carbon while that most removed from the liquid contained approximately 0.5%.

5.9.2 Pellet B

A run terminated at 1300°C showed only a very minor area of carburization. An attempt to obtain liquid products was made by reacting pellets to 1380°C and holding at temperature for the same length of time as Pellet type A. After quenching, no evidence of melting was observed but a brittle, grey ash-like layer was found on the surface of the pellets where they had contacted the coke bed.

Figure 5.32a shows a micrographic section at the contact point. Some carburization and sintering of the iron phase has occurred. Ahead of the carburized metal surface, some slag fragments can be identified. Figure 5.32b shows a scanning electron micrograph of the contact surface and Figure 5.32c shows an area of the pellet surface away from the coke bed for comparison, at the same magnification of 73x.

5.9.3 Pellet C

Runs to 1300°C resulted in zones of carburization similar to those shown in Figures 5.31a and 5.32a. Attempts to obtain liquid products from this pellet type were quite successful. A run terminated after 245 minutes at 1352 ± 5°C gave partially molten products as shown in Figures 5.33a and b. The unfused pellet portion shows a carbon concentration of approximately 0.8% (grain boundary and Widmanstätten cementite) in areas adjacent to the liquid while a carbon content of 0.7% was observed at points most distant from the liquid. The liquid is estimated to have contained approximately 3% carbon.
Fig. 5.32a Pellet B. Carburized zone in contact with coke bed. Etched with a 2% Nital solution. Magnification 40x or ___________ = 250 μm.

Fig. 5.32b Pellet B. Scanning electron micrograph of pellet surface contacting coke bed. Magnification 73x.
Fig. 5.32c  Pellet B. Scanning electron micrograph of pellet surface not contacted by coke bed. Magnification 73x.
Fig. 5.33a  Pellet C. Partially molten product.

Fig. 5.33b  Pellet C. Section showing previously solid and liquid materials. Etched with a 2% Nital solution. Magnification 40x or ____ = 250 µm.
Fig. 5.33c  Pellet C. Molten products.

Fig. 5.33d  Pellet C. Structure of solidified metal product. Etched with a 2% Nital solution. Magnification 40x or \( \frac{1}{3} \) = 250 \( \mu \text{m} \).
A run terminated after 249 minutes at 1365 ± 5°C gave completely molten products as seen in Figures 5.33c and d. Samples of metal and slag were submitted for analysis and the following results obtained. The analysis of the ash content of the coke bed material used in melting runs is also included.

Ash content of the coke was found to be 8.20%.

<table>
<thead>
<tr>
<th></th>
<th>Metal</th>
<th></th>
<th>Si</th>
<th>0.097%</th>
<th>Mn</th>
<th>0.084%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>4.00%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slag:</td>
<td></td>
<td></td>
<td>SiO₂</td>
<td>33.82%</td>
<td>SiO₂</td>
<td>46.34%</td>
</tr>
<tr>
<td></td>
<td>FeO</td>
<td>0.04%</td>
<td>Fe₂O₃</td>
<td>1.59%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>4.55%</td>
<td>Al₂O₃</td>
<td>47.14%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MnO</td>
<td>0.16%</td>
<td>CaO</td>
<td>0.56%</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>42.48%</td>
<td>MgO</td>
<td>1.30%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MgO</td>
<td>12.32%</td>
<td>K₂O</td>
<td>0.49%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>K₂O</td>
<td>0.13%</td>
<td>Na₂O</td>
<td>1.88%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na₂O</td>
<td>0.48%</td>
<td></td>
<td>99.30%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

93.98%

5.10 Differential Thermal Analysis Results

Differential thermal analyses of gangue materials were performed under an argon atmosphere with a heating rate of 20°C/minute. An alumina reference sample was employed.

5.10.1 Pellet A

The results obtained for this gangue mixture indicated the formation of the first liquid phase at approximately 1210°C and the attainment of a fully liquid product at approximately 1330°C.
5.10.2 Pellet B

The results obtained for this gangue mixture did not indicate the formation of any liquid phase for temperatures up to 1400°C.

5.10.3 Pellet C

Results for this gangue mixture indicated the formation of first liquid at approximately 1220°C and the attainment of fully liquid product at approximately 1320°C.

5.11 Summary of Metallographic Observations

The salient structural features observed under the microscope for each of the pellet types during reduction with gas flow rates of 5 and 50 cc/sec. are summarized below.

Pellet A (5 cc/sec.)

(a) significant fayalite formation
(b) formation of wustite/liquid slag cores at temperatures in excess of 1200°C
(c) very significant coarsening of the metal phase
(d) formation of an iron shell

Pellet A (50 cc/sec.)

(a) minimal formation of fayalite
(b) complete metallization at temperatures of 1200°C
(c) minor coarsening of the metal phase
(d) no formation of an iron shell
(e) very minor carburization effected by the gas stream
(f) molten products of liquid and slag could be obtained at 1380°C

Pellet B (5 cc/sec.)

(a) large quantities of fayalite formed
(b) formation of wustite/liquid slag cores at temperatures in
excess of 1200°C

(c) very significant coarsening of the metal phase
(d) formation of an iron shell

**Pellet B** (50 cc/sec.)

(a) minor formation of fayalite
(b) metallization essentially complete at 1300°C
(c) minor coarsening of the metal phase
(d) no formation of iron shell
(e) no carburization effected by the gas stream
(f) no molten products obtained at 1380°C

**Pellet C** (5 cc/sec.)

(a) no interaction between iron oxides and slag to form low melting point phase (< 1200°C)
(b) formation of wustite/liquid slag cores at temperatures in excess of 1200°C
(c) significant coarsening of the metal phase at temperatures greater than 1300°C
(d) no formation of an iron shell

**Pellet C** (50 cc/sec.)

(a) slag phase did not physically influence reduction
(b) essentially complete metallization at 1200°C
(c) very marked coarsening of the metal phase at temperatures greater than 1300°C
(d) significant carburization by the gas stream at temperatures in excess of 1300°C
(e) molten products readily obtained at a temperature of less than 1380°C
CHAPTER 6

DISCUSSION OF RESULTS

6.1 Introduction

In this chapter, results of laboratory experiments are discussed and some references made to the iron blast furnace process. In Appendix 3, a more detailed discussion of the implications for blast furnace operation is included.

In Sections 6.2 and 6.3, comments are made relating to the experimental conditions employed in the investigation.

Factors governing slag formation and the influences exerted by the slag phase during laboratory reduction of single pellets are discussed in Section 6.4. These influences and the influences of the slag phase during carburization and melting of the metal (discussed in Sections 6.6 and 6.7) are felt to be of major importance to the development of the upper and lower limits, respectively, of the softening-melting zone in the blast furnace. Experimental results indicate that fluxed pellets (similar to Pellet C in this investigation) offer potential advantages over acid pellets for reducing the resistance to gas flow associated with the softening-melting zone.

Experimental results also indicate superior performance for both acid and basic pellets when highly reduced prior to attaining temperatures in excess of 1000°C and this behaviour is discussed with reference
to current philosophies of blast furnace efficiency.

6.2 Size Distributions

The size distributions of the as-received samples (Figure 5.1) are the only indication of product uniformity prior to sample selection. The results indicate Pellet A to be the most uniform and Pellet C to be the least uniform. It should, however, be stressed that all samples had been screened by the producer to remove oversize and undersize fractions. Such an operation increases the "apparent uniformity" of the commercial product. Test samples were carefully selected on both quantitative and qualitative bases in an attempt to maximize their uniformity.

6.3 Reducibility Results

6.3.1 Introduction

Reduction experiments over a range of gas flow rates (Figures 5.18 and 5.19) have shown the gas flow rate of 50 cc/sec. to be supercritical for this experimental apparatus, and the gas flow rate of 5 cc/sec. to be in the subcritical range where gas flow rate is reaction rate controlling.

While Japanese investigators have concluded that gas velocities in the blast furnace are generally greater than 3 m/sec. (supercritical), experiments using the "Upper Bed Level" gas composition profile shown in Figure 3.7b, at a flow rate of 50 cc/sec. have shown that experiments at subcritical velocities can be used to simulate portions of the blast furnace burden where gas composition (or low flow rate) retards reduction.

In Section 3.1.2, upper levels of ore layers in the blast furnace have already been shown to be areas of interest in this respect.

In the remainder of this chapter, reduction of pellets with gas
flow rates of 50 cc/sec. and 5 cc/sec. will be termed "fast" and "slow" reduction, respectively.

Pellet types A and C were frequently found to return results indicating greater than 100% reduction by the weight loss method. The weight loss method of reduction determination was used due to the impracticability of performing wet analysis on all test samples, and was found to incur errors < ± 2% for finishing temperatures of 1000°C and 1200°C.

Pellet types A and C contained significant quantities of alkali oxides in the as-received condition. During testing of these pellet types a white deposit analyzing 7.95% Na₂O and 32.2% K₂O was found on the outlet end of the gas tube. Such a deposit was not observed during the reduction of type B pellets, and it is felt that the observed percent reduction values in excess of 100% may indicate the reduction and gasification of alkali oxides from Pellet types A and C, since the alkali content of Pellet B was considerably lower and percent reduction figures obtained for this pellet type never exceeded 100%.

As pointed out in Section 4.1, reproducibility is a problem frequently associated with experiments involving industrial quality pellets. In light of this fact almost all experimental runs were duplicated and multiple tests terminating at 1000°C, were performed on pellet types A and C under experimental conditions of slow reduction on the central temperature profile. This condition was chosen to reflect a "worst case" with respect to experimental control parameters and rate of reduction. Six tests on Pellet A returned a mean reduction of 57.7%, with a standard deviation of 1.6%, while five tests on Pellet A showed an average reduction of 60.4%, with a standard deviation of 3.3%. These
values are considered to be acceptable.

6.3.2 "Centre" and "Wall" Profile Similarities in Reducibility

Figures 5.2 to 5.9 show that for each pellet type and for both fast and slow reduction, marked similarities exist between results obtained by using "wall" and "centre" temperature-gas profiles. Microstructural features were also observed to be quite similar for the two experimental conditions.

It is felt that these observed similarities are due to the fact that during the 700°C to 1100°C temperature range, observed to be most critical for metallization and slag formation, the two temperature profiles and, to a lesser extent, the two gas composition profiles, are quite similar. The bases for selecting these profiles have already been discussed, and it should be noted that both Japanese and Russian quenched furnace investigators (2-9), also report strong correspondence between isothermal and isoreduction lines.

Further discussion of reduction behaviour is confined to results obtained using the centre temperature-gas profile.

6.3.3 Reducibilities of the Different Pellet Types

Figures 5.2, 5.5 and 5.7 for slow reduction show quite similar form, as is to be expected for reduction under conditions where the flow rate of the reducing gas is reaction rate controlling.

Figures 5.3, 5.7 and 5.8, however, for reduction with a supercritical gas velocity, do reflect the intrinsic reducibilities of the different ore types. Pellet type B shows a noticeably lower rate of reduction than do pellet types A and C.

Percentage reduction figures recorded for "fast" and "slow" reduction runs terminated at 1000°C (R₁₀₀₀) are presented in Table 6.1 with
ISO Reducibility Test results for easy comparison. Details of the ISO test were reported in Section 3.3.

Table 6.1

<table>
<thead>
<tr>
<th>Pellet Type</th>
<th>&quot;Fast&quot; Reduction R_{1000}</th>
<th>&quot;Slow&quot; Reduction R_{1000}</th>
<th>ISO Test Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>81</td>
<td>58</td>
<td>24.8</td>
</tr>
<tr>
<td>B</td>
<td>67</td>
<td>57</td>
<td>19.25</td>
</tr>
<tr>
<td>C</td>
<td>78</td>
<td>60</td>
<td>25.0</td>
</tr>
</tbody>
</table>

While % R_{1000} results for Pellet types A and B under slow reduction may, in part, reflect the formation of significant quantities of fayalite by solid state reaction, it is felt that the figures for fast reduction have not been influenced to any significant extent due to the far smaller quantities of fayalite produced under this reduction condition. The % R_{1000} values for Pellet type C are not felt to reflect any physical influence of the slag phase.

Pellet types A and B are both acidic pellets and the lower reducibility of Pellet B under these test conditions is felt to be attributable to its magnetitic origin (whereas Pellet A is made from haematite ore). The lower reducibility of magnetite ores has already been mentioned in Section 2.3.2.

It should be borne in mind that Pellet types A and B are produced on straight grate and grate-kiln type machines, respectively, and the possibilities of influence due to differences of thermal history during induration should not be ignored.

While basic pellets do not usually show as marked an increase in reducibility over acid pellets as does basic sinter over acid sinter.
(due to differences in pore structure and development)\(^{(71)}\). Pellets B and C allow a good comparison to be made here. Both pellets are produced on grate-kiln machines from magnetite ores having similar particle size distributions and specific surface areas.

The results listed in Table 6.1 indicate that a significant increase in pellet reducibility can be achieved by the addition of basic oxides to the raw concentrate before balling and induration.

6.4 Formation and Influence of Slag During Reduction

6.4.1 Pellet A

During fast reduction of this pellet, appreciable quantities of liquid slag were first observed after quenching from a temperature of 1300°C. Percentage reduction figures and qualitative electron microprobe analysis suggest this slag to be rich in MnO and SiO\(_2\) and deficient in FeO. The temperature of first liquid formation in the system MnO-SiO\(_2\) is 1251°C\(^{(12)}\) and suggests slag formation to have resulted from reaction between silica gangue particles and unreduced MnO. This slag is not considered to have influenced the reduction of iron oxide to any significant degree.

While the manganese content of these pellets was found to be heterogeneously distributed in the as-received condition, electron microprobe analysis of wustite grains in a sample quenched after slow reduction to 1100°C indicates greatly increased homogeneity of manganese distribution.

A continuous series of solid solutions exist in the ternary system FeO-MnO-SiO\(_2\) between fayalite (Fe\(_2\)SiO\(_4\)) and tephroite (Mn\(_2\)SiO\(_4\)) as shown in Figure 6.1. At temperatures in excess of 900°C, considerable quantities of a fayalite-like phase, belonging to this series of solid
Fig. 6.1a System FeO·2FeO·SiO₂·2MnO·SiO₂-MnO; liquidus surface.

Fig. 6.1b System 2FeO·SiO₂·2MnO·SiO₂.
solutions, were formed by reaction in the solid state. First liquid in the system FeO-SiO$_2$ is formed at a temperature of 1177°C (Figure 2.8), and at temperatures of 1200°C and greater, significant quantities of liquid slag phase were found in slowly reduced pellets, accumulating at central and surface locations.

Slag remaining in central locations wetted the unreduced wustite particles and caused considerable coarsening and rounding of these grains. The precipitation of secondary wustite from central slag also indicates that the slag was dissolving the wustite, with complete dissolution at temperatures between 1300°C and 1380°C resulting in large central cavities. The wetting behaviour of the slag on the wustite grains retarded reduction by greatly decreasing the wustite surface area available for reduction, and indeed restricted active metallization to small volumes at the surface of the "cored" central region.

The slag observed at the surface of the pellet exhibited wustite precipitation after quenching from 1200°C, indicating an FeO content in excess of 75%. The microprobe analyses of surface slag phases observed after quenching from 1300°C indicate an FeO content of only 40%. An influx of ferrous oxide following collapse of the central core caused an increased surface slag FeO content after reaction to 1380°C.

The presence of large quantities of slag at the pellet surface is believed to have hindered reduction in two ways. Firstly, the reduction of surface porosity of the pellet has inhibited the passage of reagent and product gases to and from the pellet interior. Secondly, iron precipitation, due to reduction of FeO from surface slag (which microprobe analysis and precipitate observations indicate to have occurred within the temperature range 1200°C - 1300°C), is believed to have been
responsible for the formation of the iron shell observed at the pellet surface.

The formation of iron shells on acid pellets has previously been reported by Turkdogan (1) and others but no explanation for their formation has previously been offered.

6.4.2 Pellet B

Owing to the lower reducibility of this pellet and the large number of silica particles occluding fine ore particles, the formation of some fayalite did occur even during "fast" reduction. The quantities of fayalite formed during "fast" reduction were not sufficient to greatly hinder reduction reactions, causing only minor "coring" of wustite in central regions at 1200°C.

During slow reduction of Pellet B very significant quantities of fayalite were formed and are thought to have significantly retarded reduction by the same methods as discussed for Pellet type A. Again, microstructural observations and electron probe analyses strongly suggest that the formation of an extensive iron shell at 1300°C has been due to the precipitation of iron reduced from FeO-rich slag which accumulated at the surfaces at temperatures as low as 1200°C.

6.4.3 Pellet C

During "fast" reduction of this pellet type, metallization was observed to be complete prior to the formation of the liquid slag phase. Therefore, the only influence upon reduction which can be ascribed to the slag phase in this case, is the positive one of increasing the reducibility of the parent magnetite concentrate. The heavy carburization occurring at temperatures in excess of 1300°C, (which must be viewed as advantageous in terms of blast furnace
operation) will be shown in a later section to be associated with the increased reducibility of FeO from iron silicate slags which accompanies increased basicity of such slags (40,41).

During "slow" reduction, fayalite formation did not occur, but at temperatures of approximately 1200°C and greater, reduction retardation, by the formation of liquid slag in association with wustite in the pellet interior, was observed. The liquid slag wetted the wustite grains and reduced their surface area available for reaction and caused the zone of active metallization to be confined to a very small volume.

Figure 6.2 shows the system \(2\text{CaO} \cdot \text{FeO} \cdot 2\text{SiO}_2 - 2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2\) which is relevant to this discussion. The left-hand side of the diagram represents compositions similar to that quantitatively suggested by microprobe analysis of slag associated with wustite. Compositions to the right of the diagram are similar to the microprobe analysis of slag found in metallized regions, the increased liquidus temperature being consistent with the first observation of previously liquid slag in such regions being for pellets quenched from 1300°C.

While the accumulation of slag at surface regions at a temperature of 1300°C is thought to have caused retardation to further reduction by lowering surface porosity, the formation of an iron shell was not observed. This is thought to be due to the low residual FeO content of the slag phase at the surface; any quantities of iron precipitated upon reduction of the residual FeO being insufficient for shell formation.

6.4.4 Summary

During the reduction of acid pellets, considerable quantities of fayalite and resultant ferrosilicate slag may be produced and cause considerable retardation of further reduction. This investigation has
Fig. 6.2 System $2\text{CaO} \cdot \text{FeO} \cdot 2\text{SiO}_2$ (Fe-Akermanite)-$2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ (Akermanite). Heavy dashed lines refer to binary equilibrium, and light dashed lines enclose areas where one or more phases cannot be expressed in terms of the melilitite components; some $\text{Fe}_2\text{O}_3$ is present in the liquids. (12)
shown that the local composition of the gas phase and sample temperature are critical to the formation of fayalite, as clearly indicated by Figure 6.3. The problems associated with early slag formation can be avoided if reduction conditions can be maintained within the field Iron + Silica shown at the bottom of Figure 6.3.

During the reduction of basic pellets, fayalite formation is not probable. The lower slag liquidus temperatures usually associated with increased FeO contents of these slags can, however, cause some retardation to reduction reactions by a liquid slag phase, if formed prior to complete metallization. The local gas-phase composition and pellet temperature are also the critical variables in this case.

The results of this work indicate that while the deleterious effects of slag influence can be avoided by "fast" reduction of all pellet types, the problems encountered in "slow" reduction of the basic pellet, type C, were considerably less severe than those encountered with acid Pellet types A and B.

Possible Advantages are indicated for blast furnace operation by the replacement of acid pellets with basic pellets in that the onset of softening behaviour under load is likely to be delayed until lower levels (higher temperatures) with resultant decrease in the depth (and gas resistance) of the softening-melting layer.

6.5 Swelling and Cracking Behaviour

6.5.1 Pellet A

Comparison of Figures 5.10 and 5.11 for the centre profile shows that considerably greater expansion occurred for pellets reduced slowly than for those reduced rapidly. This is most probably due to the early formation of an extensively metallized surface zone which
Fig. 6.3 Stable phases in system Fe-Si-O at low amounts of silicon.
inhibited pellet swelling in the latter case. The strengthening influence of the metallized zone is also expressed in the reduced frequency of pellet cracking observed for both central and wallside temperature profiles.

At temperatures in excess of 1100°C, the observed rate of volume decrease is significantly greater for pellets reduced slowly than for those rapidly reduced. This accelerated sintering was observed metallographically to be associated with the presence of large quantities of liquid slag capable of wetting the solid metal.

The low peak swelling value shown in Figure 5.12 cannot be attributed to the presence of an iron shell, but is probably due to the great length of time available for the haematite to magnetite transformation to occur in this case. Associated with this transformation are a change of crystal structure (hexagonal to cubic) and an increase in specific volume. Stresses resulting from the transformation are likely to be lower in the case of slower reduction.

6.5.2 Pellet B

Cracking was observed for this pellet type under all experimental conditions. This poor behaviour is most probably due to induration at too high a temperature for the particular raw material strength. Such over-firing can result in residual stresses which can cause cracking when combined with the volume change (+ 8%) associated with the haematite to magnetite transformation [25].

Figures 5.13 and 5.14 show similar peak swelling values for "slow" and "fast" reduction but at temperatures in excess of 1100°C slowly reduced samples show higher rates of shrinkage. This accelerated shrinkage has again been observed to be associated with the presence
of large quantities of liquid slag.

6.5.3 Pellet C

Figures 5.15 to 5.17 show similar swelling and shrinkage behaviours for this pellet type over the temperature range up to 1300°C. This is consistent with the observed similarities in slag behaviour with respect to the metal phase over this temperature range. Table 5.1 shows significant reductions in cracking frequency with increased rates of reduction. This is again due to the early formation of a strong, metallized surface zone.

The marked contraction of rapidly reduced pellets between 1300°C and 1380°C has been observed to be associated with significant carburization of the metal phase. This will be shown in Section 6.6 to be dependent upon the FeO content of the slag phase.

6.5.4 Summary

In the blast furnace, excessive swelling (> 20%) and cracking are usually associated with loss of strength and production of fines. These forms of degradation are to be avoided since they are associated with decreased permeability and lower productivity.

Rapid reduction has been shown to have a positive influence in this regard for Pellet types A and C but could not alleviate the problems encountered with Pellet type B.

The presence of significant quantities of liquid slag has been demonstrated to accelerate the rate of pellet shrinkage due to sintering of the metallic phase. While this does not cause problems in single pellet tests, very major problems may be encountered in the blast furnace where neighbouring pellets may sinter, soften and stick together under the compressive load of overlying burden (~ 2 Kg/cm²)
to form a dense composite having high gas flow resistance. This effect has been observed to be potentially more dangerous in the case of acid pellets where liquid slag may occur over a lower and wider temperature range.

6.6 Carburization From the Gaseous Phase

Results presented in Table 5.2 indicate that carburization via the gaseous phase is significantly easier in the case of basic pellets than for acid pellets.

Table 6.2 shows calculated values of austenite carbon content (wt%) in equilibrium with slags of Pellets A, B, and C as a function of slag FeO content. Calculations have been made for a temperature of 1300°C and two values of carbon monoxide partial pressure according to the reaction:

\[ \text{FeO}_{\text{slag}} + C_{\text{Fe}} = \text{Fe}_3 + \text{CO}(g) \]

\[ \Delta G^o = -35,350 - 35.9 T \text{ kcal/mole} \]

These calculations are based upon values of carbon activity in γ iron from Elliot et al. (63) and FeO activities have been taken from the following sources:

(a) System SiO₂-MnO-FeO at 1500°C: Bell (64)
(b) System SiO₂-FeO at 1350°C: Bodsworth (65)
(c) System SiO₂-CaO-FeO at 1600°C: Elliot (66)

The following simplifying assumptions have been made:

(a) The gaseous phase contains no CO₂.
(b) The idealized slag systems above adequately represent the actual pellet slags.
(c) MnO is not reduced in the case of Pellet A.
(d) In the case of Pellet type C, the alumina and magnesia contents have been added to the silica and lime contents respectively.
Table 6.2

<table>
<thead>
<tr>
<th>Pellet A</th>
<th>Pellet B</th>
<th>Pellet C</th>
</tr>
</thead>
<tbody>
<tr>
<td>% FeO</td>
<td>% C</td>
<td>% C</td>
</tr>
<tr>
<td>$P_{CO} = 0.44$</td>
<td>$P_{CO} = 0.7$</td>
<td>$P_{CO} = 0.44$</td>
</tr>
<tr>
<td>40</td>
<td>&lt; .02</td>
<td>&lt; .02</td>
</tr>
<tr>
<td>20</td>
<td>.02</td>
<td>.02</td>
</tr>
<tr>
<td>10</td>
<td>.03</td>
<td>.03</td>
</tr>
<tr>
<td>5</td>
<td>.04</td>
<td>.10</td>
</tr>
<tr>
<td>.2</td>
<td>.16</td>
<td>.27</td>
</tr>
</tbody>
</table>

* $SiO_2$ saturation occurs at 57% FeO for this system at 1300°C.
The data available do not allow calculations to be made for FeO contents lower than 2%.

The value of $P_{CO} = 0.44$ atmospheres corresponds to the conditions of this investigation while the value $P_{CO} = 0.7$ atmospheres is more representative of lower regions of the blast furnace.

It is well known that FeO is more easily reduced from basic than acidic slags, and this, combined with the values shown in Table 6.2 and the results of microprobe analysis, offers some explanation for the experimentally observed levels of gaseous carburization reported in Table 5.2.

The steep gradients of carbon concentration observed in areas contacting a coke bed can also be understood when the known greater efficiency of solid carbon (with respect to carbon monoxide gas) as a reducing agent for FeO is taken into consideration.

The microprobe analyses reported in Section 5.9.1 for slag in contact with a carburized region of a type A pellet correspond favourably with the calculated values reported in Table 6.2.

6.7 Melting Behaviours

The observations of melting behaviour, combined with the gangue material melting points, obtained by differential thermal analysis, indicate that the slag phase exercises a strong influence over melting behaviour.

Figure 6.4 shows a portion of the iron-carbon equilibrium phase diagram. Points A and C show the composition of solid material at the appropriate solid/liquid interface.

The higher temperature and longer time required to obtain liquid products from Pellet A than from Pellet C are consistent with the lower
Fig. 6.4 Part of the Iron Carbon Phase Diagram.
degree of carburization occurring from the gaseous phase in the case of Pellet A.

The liquidus temperatures of gangue components in Pellet types A and C were found to be quite similar, indicating the reduction of residual FeO, which is required for carburization, to be of major importance in obtaining a liquid product. (It is assumed that liquid slag viscosities are not great enough to exercise any controlling influence). The enhanced kinetics of FeO reduction accompanying increased slag basicity (40,41) therefore indicate a decided advantage for basic pellets when a molten product is desired. Such an advantage could have important implications for the lower limit of the softening-melting zone in the blast furnace.

Slag droplets were noted at the surface of dissolving pellet caps of Pellet types A and C and the highly carburized basic pellets (as shown in Figure 5.29c). The expulsion of these droplets was only observed for pellets in which carburization of the metal phase, to an extent of 0.5% or greater, had occurred. Similar effects have been observed by Japanese investigators to immediately precede melting (67).

It is possible that this slag is squeezed to the surface by the coarsening metal phase, and that this effect might be greatly intensified by the elimination of CO gas bubbles produced by reduction of residual ferrous oxide in the slag. In this respect Figure 5.33c is very interesting in that it shows gas bubbles to have been present at the slag/metal interface at the time of quenching.

Failure to obtain a molten product from Pellet B was almost certainly due to solidification of the slag phase upon reduction of residual FeO, as Table 6.2 and the gangue melting point indicate to be.
necessary at the observed level of carburization. Following some
initial carburization (while in contact with the coke bed) sintering
of the metallic phase occurred, reducing the metal/coke contact area
and leaving a solid slag skeleton which provided an effective barrier
to further rapid carburization.

The coke ash analysis reported in Section 5.8 suggests a melting
point in excess of 1600°C and it should be noted that a coke ash skele-
ton may also have acted to retard carburization. A coke ash skeleton
could even retard the carburization of a pellet whose slag did not so-
olidify if the ash were not soluble in the liquid slag.

The attainment of liquid products from pellets developing high
melting point slags (>1400°C) upon residual FeO reduction, is clearly
difficult due to limitations imposed by the slag phase. Such limita-
tions may have important implications for the location of the blast
furnace softening-melting zone and the nature of events occurring at
its lower limit. At this lower limit, rapid melting of the metal phase
and high fluidity of the slag phase are to be desired in order to main-
tain a "clean" structure offering minimum resistance to gas flow.

The results of wet analysis of melt products reported in Chapter 5
compare quite favourably with those of Sasaki et al. (6) (for samples
removed from the dripping zone of Hirohata No. 1 and Kukioka No. 4
blast furnaces) with respect to C, Si and Mn contents of the metal phase
and the reduction state of the slag phase.

6.8 The Influence of Slag on Metal Phase Morphology

During the course of this investigation, the presence of liquid
slag phase has been observed to be responsible for considerable modifi-
cation to the structure of the metal phase. Some examination of the
surface energies involved is indicated.

The measurement of surface and interfacial energies is experimentally very difficult, and the values given in this discussion should be regarded as being approximate only.

Figure 6.5 indicates the surface tension of a number of fused silicate systems. The surface energy of solid iron is approximately $2000 \text{ ergs/cm}^2$ and that of solid wustite is approximately $800 \text{ ergs/cm}^2$.

In order to obtain an indication of the energy associated with the formation of an interface between two phases, Antanov's Rule:

$$|\sigma_{\alpha/\beta} - \sigma_{\gamma/\beta}| = \sigma_{\alpha/\gamma},$$

where $\alpha$, $\beta$ and $\gamma$ denote the phases in question, can be used. It should, however, be stressed that this "rule" offers only a first approximation and has, in some cases, been found to give quite erroneous results.

A surface tension of $x \text{ dynes/cm}$ is consistent with a surface energy of $x \text{ ergs/cm}^2$.

Application of Antanov's Rule to the system solid FeO/liquid fayalite ($\text{Fe}_2\text{SiO}_4$) gives an interfacial energy of approximately $400 \text{ ergs/cm}^2$, a value significantly less than the sum of the surface energies of the two individual phases. The wetting behaviour of fayalite (and indeed all ferrosilicate slags by inspection of Figure 6.5) on solid FeO is indicated:

A similar calculation for the interface formed between liquid fayalite (or ferrosilicate slag) and solid iron also concurs with the observed wetting behaviour.

The values from Figure 6.5 for many MnO-$\text{SiO}_2$ and CaO-$\text{SiO}_2$ melts can also be seen to indicate wetting of both solid wustite and solid iron for wide ranges of melt composition in these slag systems.
Fig. 6.5. Surface tension in some silicate systems (68).
The greatest surface energy encountered in the pellet systems under examination is that of a free solid iron surface, and the greatest reduction of the total surface energy of the system is to be achieved by simply reducing the total free surface area of the metallic phase.

In experiments where rapid reduction resulted in the formation of a very limited volume of liquid slag, some significant reduction in total metal surface area did occur by solid state sintering. This phenomenon is associated with the diffusion of vacancies through the solid crystal lattice.

In experiments where a liquid slag phase was present in significant quantities, that slag was observed to migrate towards the surface of the pellet and there to be associated with considerable coarsening of and alteration to the morphology of the iron.

As mentioned in Chapter 2, the size of iron particles formed during the reduction process increases with the temperature at which metallization occurs. In the present case of reduction under conditions of continually increasing temperature, the finest iron (and pore) structure develops at the pellet surface. The observed migration of slag to surface regions can therefore be explained in that it allows maximum reduction of surface energy by the limited volume of slag available to wet the metal surfaces.

Figure 6.6 shows slag and metal phases at the surface of an acid pellet (type A) quenched from 1200°C. Metal surfaces contacted by slag are clearly smoother than those not contacted and so represent sites of reduced energy. In this case three possible explanations exist for the observed structure:

(a) reduction of FeO from the slag phase and the associated growth
Fig. 6.6  Surface view of a type A pellet after "slow" reduction to 1200°C showing the influence of slag in modifying metal morphology.
Magnification 400x or \( \frac{1}{25} \) = 25 μm.
of the metal phase.

(b) rapid relocation of iron atoms by diffusion along the interfacial boundary.

(c) transport of iron through the slag from rough (or high curvature) surfaces to smooth (or low curvature) surfaces of lower energy by processes of dissolution, diffusion and subsequent reprecipitation.

It should also be pointed out that the viscosity of the slag phase must be expected to exert strong influence over its ability to influence the morphology of the metal phase. Silicate slags containing very low levels of FeO are known to be very viscous over the temperature range of this investigation. The very minor changes observed for Pellet type B containing FeO deficient slags, at temperatures above 1300°C, may be due to the high viscosity expected of the slag phase.

It has been noted in previous sections that iron containing appreciable quantities of carbon (> .02%) coarsened to a significantly greater degree than iron containing no carbon. The observation of such an effect at the surface of a type B pellet (Figure 5.32a), in which the slag phase was solid, indicates that this effect is due only to a phenomenon occurring in the metal.

Associated with increased carbon content are both an increase in the austenite lattice parameter (approximately 1% at 0.7% C), and an increase in the homologus temperature $\frac{T}{T_M}$ (where $T_M$ is the absolute melting point of the solid). While changes in either of these properties can cause changes in the mechanical response of a metal when stressed, and increased diffusivity of carbon, it is not felt that the effect can be satisfactorily explained at this stage.
6.9 Implications for the Iron Blast Furnace

As pointed out in Chapter 2, the structure and behaviour of the softening-melting zone in the blast furnace are vital to its performance as a gas distributor to the furnace shaft or lumpy zone above, where the majority of reduction must be performed.

The nature of the softening-melting zone is largely determined by the materials reporting to it from above. This investigation has shown that, by varying the rate of pellet reduction, very significant differences in behaviour at elevated temperatures (>1100°C) can be achieved.

As stated earlier, Japanese researchers and operators have already concluded that optimum blast furnace operation is consistent with optimization of the softening-melting zone.

The more traditional view of blast furnace efficiency and optimization is shown in Figure 6.7 (69). This diagram considers blast furnace optimization in terms of thermal requirements and shaft gas utilization. The optimum point is indicated at approximately 39% direct reduction, that is to say, 39% of total iron ore reduction occurring at temperatures in excess of 1000°C.

In this investigation, in which some fundamental blast furnace conditions have been simulated, degrees of reduction of approximately 55-60% and 75-80% have been observed for "slow" and "fast" reduction to 1000°C, respectively. These values correspond to direct reduction rates of 40-45% and 20-25%, respectively.

In a conventionally operated blast furnace, clearly some acid pellets (and other acid materials) can be expected to form very significant quantities of fayalite during reduction and to contain large volumes of liquid slag at temperatures of 1200°C and above. In
Fig. 6.7 Illustration of the relationship between degree of direct reduction and carbon consumption in the blast furnace.
addition to being difficult to reduce and retarding carburization and melting phenomena, these slags are known to be associated with burden softening and refractory attack.

While the results of this investigation indicate that the use of fluxed pellets may not completely avoid the problems mentioned above, they do indicate that the onset of liquid slag can be delayed and that the volume of primary slag produced can be reduced by the addition of basic oxides. These effects may prove advantageous in delaying and reducing the softening behaviour in the blast furnace which is responsible for the greatest portion of the high gas flow resistance offered by the softening-melting zone.

While Figure 6.7 clearly shows that blast furnace operation with direct reduction rate of 20 or 25% incurs an enormous penalty of some 100 kg of carbon consumption per ton of hot metal produced, the results of this investigation suggest that some benefits may be achieved in terms of performance, related to softening-melting zone behaviour, at the expense of smaller decreases in the rate of direct reduction.
CHAPTER 7

SUMMARY AND CONCLUSIONS

The aim of this work was to study the development and influence of the primary slag phase formed during reduction of iron ore pellets when subjected to conditions simulating those encountered in the iron blast furnace.

The apparatus employed did not allow complete simulation of the blast furnace environment in the following respects:

1. It was not possible to impose a compressive load during reduction similar to that provided by overlying burden materials in the blast furnace.

2. The reducing gas stream contained only CO, CO₂ and Ar (substituted for N₂) and lacked the species H₂, H₂O, K, Na, S₂, SiO and others known to be present in smaller but often significant quantities in the blast furnace.

Samples were quenched from intermediate and final points of experimental time-temperature-gas composition profiles and examined physically, metallographically and using the electron microprobe analyzer.

Despite the aforementioned experimental limitations, the results of this investigation allow some useful insights into the blast furnace process and allow the following conclusions to be drawn:
1. Significant quantities of fayalite (Fe₂SiO₄) may be formed when acid pellets are subjected to temperatures in excess of 1000°C prior to complete metallization due to solid state reaction between silica and wustite.

2. The extent of fayalite formation increases with lower intrinsic reducibility of the ore and increased areas of contact between silicate gangue and ore particles.

3. Extensive fayalite production can result in the formation of large quantities of ferrosilicate slag which can act to retard the rate of further pellet reduction and lead to the formation of iron shells at the pellet surface.

4. Fayalite production can be avoided in the iron blast furnace.

5. Problems of reduction retardation due to the formation of liquid slag may be encountered in basic pellets but the temperature required for such behaviour is greater than in the case of acid pellets.

6. Carburization and melting of commercial pellets are greatly influenced by the previous history of reduction, residual slag FeO content and slag phase melting point.
APPENDIX 1

ACCURACY OF VOLUME MEASUREMENTS
BY THE MERCURY VOLUMENOMETER

Chromium plated steel ball bearings having a range of precisely known diameters were used to test the accuracy of the volumenometer. Volumes of the balls were calculated from the known diameters and measured with the volumenometer. The measured values appearing in Table A1 are averaged over five observations, this method being similar to that used to determine the volume of test pellets.

It should be noted from Table 1 that the greatest relative errors occur at volumes less than those encountered in this work and that the greatest absolute error observed is .025 cc.
Table Al: Accuracy of the Mercury Volumenometer

<table>
<thead>
<tr>
<th>Ball Bearing Diameter (cm)</th>
<th>Calculated Volume (cc)</th>
<th>Measured Volume (cc)</th>
<th>Greatest Absolute Error (cc)</th>
<th>Greatest Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.634</td>
<td>0.133</td>
<td>0.14 ± 0.005</td>
<td>+0.012</td>
<td>+9.02</td>
</tr>
<tr>
<td>0.793</td>
<td>0.261</td>
<td>0.25 ± 0.005</td>
<td>-0.016</td>
<td>-6.13</td>
</tr>
<tr>
<td>0.951</td>
<td>0.450</td>
<td>0.43 ± 0.005</td>
<td>-0.025</td>
<td>-5.55</td>
</tr>
<tr>
<td>1.268</td>
<td>1.067</td>
<td>1.08 ± 0.005</td>
<td>+0.018</td>
<td>+1.70</td>
</tr>
<tr>
<td>1.586</td>
<td>2.089</td>
<td>2.08 ± 0.005</td>
<td>-0.014</td>
<td>-0.67</td>
</tr>
<tr>
<td>1.905</td>
<td>3.594</td>
<td>3.61 ± 0.005</td>
<td>+0.021</td>
<td>+0.58</td>
</tr>
</tbody>
</table>
## APPENDIX 2A  SIZE DISTRIBUTION OF AS-RECEIVED PELLET SAMPLES

<table>
<thead>
<tr>
<th>Screen Opening (inches)</th>
<th>Wt. (g) Retained</th>
<th>Wt. (g) Retained</th>
<th>Cum.% Retained</th>
<th>Wt. (g) Retained</th>
<th>Cum.% Retained</th>
<th>Wt. (g) Retained</th>
<th>Cum.% Retained</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/4&quot;</td>
<td>0</td>
<td>0</td>
<td>100.0</td>
<td>24.7</td>
<td>0.35</td>
<td>99.65</td>
<td>99.5</td>
</tr>
<tr>
<td>5/8&quot;</td>
<td>0</td>
<td>0</td>
<td>100.0</td>
<td>0</td>
<td>0</td>
<td>99.65</td>
<td>760.9</td>
</tr>
<tr>
<td>9/16&quot;</td>
<td>0</td>
<td>0</td>
<td>100.0</td>
<td>120.8</td>
<td>1.72</td>
<td>97.93</td>
<td>8.92</td>
</tr>
<tr>
<td>1/2&quot;</td>
<td>815.1</td>
<td>9.21</td>
<td>100.0</td>
<td>1810.6</td>
<td>25.83</td>
<td>72.10</td>
<td>41.03</td>
</tr>
<tr>
<td>7/16&quot;</td>
<td>4213.2</td>
<td>47.56</td>
<td>90.79</td>
<td>3863.8</td>
<td>55.12</td>
<td>16.98</td>
<td>27.56</td>
</tr>
<tr>
<td>3/8&quot;</td>
<td>3354.7</td>
<td>37.90</td>
<td>42.23</td>
<td>1135.5</td>
<td>16.20</td>
<td>0.78</td>
<td>5.42</td>
</tr>
<tr>
<td>5/16&quot;</td>
<td>416.7</td>
<td>4.71</td>
<td>5.33</td>
<td>26.5</td>
<td>0.38</td>
<td>0.40</td>
<td>2.17</td>
</tr>
<tr>
<td>1/4&quot;</td>
<td>49.0</td>
<td>0.56</td>
<td>0.62</td>
<td>14.2</td>
<td>0.20</td>
<td>0.20</td>
<td>1.44</td>
</tr>
<tr>
<td>20 mesh (.0382&quot;)</td>
<td>0.0</td>
<td>0.00</td>
<td>0.00</td>
<td>0</td>
<td>0.00</td>
<td>0.20</td>
<td>0.22</td>
</tr>
<tr>
<td>-20 mesh</td>
<td>5.1</td>
<td>0.06</td>
<td>14.2</td>
<td>0.20</td>
<td>24.9</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>8,853.8</td>
<td>100.0</td>
<td>7,010.3</td>
<td>100.0</td>
<td>11,082.6</td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX 2B

EXPERIMENTAL OBSERVATIONS OF DEGREE OF REDUCTION, SWELLING INDEX AND CRACKING BEHAVIOUR
### Pellet A

**Condition:** Centre Profile. Gas Flow Rate = 5 cc/sec.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Finishing Temp. °C</th>
<th>Initial Weight $W_0$ (g)</th>
<th>Final Weight $W_f$ (g)</th>
<th>Initial Volume $V_0$ (cc)</th>
<th>Final Volume $V_f$ (cc)</th>
<th>Reduction</th>
<th>$\frac{\Delta V}{V_0}$ (%)</th>
<th>Cracked?</th>
</tr>
</thead>
<tbody>
<tr>
<td>A29</td>
<td>750</td>
<td>3.5941</td>
<td>3.3291</td>
<td>0.90</td>
<td>1.03</td>
<td>30.1</td>
<td>+14.4</td>
<td>YES</td>
</tr>
<tr>
<td>A102</td>
<td>750</td>
<td>3.5286</td>
<td>3.2492</td>
<td>0.92</td>
<td>1.01</td>
<td>28.1</td>
<td>+12.1</td>
<td>YES</td>
</tr>
<tr>
<td>A31</td>
<td>900</td>
<td>3.4227</td>
<td>3.2743</td>
<td>0.83</td>
<td>1.04</td>
<td>38.9</td>
<td>+25.3</td>
<td>NO</td>
</tr>
<tr>
<td>A107</td>
<td>900</td>
<td>3.4736</td>
<td>3.0147</td>
<td>0.94</td>
<td>1.05</td>
<td>46.9</td>
<td>+11.7</td>
<td>YES</td>
</tr>
<tr>
<td>A106</td>
<td>1000</td>
<td>3.4008</td>
<td>2.8402</td>
<td>0.91</td>
<td>0.98</td>
<td>58.5</td>
<td>± 7.7</td>
<td>NO</td>
</tr>
<tr>
<td>A1</td>
<td>1000</td>
<td>3.5589</td>
<td>2.9548</td>
<td>0.89</td>
<td>1.00</td>
<td>58.2</td>
<td>+12.4</td>
<td>NO</td>
</tr>
<tr>
<td>A123</td>
<td>1000</td>
<td>3.5860</td>
<td>2.9723</td>
<td>0.98</td>
<td>1.19</td>
<td>60.7</td>
<td>+21.4</td>
<td>NO</td>
</tr>
<tr>
<td>A124</td>
<td>1000</td>
<td>3.5476</td>
<td>2.9914</td>
<td>0.95</td>
<td>1.10</td>
<td>55.6</td>
<td>+15.8</td>
<td>NO</td>
</tr>
<tr>
<td>A125</td>
<td>1000</td>
<td>3.4112</td>
<td>2.8872</td>
<td>0.92</td>
<td>1.22</td>
<td>54.6</td>
<td>+32.6</td>
<td>NO</td>
</tr>
<tr>
<td>A126</td>
<td>1000</td>
<td>3.5112</td>
<td>2.9334</td>
<td>0.95</td>
<td>1.19</td>
<td>58.3</td>
<td>+25.2</td>
<td>YES</td>
</tr>
<tr>
<td>A2</td>
<td>1100</td>
<td>3.5613</td>
<td>2.8081</td>
<td>0.92</td>
<td>0.90</td>
<td>72.5</td>
<td>-2.2</td>
<td>NO</td>
</tr>
<tr>
<td>A103</td>
<td>1100</td>
<td>3.4139</td>
<td>2.6724</td>
<td>0.91</td>
<td>0.99</td>
<td>77.0</td>
<td>+8.8</td>
<td>NO</td>
</tr>
<tr>
<td>A105</td>
<td>1200</td>
<td>3.4758</td>
<td>2.7010</td>
<td>0.94</td>
<td>0.67</td>
<td>79.1</td>
<td>-28.7</td>
<td>NO</td>
</tr>
<tr>
<td>A3</td>
<td>1200</td>
<td>3.5371</td>
<td>2.7030</td>
<td>0.88</td>
<td>0.75</td>
<td>80.8</td>
<td>-14.8</td>
<td>NO</td>
</tr>
<tr>
<td>A4</td>
<td>1300</td>
<td>3.4825</td>
<td>2.5700</td>
<td>0.87</td>
<td>0.61</td>
<td>90.7</td>
<td>-31.0</td>
<td>NO</td>
</tr>
<tr>
<td>A104</td>
<td>1300</td>
<td>3.5114</td>
<td>2.5531</td>
<td>0.95</td>
<td>0.62</td>
<td>96.8</td>
<td>-34.7</td>
<td>YES</td>
</tr>
<tr>
<td>A101</td>
<td>1380</td>
<td>3.3504</td>
<td>2.3800</td>
<td>0.96</td>
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### Pellet A

**Condition:** Centre Profile, Gas Flow Rate = 50 cc/sec.

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<th>$W_0$ (g)</th>
<th>$W_f$ (g)</th>
<th>$V_0$ (cc)</th>
<th>$V_f$ (cc)</th>
<th>% Reduction</th>
<th>$\Delta V/V_0$ (%)</th>
<th>Cracked?</th>
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Pellet A

Condition: Wall Profile. Gas Flow Rate = 5 cc/sec.

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<th>Final Weight $W_f$ (g)</th>
<th>Initial Volume $V_0$ (cc)</th>
<th>Final Volume $V_f$ (cc)</th>
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<th>$\Delta V/V_0$ (%)</th>
<th>Cracked?</th>
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Pellet A

Condition: Wall Profile. Gas Flow Rate = 50 cc/sec.

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<th>Initial Weight $W_0$ (g)</th>
<th>Final Weight $W_f$ (g)</th>
<th>Initial Volume $V_0$ (cc)</th>
<th>Final Volume $V_f$ (cc)</th>
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<th>$\frac{\Delta V}{V_0}$ (%)</th>
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### Pellet B

**Condition:** Centre Profile. Gas Flow Rate = 5 cc/sec.

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Pellet B

Condition: Centre Profile. Gas Flow Rate = 50 cc/sec.

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<th>Final Volume $V_f$ (cc)</th>
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### Pellet B

**Condition:** Wall Profile. **Gas Flow Rate = 5 cc/sec.**

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<th>Final Weight ( W_f ) (g)</th>
<th>Initial Volume ( V_0 ) (cc)</th>
<th>Final Volume ( V_f ) (cc)</th>
<th>Reduction</th>
<th>( \frac{\Delta V}{V_0} ) (%)</th>
<th>Cracked?</th>
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<td>2.7348</td>
<td>0.92</td>
<td>0.76</td>
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**Pellet B**

Condition: Wall Profile. Gas Flow Rate = 50 cc/sec.

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<th>Run No.</th>
<th>Temp. °C</th>
<th>Initial Weight $W_o$ (g)</th>
<th>Initial Volume $V_o$ (cc)</th>
<th>Final Weight $W_f$ (g)</th>
<th>Final Volume $V_f$ (cc)</th>
<th>% Reduction</th>
<th>$\frac{\Delta V}{V_o}$ (%)</th>
<th>Cracked?</th>
</tr>
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<tr>
<td>B37</td>
<td>1000</td>
<td>3.4698</td>
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<td>2.7929</td>
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<td>2.7018</td>
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<td>B39</td>
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Pellet C

Condition: Centre Profile. Gas Flow Rate = 5 cc/sec.

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<th>Run No.</th>
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<th>Initial Weight $W_O$ (g)</th>
<th>Final Weight $W_f$ (g)</th>
<th>Initial Volume $V_O$ (cc)</th>
<th>Final Volume $V_f$ (cc)</th>
<th>Reduction $\frac{V_f}{V_O}$ (%)</th>
<th>Cracked?</th>
</tr>
</thead>
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<tr>
<td>C29</td>
<td>750</td>
<td>3.3291</td>
<td>3.1146</td>
<td>0.85</td>
<td>0.96</td>
<td>23.8</td>
<td>YES</td>
</tr>
<tr>
<td>C102</td>
<td>750</td>
<td>3.4737</td>
<td>3.2116</td>
<td>0.93</td>
<td>1.09</td>
<td>27.3</td>
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<tr>
<td>C31</td>
<td>900</td>
<td>3.2743</td>
<td>2.9387</td>
<td>0.85</td>
<td>0.98</td>
<td>37.1</td>
<td>YES</td>
</tr>
<tr>
<td>C107</td>
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<td>3.6224</td>
<td>3.2341</td>
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<td>1.06</td>
<td>38.8</td>
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<tr>
<td>C106</td>
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<td>3.4367</td>
<td>2.8420</td>
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<td>C1</td>
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<td>3.3860</td>
<td>2.8708</td>
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<td>55.0</td>
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<tr>
<td>C123</td>
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<td>3.5443</td>
<td>2.8800</td>
<td>0.93</td>
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<td></td>
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<tr>
<td>C124</td>
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<td>3.4915</td>
<td>2.9240</td>
<td>0.92</td>
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<td>58.4</td>
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<tr>
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<td>2.9566</td>
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<td>1.17</td>
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<tr>
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<td>3.6007</td>
<td>2.9825</td>
<td>1.02</td>
<td>1.15</td>
<td>62.1</td>
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<tr>
<td>C2</td>
<td>1100</td>
<td>3.5314</td>
<td>2.7925</td>
<td>0.88</td>
<td>0.87</td>
<td>75.6</td>
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<tr>
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<td>2.6913</td>
<td>0.92</td>
<td>0.66</td>
<td>75.6</td>
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<td>1200</td>
<td>3.3847</td>
<td>2.6155</td>
<td>1.00</td>
<td>0.80</td>
<td>82.4</td>
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<tr>
<td>C3</td>
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<td>2.5431</td>
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<td>0.66</td>
<td>95.7</td>
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<td>C104</td>
<td>1300</td>
<td>3.3901</td>
<td>2.4728</td>
<td>0.92</td>
<td>0.66</td>
<td>97.8</td>
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<tr>
<td>C101</td>
<td>1380</td>
<td>3.5655</td>
<td>2.8313</td>
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<td>0.53</td>
<td>74.4</td>
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### Pellet C

**Condition**: Centre Profile, Gas Flow Rate = 50 cc/sec.

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<th>Finishing Temp. °C</th>
<th>Initial Weight $W_0$ (g)</th>
<th>Final Weight $W_F$ (g)</th>
<th>Initial Volume $V_0$ (cc)</th>
<th>Final Volume $V_F$ (cc)</th>
<th>Reduction</th>
<th>$\frac{\Delta V}{V_0}$ (%)</th>
<th>Cracked?</th>
</tr>
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<tbody>
<tr>
<td>C135</td>
<td>750</td>
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<td>3.1300</td>
<td>0.98</td>
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<td>43.3</td>
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<td>3.1453</td>
<td>1.03</td>
<td>1.20</td>
<td>42.5</td>
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<td>900</td>
<td>3.4020</td>
<td>2.8919</td>
<td>0.93</td>
<td>1.12</td>
<td>54.2</td>
<td>+20.4</td>
<td>YES</td>
</tr>
<tr>
<td>C134</td>
<td>900</td>
<td>3.3919</td>
<td>2.8028</td>
<td>0.86</td>
<td>1.01</td>
<td>62.8</td>
<td>+17.4</td>
<td>NO</td>
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<td>2.7381</td>
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<td>77.0</td>
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<td>97.0</td>
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<td>2.5892</td>
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<td>2.8033</td>
<td>1.00</td>
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<td>2.7403</td>
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<td>0.79</td>
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<td>1.01</td>
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<td>0.41</td>
<td>100.4</td>
<td>-55.9</td>
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Pellet C

Condition: Wall Profile. Gas Flow Rate = 5 cc/sec.

<table>
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<tr>
<th>Run No.</th>
<th>Finishing Temp. °C</th>
<th>Initial Weight W₀ (g)</th>
<th>Final Weight W_f (g)</th>
<th>Initial Volume V₀ (cc)</th>
<th>Final Volume V_f (cc)</th>
<th>Reduction</th>
<th>ΔV/V₀ (%)</th>
<th>Cracked?</th>
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<tbody>
<tr>
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<td>3.4283</td>
<td>3.2312</td>
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<td>3.4276</td>
<td>3.1914</td>
<td>0.96</td>
<td>1.02</td>
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<td>+6.3</td>
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<td>3.5589</td>
<td>3.3394</td>
<td>0.86</td>
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<td>22.3</td>
<td>+17.4</td>
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<td>3.1331</td>
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**Pellet C**

**Condition:** Wall Profile.  *Gas Flow Rate = 50 cc/sec.*

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Finishing Temp. °C</th>
<th>Initial Weight $W_0$ (g)</th>
<th>Final Weight $W_f$ (g)</th>
<th>Initial Volume $V_0$ (cc)</th>
<th>Final Volume $V_f$ (cc)</th>
<th>Reduction</th>
<th>$\Delta V/V_0$ (%)</th>
<th>Cracked?</th>
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<tr>
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<td>52.7</td>
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## APPENDIX 2C

### Pellet A (Centre temperature profile)

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<th>Run No.</th>
<th>Gas Flow Rate cc/sec.</th>
<th>Finishing Temp. °C</th>
<th>Initial Weight $W_0$ (g)</th>
<th>Final Weight $W_f$ (g)</th>
<th>Initial Volume $V_0$ (cc)</th>
<th>Final Volume $V_f$ (cc)</th>
<th>$R_{1000}$</th>
<th>$\frac{AV}{V_0}$ (%)</th>
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<tbody>
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<td>5</td>
<td>1000</td>
<td>3.4008</td>
<td>2.8402</td>
<td>0.91</td>
<td>0.98</td>
<td>58.5</td>
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</tr>
<tr>
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<td>1000</td>
<td>3.5589</td>
<td>2.9548</td>
<td>0.89</td>
<td>1.10</td>
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<td>+12.4</td>
</tr>
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<td>3.5860</td>
<td>2.9723</td>
<td>0.98</td>
<td>1.19</td>
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<td>3.5476</td>
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<td>0.95</td>
<td>1.10</td>
<td>55.6</td>
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<td>2.8872</td>
<td>0.92</td>
<td>1.22</td>
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<td>0.94</td>
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<td>0.93</td>
<td>76.8</td>
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<td>0.92</td>
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<td>0.89</td>
<td>85.2</td>
<td>- 4.3</td>
</tr>
</tbody>
</table>
Pellet C  (Centre temperature profile)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Gas Flow Rate cc/sec</th>
<th>Finishing Temp. °C</th>
<th>Initial Weight $W_0$ (g)</th>
<th>Final Weight $W_f$ (g)</th>
<th>Initial Volume $V_o$ (cc)</th>
<th>Final Volume $V_f$ (cc)</th>
<th>$R_{1000}$</th>
<th>$\frac{\Delta V}{V_o}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C106</td>
<td>5</td>
<td>1000</td>
<td>3.4367</td>
<td>2.8420</td>
<td>0.98</td>
<td>1.03</td>
<td>62.6</td>
<td>+ 5.1</td>
</tr>
<tr>
<td>C1</td>
<td>5</td>
<td>1000</td>
<td>3.3860</td>
<td>2.8708</td>
<td>0.81</td>
<td>1.01</td>
<td>55.0</td>
<td>+ 24.7</td>
</tr>
<tr>
<td>C123</td>
<td>5</td>
<td>1000</td>
<td>3.5443</td>
<td>2.8800</td>
<td>0.93</td>
<td>Not Determined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C124</td>
<td>5</td>
<td>1000</td>
<td>3.4915</td>
<td>2.9240</td>
<td>0.92</td>
<td>1.02</td>
<td>58.4</td>
<td>+ 10.9</td>
</tr>
<tr>
<td>C125</td>
<td>5</td>
<td>1000</td>
<td>3.5946</td>
<td>2.9566</td>
<td>1.03</td>
<td>1.17</td>
<td>64.2</td>
<td>+ 13.6</td>
</tr>
<tr>
<td>C126</td>
<td>5</td>
<td>1000</td>
<td>3.6007</td>
<td>2.9825</td>
<td>1.02</td>
<td>1.15</td>
<td>62.1</td>
<td>+ 12.7</td>
</tr>
<tr>
<td>C142</td>
<td>10</td>
<td>1000</td>
<td>3.6687</td>
<td>2.9171</td>
<td>1.00</td>
<td>1.07</td>
<td>74.1</td>
<td>+ 7.0</td>
</tr>
<tr>
<td>C143</td>
<td>10</td>
<td>1000</td>
<td>3.6147</td>
<td>2.8807</td>
<td>1.01</td>
<td>1.11</td>
<td>73.4</td>
<td>+ 10.9</td>
</tr>
<tr>
<td>C141</td>
<td>25</td>
<td>1000</td>
<td>3.6571</td>
<td>2.8816</td>
<td>1.00</td>
<td>1.04</td>
<td>76.6</td>
<td>+ 4.0</td>
</tr>
<tr>
<td>C144</td>
<td>25</td>
<td>1000</td>
<td>3.8312</td>
<td>2.9768</td>
<td>1.04</td>
<td>1.13</td>
<td>81.3</td>
<td>+ 8.7</td>
</tr>
<tr>
<td>C131</td>
<td>50</td>
<td>1000</td>
<td>3.4792</td>
<td>2.7381</td>
<td>0.93</td>
<td>0.99</td>
<td>77.0</td>
<td>+ 6.5</td>
</tr>
<tr>
<td>C132</td>
<td>50</td>
<td>1000</td>
<td>3.4262</td>
<td>2.6616</td>
<td>0.93</td>
<td>0.95</td>
<td>80.6</td>
<td>+ 2.1</td>
</tr>
</tbody>
</table>
Pellet Types A and C

Upper Bed Level Gas Composition Profile (Gas Flow Rate = 50 cc/sec., Centre Temperature Profile)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Finishing Temp. °C</th>
<th>Initial Weight $W_0$ (g)</th>
<th>Final Weight $W_f$ (g)</th>
<th>Initial Volume $V_o$ (cc)</th>
<th>Final Volume $V_f$ (cc)</th>
<th>% Reduction</th>
<th>$\frac{\Delta V}{V_o}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A147</td>
<td>1000</td>
<td>3.3365</td>
<td>2.9017</td>
<td>0.92</td>
<td>1.06</td>
<td>46.2</td>
<td>+15.2</td>
</tr>
<tr>
<td>A148</td>
<td>1200</td>
<td>3.5190</td>
<td>2.8069</td>
<td>0.92</td>
<td>0.80</td>
<td>71.9</td>
<td>-13.0</td>
</tr>
<tr>
<td>C147</td>
<td>1000</td>
<td>3.2106</td>
<td>2.7431</td>
<td>0.95</td>
<td>1.02</td>
<td>52.6</td>
<td>+ 7.4</td>
</tr>
<tr>
<td>C148</td>
<td>1200</td>
<td>3.8850</td>
<td>3.0936</td>
<td>1.00</td>
<td>1.00</td>
<td>73.7</td>
<td>+ 0.0</td>
</tr>
</tbody>
</table>
APPENDIX 3

IMPLICATIONS OF THIS WORK TO BLAST FURNACE OPERATION

A3.1 The Conventional Layered Burden

As pointed out in Sections 3.1.2 and 6.3.1, due to the CO regenerative nature of the coke layers, ore particles occupying upper levels of a ferrous burden layer are exposed to furnace gases of lower reducing potential than those in lower parts of the same layer (but occupying the same furnace radial position). The results of quenched furnace investigations indicate this to be a long-term effect, operative right down to the softening-melting layer (6).

The results of this investigation indicate that material at the bottom of an individual ore layer (i.e., adjacent to CO regenerative coke layers) will be reduced rapidly with a minimum of problems associated with the early generation of liquid slag.

The degree of direct reduction usually associated with efficient modern blast furnace operation (approximately 40%) indicates that materials at upper levels of the ore layer are likely to be reduced less rapidly. In the case of acid burden materials, slow reduction can lead to the formation of significant quantities of fayalite slag prior to complete reduction. Basic materials may also form significant quantities of slag but, in this case the slags produced are less difficult to reduce and usually not quite so troublesome due to their higher melting points.
During charging of the blast furnace by the more conventional bell-type devices, radial variations in layer thickness are usually encountered due to variations in material falling and rolling properties. These variations are generally more pronounced in large furnaces owing to the relationship between throat radius \( r \) and batch volumes \( r^3 \).

Radial variations in layer geometry can obviously result in similar radial variations in the mean rate of ore layer reduction and hence in the proportion of troublesome liquid slag produced in materials not situated adjacent to coke layers.

Recent developments, such as moveable throat armour and the Paul Wurth bell-less top have given operators of large furnaces considerably greater control over burden distribution. While this has certainly allowed some control over the volume, nature and location of primary slag production, most efforts have to this point been directed towards optimization of the more easily accessible lumpy zone of the furnace.

The high pressure drop and low permeability associated with the softening-melting zone have already been discussed in Chapter 2, and it is clear from both quenched furnace and laboratory investigations that the early formation of large volumes of primary slag are the major contributors to this high gas resistance.

During this investigation, it has not been possible to examine the influence of compressive forces to which partially reduced materials in the blast furnace are exposed. The results of other investigations clearly indicate, however, that compressive forces can cause partially reduced ore particles (particularly pellets) to rupture. This tendency has been shown by Barnaba (45) to be more marked at low
degrees of reduction, presumably because of a thinner, layer of strong metallized material.

Japanese workers (74) have recognized that the spherical geometry of pellets is the worst possible in this respect due to the minimal surface area to volume ratio and attempts have been made to alter the geometry of agglomerates made from fine concentrates.

When rupturing occurs, any liquid slag phase present can be squeezed from the interior of the ore particle and enter the spaces between individual particles of the layer or bed. Hence the porosity of the layer is reduced not only by compaction but also by liquid slag expulsion into the interstices between particles.

Once expelled from the ore particle interior, liquid slag may come into contact with the bulk furnace gas stream which is likely to be both richer and more abundant than the gas previously encountered inside the ore particle. Reduction of ferrous oxide contained by the slag phase will result in metal deposition (so causing further consolidation) and may even cause solidification of the reduced slag due to elevation of the liquidus temperature upon FeO removal.

In the event that gravitational effects cause the slag to move to the bottom of the layer prior to reduction (as observed by Barnaba (45) and others (5, 6)), the calculations for metal phase carburization in Chapter 6 clearly indicate that carburization of reduced pellets at the bottom of the bed becomes much more difficult.

Thus, the production of significant volumes of liquid slag in pellets reduced slowly at the top of an ore layer can, upon expulsion into the bed's porous volume, significantly contribute to further compaction and consolidation of the bed and inhibit carburization of
metallics.

If slag is sufficiently fluid it is possible that it may leave the ore layer in which it was produced and drip into the underlying layer of coke. Such phenomena have been observed in quenched furnaces by Japanese investigators\(^{(4,5)}\). Upon contact with the solid coke it is likely that any residual FeO content would be reduced rapidly, and in the case of acid slags, the resultant elevation of the liquidus temperature would cause the slag to freeze. The ramifications of such a phenomenon must be expected to be very serious since the coke layers, or slits, in the softening-melting zone have been shown to be the principal route for gas distribution to the lumpy zone.

The above effects must be expected to be more severe in the case of acid slags than their basic counterparts due to their usually higher FeO contents, their lower melting points and their usually-greater increase in liquidus temperature with FeO removal. This is in keeping with the operational experience that flame temperatures must in general be restricted to lower levels in acid burden operation than in operation with basic burdens, and also for operation at higher levels of silicon in the hot metal.

Large short-term variations in such operational parameters as flame temperature and blast penetration are known to cause operational problems of irregularity and uneven burden descent. It is the opinion of this author that these effects may be due to sudden changes in effective coke slit cross-sectional area available for gas flow. Such changes might result from altered conditions of slag flow and composition consistent with the changed conditions of furnace operation.

It should be pointed out here that, especially in the case of acid
slags, the reduction of alkali metal oxides from the slag phase might cause similar problems since the presence of these oxides dramatically lowers the melting points of many acid slag compositions. Japanese investigators report alkali reduction and gasification to be most active at the lower limit of the softening-melting zone where these effects would be most serious (6).

The results of this investigation support Japanese suggestions (5) that the slag phase plays the major role in determining carburization of the metal which in turn is the event considered to control the lower limit of the melting zone. The results also indicate that melting can be expected to occur at lower temperatures in the case of basic burden materials. Many operations are today based (for reasons of economy, material availability and also proven productivity) upon burdens comprised of significant proportions of both acid and basic materials. In Figure Al some possible geometrical arrangements for the softening-melting zone are presented schematically. These arrangements are based upon alternative material distribution patterns at the furnace stock-line and probable different softening-melting behaviour of these different ore types. (Acid ores are presumed to have higher meltdown temperatures and wider thermal ranges of softening behaviour than basic ores.)

Also indicated in Figure Al are coke slits, representing the paths of minimum gas resistance through the softening-melting zone.

It will be noted that while the number of slits available for gas flow is approximately the same for Figures Al(a) and (b), their length and hence flow resistance are greater for the case of an acid burden. Figure Al(c) shows that the charging of acid material to the walls and
Fig. A1 Possible geometric arrangements of the softening-melting zone.
basic materials to the centre is expected to greatly reduce the number of slits available for gas flow while the reverse charging technique has the opposite and obviously more desirable effect.

It should be pointed out that in presenting Figure A1 some very broad and possibly inaccurate assumptions are made but it is believed that this type of representation is valuable in indicating the possibilities which exist for controlling furnace operation by the careful selection of raw materials and charging procedure most conducive to optimization of the softening-melting zone.

Figure A2 is taken from a recent paper by Wakayama et al. (8) and shows two idealized forms of the softening-melting zone. The authors conclude that the form marked β is desirable to stabilize furnace operation and optimize shaft gas utilization.

The preceding discussion has been based on the behaviour of ferrous materials during their descent through the blast furnace, but the behaviour of coke should not be neglected. The importance of coke quality to the softening-melting (or cohesive) zone and lower regions of the blast furnace are well illustrated in Figure A3 which is due to Ishikawa (70).

A3.2 Possibilities for Stack Injection

The possibility of achieving significant gains in furnace productivity by the injection of reducing gases into the furnace shaft at the bosh level has been recognized for some years. While advantages similar to those available to operation with prereduced burden have been shown to be both theoretically and practically feasible, economic factors have to date limited large-scale investigations.

Many of the factors giving rise to troublesome softening behaviour
Fig. A2  Distribution of the volume of blast passing through the softening-melting zone.
Fig. A3  Coke quality influences on blast furnace operation (70).
and retardation of metal melting due to the presence of FeO-rich slag are due to burden materials reaching relatively high temperatures (say 1200°C) while still only partially reduced. Stack gas injection offers a possible solution to these problems by allowing the introduction of an additional increment of reducing gases to the lumpy zone, so permitting lower residual levels of FeO to be reached before the material is exposed to the high temperature areas of the furnace. Additional kinetic advantages may also be available if high proportions of hydrogen are present in the injected gas stream.

The major problems associated with stack injection are presently those relating to the development of technological expertise in achieving satisfactory penetration and mixing of the injected gases with bosh gases.

A3.3 Possibilities of Mixed Burdening

The coke and ore particles charged to the blast furnace generally have a particle diameter ratio of approximately 4:1. This ratio, and the productivity requirement that burden permeability be maximized make it essential that these materials be kept separate in the blast furnace.

While this criterion is satisfied within practical limits by the conventional layered burden, the findings of this investigation indicate that "gas starvation" and the problems of early slag production associated with lower rates of reduction of ore materials are also inherently associated with the layered burden.

Recent work by Standish (72) has shown that the numerous ore/coke interfaces formed in a layered burden can be responsible for very significant resistances to gas flow, particularly when significant size
differences exist between the two materials.

Standish has also recently pointed out that in some cases, the total resistances for mixtures of materials may be less than those for the equivalent layered structures (72).

A burden in which ore and coke particles (having compatible size distributions) are well mixed before charging and charged in such a manner as to prevent segregation at the furnace stockline, may prove feasible in the future. With such a burden, all ore particles would be situated adjacent to gas regenerating coke particles and all ore particles would be expected to reduce rapidly.

While such an operation would be expected to avoid the problems of early slag formation and allow high wind volumes to be blown (assuming the burden permeability to have been significantly increased due to the elimination of most ore softening problems) certain drawbacks and potential dangers need to be pointed out.

Firstly, it is possible that in mixed burden operation, shaft gas efficiency would be lower, implying higher fuel rates as mentioned in Chapter 6. While this seems disastrous at first glance, it should be remembered that the CO-rich top gas resulting from such an operation is a very useful energy source. The economics of such an operation would vary from plant to plant and are beyond the realm of this discussion.

Secondly, work by Japanese and German investigators (3, 73) has shown that under conventional layered burden operation, the softening-melting zone and the bosh walls are responsible for supporting the great weight of the burden in the lumpy zone. In a mixed burden operation it is possible that the softening-melting zone would not exist in a form capable of similar supporting behaviour. In such an event, a
very significant load would be transferred to the coke in the hearth of the furnace. In addition to modifying tuyeres, raceway, hearth and taphole behaviour from what we know today, this must be expected to place very severe demands on coke quality.

Thirdly, in the event of an operational mishap, there is the possibility that the entire furnace volume would become a "softening-melting zone" and recovery from such a situation would undoubtedly be a major task.
APPENDIX 4

COMPUTER OUTPUTS FOR ELECTRON MICROPROBE RESULTS

The following pages contain computer printouts of electron microprobe results. These results have been converted to percentage oxide. The statistical values given are those relating to the fields analyzed and not those relating to the machine.

For the great majority of analyses reported in this work the number of counts generated was in excess of 10,000. Such a value corresponds to a precision in analysis of 1%. Greater precision is achieved at higher count numbers (0.1% for 100,000 counts) and lower precision at lower count numbers (10% for only 100 counts).

A more detailed account of errors associated with microprobe analysis can be found in the literature (76).
### MICROPROBE ANALYSIS A 1100

**Date:** 79/03/0

**Submitted by:** R. Nightingale

**Description:** As received

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>68.41 ± 0.39</td>
<td>38.32 ± 0.43</td>
</tr>
<tr>
<td>Mn</td>
<td>14.96 ± 0.05</td>
<td>7.04 ± 0.03</td>
</tr>
<tr>
<td>O</td>
<td>28.53 ± 0.40</td>
<td>61.64 ± 0.44</td>
</tr>
</tbody>
</table>

Σ 98.72

* Determined by difference.

---

### MICROPROBE ANALYSIS A 1760

**Date:** 79/03/0

**Submitted by:** R. Nightingale

**Description:** AO Gangue

**Mean Chemical Composition and Two Sigma Limits Based on 19 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>55.67 ± 0.36</td>
<td>33.67 ± 0.32</td>
</tr>
<tr>
<td>O</td>
<td>33.33 ± 0.36</td>
<td>66.73 ± 0.32</td>
</tr>
</tbody>
</table>

Σ (100.01 ± 77.95) 9%

* Determined by difference.

---

### MICROPROBE ANALYSIS A 802

**Date:** 79/03/0

**Submitted by:** R. Nightingale

**Description:** As received

**Mean Chemical Composition and Two Sigma Limits Based on 19 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>45.89 ± 4.41</td>
<td>56.61 ± 5.80</td>
</tr>
<tr>
<td>Mn</td>
<td>22.35 ± 1.20</td>
<td>12.79 ± 1.23</td>
</tr>
<tr>
<td>O</td>
<td>32.70 ± 3.09</td>
<td>60.59 ± 6.80</td>
</tr>
</tbody>
</table>

Σ 97.71

* Determined by difference.
### Microprobe Analysis A 600

**Submitted by:** R. Nightingale  
**Pellet A**  
**Description:** Mostite AC100  
**Quenched from 1100°C**  
**Slow Reduction**

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>74.55</td>
<td>47.75</td>
</tr>
<tr>
<td>Mn</td>
<td>2.91</td>
<td>1.90</td>
</tr>
<tr>
<td>S</td>
<td>22.53</td>
<td>50.35</td>
</tr>
</tbody>
</table>

**Determined by Difference**

---

### Microprobe Analysis A 100

**Submitted by:** R. Nightingale  
**Pellet A**  
**Description:** FAYALITE-I100AC  
**Quenched from 1100°C**  
**Slow Reduction**  
**Fayalite**

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>49.19</td>
<td>25.66</td>
</tr>
<tr>
<td>Mn</td>
<td>9.69</td>
<td>2.91</td>
</tr>
<tr>
<td>Si</td>
<td>31.32</td>
<td>56.93</td>
</tr>
</tbody>
</table>

**Determined by Difference**

---

### Microprobe Analysis A 300

**Submitted by:** R. Nightingale  
**Pellet A**  
**Description:** SFCE-FAY 1300A  
**Quenched from 1300°C**  
**Fayalite**

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
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<td>Fe</td>
<td>32.66</td>
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<tr>
<td>Mn</td>
<td>18.81</td>
<td>13.68</td>
</tr>
<tr>
<td>Si</td>
<td>32.96</td>
<td>58.12</td>
</tr>
</tbody>
</table>

**Determined by Difference**
### MICROPROBE ANALYSIS A 1200

**Date:** 1970.37

**Submitted by:** R. Nightingale

**Pellet A: Quenched from 1300°C**

**Description:** ACT 1300-PROBES 
Slow Reduction

**Si-rich phase**

**Mean Chemical Composition and Two Sigma Limits Based on 17 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>11.51</td>
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<tr>
<td>Mn</td>
<td>14.06</td>
<td>5.56</td>
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<tr>
<td>Si</td>
<td>17.79</td>
<td>7.11</td>
</tr>
<tr>
<td>O</td>
<td>56.64</td>
<td>1.40</td>
</tr>
</tbody>
</table>

\[ \pm 7.35 \]

* Determined by difference

### MICROPROBE ANALYSIS A 700

**Date:** 1970.37

**Submitted by:** R. Nightingale

**Pellet A: Slow Reduction**

**Description:** WUSTITE - ACT 1300 Quenched from 1200°C

**Si-rich Wustite**

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>74.10</td>
<td>47.14</td>
</tr>
<tr>
<td>Mn</td>
<td>2.32</td>
<td>1.89</td>
</tr>
<tr>
<td>O</td>
<td>22.58</td>
<td>3.01</td>
</tr>
</tbody>
</table>

\[ \pm 6.30 \]

* Determined by difference

### MICROPROBE ANALYSIS A 801

**Date:** 1970.37

**Submitted by:** R. Nightingale

**Pellet A: Slow Reduction**

**Description:** A009 - R. Nightingale Quenched from 1380°C

**Wustite at core surface**

**Mean Chemical Composition and Two Sigma Limits Based on 14 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>66.32</td>
<td>34.15</td>
</tr>
<tr>
<td>Mn</td>
<td>10.96</td>
<td>14.14</td>
</tr>
<tr>
<td>O</td>
<td>22.72</td>
<td>50.58</td>
</tr>
</tbody>
</table>

\[ \pm 0.49 \]

* Determined by difference
### Microprobe Analysis A 1300

**Date:** 79/03/0

**Description:** AC1300 — Smooth, quenched from 1380°C, similar slag phase

**Mean Chemical Composition and Two Sigma Limits Based on 12 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
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<tbody>
<tr>
<td>Fe</td>
<td>53 ± 47</td>
<td>23 ± 20</td>
</tr>
<tr>
<td>Mn</td>
<td>13 ± 59</td>
<td>11 ± 23</td>
</tr>
<tr>
<td>Si</td>
<td>13 ± 53</td>
<td>11 ± 55</td>
</tr>
<tr>
<td>O</td>
<td>47 ± 28</td>
<td>71 ± 97</td>
</tr>
</tbody>
</table>

*Determined by Difference*  

79-07

### Microprobe Analysis A 500

**Date:** 79/03/0

**Description:** Centre A1300C — Slow reduction, Fayalite at surface

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>31.30 ± 0.67</td>
<td>15.58 ± 0.48</td>
</tr>
<tr>
<td>Mn</td>
<td>18.25 ± 0.42</td>
<td>9.09 ± 0.30</td>
</tr>
<tr>
<td>Si</td>
<td>13.54 ± 0.38</td>
<td>13.18 ± 0.45</td>
</tr>
<tr>
<td>O</td>
<td>36.42 ± 1.02</td>
<td>62.15 ± 1.03</td>
</tr>
</tbody>
</table>

*Determined by Difference*  

54-25

### Microprobe Analysis A 1600

**Date:** 79/03/0

**Description:** AC1300 — 0.02C A at metal

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>2.49 ± 0.7</td>
<td>0.95 ± 0.18</td>
</tr>
<tr>
<td>Mn</td>
<td>1.34 ± 0.59</td>
<td>0.70 ± 0.30</td>
</tr>
<tr>
<td>Si</td>
<td>3.93 ± 0.53</td>
<td>2.68 ± 0.33</td>
</tr>
<tr>
<td>O</td>
<td>51.21 ± 1.11</td>
<td>63.17 ± 0.93</td>
</tr>
</tbody>
</table>

*Determined by Difference*  

79-70
### MICROPORBE ANALYSIS A 1400

**DATE**: 79/03/0

**SUBMITTED BY**: R NIGHTINGALE

**Description**: AC1300 0.02C 0 Fast Reduction

**Slag Phase**: B at metal with 0.02C

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>7.05 ± 1.24</td>
<td>2.99 ± 1.11</td>
</tr>
<tr>
<td>Mn</td>
<td>28.14 ± 0.72</td>
<td>11.29 ± 0.37</td>
</tr>
<tr>
<td>Si</td>
<td>0.89 ± 0.32</td>
<td>17.64 ± 0.36</td>
</tr>
<tr>
<td>O</td>
<td>49.93 ± 3.56</td>
<td>68.07 ± 8.95</td>
</tr>
</tbody>
</table>

* DETERMINED BY DIFFERENCE

**SUBMITTED BY**: R NIGHTINGALE

**Description**: AO15 R NIGHTINGALE Quenched from 1300°C

**Pellet A**: Fast Reduction, Slag at 0.02C metal

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>26 ± 0.07</td>
<td>11 ± 0.33</td>
</tr>
<tr>
<td>Mn</td>
<td>33.68 ± 0.64</td>
<td>14.73 ± 0.58</td>
</tr>
<tr>
<td>Si</td>
<td>21.65 ± 0.59</td>
<td>18.49 ± 0.47</td>
</tr>
<tr>
<td>O</td>
<td>44.44 ± 0.78</td>
<td>66.67 ± 0.69</td>
</tr>
</tbody>
</table>

* DETERMINED BY DIFFERENCE
### MICROPROBE ANALYSIS B 100

**SUBMITTED BY:** R NIGHTINGALE  
**Description:** Ayalite  
**DATE:** 7/9/03/70  
**Pellet B, Slow Reduction**  
**Quenched from 1100°C**  

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>54.30 ± 0.89</td>
<td>28.02 ± 0.76</td>
</tr>
<tr>
<td>Si</td>
<td>13.26 ± 0.27</td>
<td>13.66 ± 0.27</td>
</tr>
<tr>
<td>O</td>
<td>32.44 ± 0.80</td>
<td>58.38 ± 0.84</td>
</tr>
</tbody>
</table>

\[ \sum = 91.05 \]

* Determined by Difference

### MICROPROBE ANALYSIS B 1200

**SUBMITTED BY:** R NIGHTINGALE  
**Description:** B0 Gangue  
**DATE:** 7/9/03/70  
**Pellet B, Gangue at 1100°C Quench**  

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>45.81 ± 0.71</td>
<td>32.52 ± 0.63</td>
</tr>
<tr>
<td>O</td>
<td>54.19 ± 0.71</td>
<td>67.48 ± 0.63</td>
</tr>
</tbody>
</table>

\[ \sum = 99.17 \]

* Determined by Difference

### MICROPROBE ANALYSIS B 600

**SUBMITTED BY:** R NIGHTINGALE  
**Description:** Wustite B0  
**DATE:** 7/9/03/70  
**Pellet B, Quenched from 1100°C**  
**Slow Reduction Wustite**  

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>75.12 ± 0.27</td>
<td>46.38 ± 0.35</td>
</tr>
<tr>
<td>O</td>
<td>24.88 ± 0.27</td>
<td>53.62 ± 0.35</td>
</tr>
</tbody>
</table>

\[ \sum = 98.48 \]

* Determined by Difference
### MICROPROBE ANALYSIS B 300

**SUBMITTED BY: R NIGHTINGALE**  
**DESCRIPTION:** FAYALITE BCT1300 CENTRE Quenched from 1300°C  
**MEAN CHEMICAL COMPOSITION AND TWO SIGMA LIMITS BASED ON 10 ANALYSES**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>53.30 ± .50</td>
<td>27.12 ± .42</td>
</tr>
<tr>
<td>Si</td>
<td>13.15 ± .14</td>
<td>13.31 ± .17</td>
</tr>
<tr>
<td>O*</td>
<td>33.59 ± .43</td>
<td>59.57 ± .42</td>
</tr>
</tbody>
</table>

*D DETERMINED BY DIFFERENCE*  

### MICROPROBE ANALYSIS B 500

**SUBMITTED BY: R NIGHTINGALE**  
**DESCRIPTION:** WUSTITE BCT300 CENTRE Quenched from 1300°C  
**MEAN CHEMICAL COMPOSITION AND TWO SIGMA LIMITS BASED ON 22 ANALYSES**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>74.46 ± .43</td>
<td>45.54 ± .83</td>
</tr>
</tbody>
</table>

*D DETERMINED BY DIFFERENCE*  

### MICROPROBE ANALYSIS B 809

**SUBMITTED BY: R NIGHTINGALE**  
**DESCRIPTION:** B009 PELLET B, SLOW REDUCTION  
**MEAN CHEMICAL COMPOSITION AND TWO SIGMA LIMITS BASED ON 9 ANALYSES**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>13.25 ± .38</td>
<td>17.61 ± .15</td>
</tr>
<tr>
<td>Si</td>
<td>19.47 ± .39</td>
<td>13.27 ± .39</td>
</tr>
<tr>
<td>O*</td>
<td>67.53 ± .49</td>
<td>62.11 ± .33</td>
</tr>
</tbody>
</table>

*D DETERMINED BY DIFFERENCE*
### Microprobe Analysis B 200

**Date:** 7/9/03

**Submitted By:** R. Nightingale

**Description:** Pellet B, Slow reduction

**Description:** Pyrolite BC1380, quenched from 1380°C

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>53.56 ± 1.49</td>
<td>27.28 ± 1.43</td>
</tr>
<tr>
<td>Si</td>
<td>12.79 ± 1.17</td>
<td>12.95 ± 2.23</td>
</tr>
<tr>
<td>O</td>
<td>33.65 ± 0.56</td>
<td>59.78 ± 0.80</td>
</tr>
</tbody>
</table>

* Determined by difference

**Microprobe Analysis B 300**

**Date:** 7/9/03

**Submitted By:** R. Nightingale

**Description:** SI rich phase BC1380: Slow reduction

**Fe-rich phase**

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>11.67 ± 0.73</td>
<td>28.00 ± 15.30</td>
</tr>
<tr>
<td>Si</td>
<td>19.62 ± 1.15</td>
<td>62.69 ± 8.31</td>
</tr>
<tr>
<td>O</td>
<td>69.71 ± 1.05</td>
<td>0.62 ± 14.24</td>
</tr>
</tbody>
</table>

* Determined by difference

**Microprobe Analysis B 400**

**Date:** 7/9/03

**Submitted By:** R. Nightingale

**Description:** Pellet B, Slow reduction

**Description:** Slag BC1380, quenched from 1380°C

**Fayalite**

**Mean Chemical Composition and Two Sigma Limits Based on 15 Analyses**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
<th>Atomic Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>49.15 ± 0.89</td>
<td>23.71 ± 0.70</td>
</tr>
<tr>
<td>Si</td>
<td>12.76 ± 1.15</td>
<td>12.24 ± 24.31</td>
</tr>
<tr>
<td>O</td>
<td>30.10 ± 0.96</td>
<td>64.05 ± 91.2</td>
</tr>
</tbody>
</table>

* Determined by difference
### Microprobe Analysis B 802

**DATE:** 79/03/0

**SUBMITTED BY:** R NIGHTINGALE

**DESCRIPTION:** R NIGHTINGALE-Oxide

1380°C

**MEAN CHEMICAL COMPOSITION AND TWO SIGMA LIMITS BASED ON 15 ANALYSES**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>70.95 ± 0.14</td>
<td>55.56 ± 0.05</td>
</tr>
<tr>
<td>Si*</td>
<td>19.86 ± 0.71</td>
<td>18.99 ± 0.32</td>
</tr>
<tr>
<td>0</td>
<td>19.09 ± 0.64</td>
<td>80.99 ± 0.50</td>
</tr>
</tbody>
</table>

* DETERMINED BY DIFFERENCE

### Microprobe Analysis B 700

**DATE:** 79/03/0

**SUBMITTED BY:** R NIGHTINGALE

**DESCRIPTION:** Wustite-Cr380PpE

1380°C

**MEAN CHEMICAL COMPOSITION AND TWO SIGMA LIMITS BASED ON 14 ANALYSES**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>73.68 ± 1.06</td>
<td>44.19 ± 1.33</td>
</tr>
<tr>
<td>O*</td>
<td>26.32 ± 1.06</td>
<td>55.81 ± 1.33</td>
</tr>
</tbody>
</table>

* DETERMINED BY DIFFERENCE

### Microprobe Analysis B 1100

**DATE:** 79/03/0

**SUBMITTED BY:** R NIGHTINGALE

**DESCRIPTION:** Cr1380s-Phase B

1380°C

**MEAN CHEMICAL COMPOSITION AND TWO SIGMA LIMITS BASED ON 15 ANALYSES**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>45.20 ± 0.19</td>
<td>57.87 ± 0.04</td>
</tr>
<tr>
<td>Si*</td>
<td>54.77 ± 0.43</td>
<td>42.13 ± 0.62</td>
</tr>
</tbody>
</table>

* DETERMINED BY DIFFERENCE

---

Note: The symbols * represent elements determined by difference.
**MICROPROBE ANALYSIS C. 100**

**SUBMITTED BY: R NIGHTINGALE**

Pellet C, quenched from 1200 C

**DESCRIPTION:** Basic 1200 C Centre, slowly reduced

**MEAN CHEMICAL COMPOSITION AND TWO SIGMA LIMITS BASED ON 15 ANALYSES**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>FE</td>
<td>17.38 ± 1.11</td>
<td>7.34 ± 0.54</td>
</tr>
<tr>
<td>SI</td>
<td>11.93 ± 2.22</td>
<td>10.00 ± 0.20</td>
</tr>
<tr>
<td>CA</td>
<td>23.81 ± 4.12</td>
<td>13.98 ± 0.32</td>
</tr>
<tr>
<td>AL</td>
<td>2.33 ± 1.13</td>
<td>2.9 ± 0.12</td>
</tr>
<tr>
<td>MG</td>
<td>0.83 ± 0.03</td>
<td>0.03 ± 0.00</td>
</tr>
<tr>
<td>O</td>
<td>46.51 ± 11.14</td>
<td>68.36 ± 0.38</td>
</tr>
</tbody>
</table>

Σ DETERMINED BY DIFFERENCE

---

**MICROPROBE ANALYSIS C. 101**

**SUBMITTED BY: R NIGHTINGALE**

Pellet C, slow red'n

**DESCRIPTION:** COO2, R NIGHTINGALE, quenched from 1200 C

**SULFUR IN METALIZED ZONE**

**MEAN CHEMICAL COMPOSITION AND TWO SIGMA LIMITS BASED ON 15 ANALYSES**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WEIGHT PERCENT</th>
<th>ATOMIC PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>FE</td>
<td>2.48 ± 0.51</td>
<td>0.99 ± 0.21</td>
</tr>
<tr>
<td>SI</td>
<td>1.44 ± 0.71</td>
<td>1.51 ± 0.55</td>
</tr>
<tr>
<td>CA</td>
<td>3.64 ± 1.32</td>
<td>15.39 ± 3.71</td>
</tr>
<tr>
<td>AL</td>
<td>3.21 ± 1.60</td>
<td>5.79 ± 1.51</td>
</tr>
<tr>
<td>MG</td>
<td>6.31 ± 0.64</td>
<td>58.75 ± 2.27</td>
</tr>
<tr>
<td>O</td>
<td>45.28 ± 1.53</td>
<td>53.11 ± 0.51</td>
</tr>
</tbody>
</table>

Σ DETERMINED BY DIFFERENCE

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REFERENCES


(44) Bentall, L., (LKAB, Malmberget, Sweden), private communications.
(48) Bentall, L., (LKAB, Malmberget, Sweden), private communications.


(67) Lu, W-K. (McMaster University, Hamilton, Ontario), private communications.


(76) The Electron Probe Microanalyzer, McMaster University, 1969, p.39.