THE HEATING AND MELTING OF METALLIC DRI PARTICLES IN STEELMAKING SLAGS

by

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ABSTRACT

The rate of heat transfer to single metallic particles of Direct Reduced Iron (DRI) in molten steelmaking slags was studied. Spherical pellets were prepared from commercial DRI and DRI produced in the laboratory. The temperature inside the pellet and the volume of gas evolved from the pellet were measured as a cold DRI pellet was plunged and then held in the hot slag. The structure of the pellet and the frozen slag shell that forms on the pellet as it is heated in molten slag were also studied. The results indicate that molten slag permeates the pore structure of the pellet after the frozen slag shell melts away. The effects of slag penetration and gas evolution are visible in the temperature measurements.

The reactivity of DRI was also investigated by heating a sample in a sealed container, in the absence of slag, and measuring the volume of gas that evolved from the sample as it was heated. The kinetics of reaction of carbon and iron oxide were described by a simple structural model for the distribution of these constituents in DRI. A model based on kinetic control at the Fe/FeO interface gave the best overall agreement with the experimental measurements.

A computer model was developed to describe the heating and melting process for an isolated DRI pellet immersed in a steelmaking slag. The effects of temperature dependent thermophysical properties, forced convection by evolving gases, slag penetration, and the thermal requirements of the reactions in the pellet are included in the model. Predictions from the model indicate that the level of steady state agitation in the slag bath has the strongest influence on the total melting time of a pellet. The total melting time is also influenced strongly by the apparent density of the pellet. The importance of other variables depends on the specific conditions of the melting environment.

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## DEFINITION OF TERMS

### Variables

- **a**: coefficient in equation 5-20
- **$A_{i-1/2}$**: inner surface area in element $i$
- **$A_{i+1/2}$**: outer surface area of element $i$
- **b**: coefficient in equation 5-20
- **B**: constant in equation 5-31
- **$B_b$**: weight change of blank collection bulb during blank run
- **$B_{CO_2}$**: weight change of $CO_2$ collection bulb during blank run
- **$B_{H_2O}$**: weight change of $H_2O$ collection bulb during blank run
- **$B_{1,2}$**: weight change of boat during blank oxidation run
- **$B_{2,3}$**: weight change of boat during blank reduction run
- **C**: coefficient in equation 5-20
- **c**: constant in equation 2-6
- **$C_i$**: specific heat of element $i$ or component $i$
- **$C_L$**: specific heat of the liquid
- **$C_p$**: specific heat of the pellet
- **$C_s$**: specific heat of the slag
- **$C_{Tr,eff}$**: effective specific heat of a transformation
- **$z_o$**: molar concentration of oxygen in $\gamma$ Fe at saturation
- **$d_b$**: bubble diameter
- **$d_e$**: mean pore diameter in the pellet
- **$d_p$**: pellet diameter
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<th>Definition</th>
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<td>$D_{\text{CO-CO}_2}$</td>
<td>binary molecular diffusion coefficient for $\text{CO-CO}_2$</td>
</tr>
<tr>
<td>$D_{\text{eff}}$</td>
<td>effective binary pore diffusion coefficient</td>
</tr>
<tr>
<td>$D_K$</td>
<td>Knudsen diffusion coefficient</td>
</tr>
<tr>
<td>$D_O$</td>
<td>diffusion coefficient for oxygen in $\gamma$ Fe</td>
</tr>
<tr>
<td>$e$</td>
<td>porosity of the pellet</td>
</tr>
<tr>
<td>$e_m$</td>
<td>microporosity of the porous iron product layer</td>
</tr>
<tr>
<td>$E_p$</td>
<td>emissivity of the pellet</td>
</tr>
<tr>
<td>$E_s$</td>
<td>emissivity of the slag</td>
</tr>
<tr>
<td>$f$</td>
<td>frequency of bubble departures</td>
</tr>
<tr>
<td>$g$</td>
<td>gravitational constant</td>
</tr>
<tr>
<td>$G$</td>
<td>mass flow rate of gas</td>
</tr>
<tr>
<td>$h$</td>
<td>heat transfer coefficient</td>
</tr>
<tr>
<td>$h_{\text{max}}$</td>
<td>maximum value of heat transfer coefficient</td>
</tr>
<tr>
<td>$h_{\text{ss}}$</td>
<td>steady state value of heat transfer coefficient</td>
</tr>
<tr>
<td>$i$</td>
<td>spatial element number</td>
</tr>
<tr>
<td>$j$</td>
<td>time element number</td>
</tr>
<tr>
<td>$k$</td>
<td>mass transfer coefficient</td>
</tr>
<tr>
<td>$k_{\text{eff}}$</td>
<td>effective thermal conductivity of pellet</td>
</tr>
<tr>
<td>$k_{\text{gas}}$</td>
<td>thermal conductivity of gas in a pore</td>
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<td>$k_{i+1/2}$</td>
<td>avg. thermal conductivity of element $i$ and $i+1$</td>
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<tr>
<td>$k_{i-1/2}$</td>
<td>avg. thermal conductivity of element $i$ and $i-1$</td>
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<td>Symbol</td>
<td>Definition</td>
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<td>------------</td>
</tr>
<tr>
<td>$k_L$</td>
<td>thermal conductivity of liquid</td>
</tr>
<tr>
<td>$k_M$</td>
<td>thermal conductivity of metal substrate</td>
</tr>
<tr>
<td>$k_{pore, eff}$</td>
<td>effective thermal conductivity of a pore</td>
</tr>
<tr>
<td>$k_{rad}$</td>
<td>effective radiation conductivity of a pore</td>
</tr>
<tr>
<td>$k_s$</td>
<td>thermal conductivity of slag</td>
</tr>
<tr>
<td>$K$</td>
<td>carbon gasification equilibrium constant</td>
</tr>
<tr>
<td>$k^I$</td>
<td>Fe/FeO equilibrium constant</td>
</tr>
<tr>
<td>$L_i$</td>
<td>latent heat of fusion of component $i$</td>
</tr>
<tr>
<td>$L_p$</td>
<td>latent heat of fusion of the pellet</td>
</tr>
<tr>
<td>$L_s$</td>
<td>latent heat of fusion of slag</td>
</tr>
<tr>
<td>$m_L$</td>
<td>mass of liquid</td>
</tr>
<tr>
<td>$m_{p,i}$</td>
<td>mass of pellet solids in element $i$</td>
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<tr>
<td>$m_{(rem)}$</td>
<td>mass of slag remaining in an element</td>
</tr>
<tr>
<td>$m_{(in)}$</td>
<td>mass of slag entering an element</td>
</tr>
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<td>$M^X_{i}$</td>
<td>modulus defined by equation 5-2b</td>
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<tr>
<td>$M^X_{i-1}$</td>
<td>modulus defined by equation 5-2c</td>
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<tr>
<td>$M_{FeO}$</td>
<td>molecular weight of FeO</td>
</tr>
<tr>
<td>$n$</td>
<td>density of active bubbling sites on surface</td>
</tr>
<tr>
<td>$n$</td>
<td>exponent in equation 2-8</td>
</tr>
<tr>
<td>$n$</td>
<td>total number of data points</td>
</tr>
<tr>
<td>$N_{(+)}$</td>
<td>modulus defined by equation 5-18b</td>
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</table>
\( N_{(-)} \) modulus defined by equation 5-18c

\( P \) pressure

\( P_1 \) variable defined by equation 5-20b

\( P_2 \) variable defined by equation 5-20

\( P_3 \) variable defined by equation 5-21b

\( P_4 \) variable defined by equation 5-21c

\( q_i \) volumetric rate of heat generation in element \( i \)

\( Q \) gas flow rate

\( Q \) activation energy

\( Q_i \) modulus defined by equation 5-2d

\( r \) radius

\( r_i \) radial distance to nodal point in element \( i \)

\( r_s \) mean pore radius in the iron product layer

\( R \) radial distance to surface of pellet, present time step

\( R_0 \) initial pellet radius

\( R \) radius of wustite core in a DRI grain

\( R_0^* \) radius of a DRI grain

\( R' \) radial distance to surface of pellet, next time step

\( R' \) gas constant

\( R \) no. of points on each side of data point \( i \) used in
gas evolution rate calculation (cf. Appendix C)

\( s \) thickness of retained layer of liquid

\( S \) spreading coefficient

\( t \) time
<table>
<thead>
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<th>Description</th>
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<tr>
<td>( t_j )</td>
<td>time at time step ( j )</td>
</tr>
<tr>
<td>( t_{\text{max}} )</td>
<td>time at which maximum rate of gas evolution occurs</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature</td>
</tr>
<tr>
<td>( T_i )</td>
<td>temperature of element ( i ), present time step</td>
</tr>
<tr>
<td>( T_i^* )</td>
<td>temperature of element ( i ), next time step</td>
</tr>
<tr>
<td>( T_{\text{ML}} )</td>
<td>slag liquidus temperature</td>
</tr>
<tr>
<td>( T_{\text{MP}} )</td>
<td>pellet melting temperature</td>
</tr>
<tr>
<td>( T_{\text{MS}} )</td>
<td>slag solidus temperature</td>
</tr>
<tr>
<td>( T_0 )</td>
<td>initial pellet temperature</td>
</tr>
<tr>
<td>( T_\infty )</td>
<td>slag bath temperature</td>
</tr>
<tr>
<td>( U_o )</td>
<td>withdrawal velocity</td>
</tr>
<tr>
<td>( v )</td>
<td>volume of sample</td>
</tr>
<tr>
<td>( v_i )</td>
<td>volume of element ( i )</td>
</tr>
<tr>
<td>( v_{\text{ip}} )</td>
<td>volume of element being penetrated by molten slag</td>
</tr>
<tr>
<td>( V )</td>
<td>volume of gas</td>
</tr>
<tr>
<td>( V_{\text{STP},j} )</td>
<td>cumulative volume of gas evolved to time step ( j ) at STP</td>
</tr>
<tr>
<td>( V_{T,j} )</td>
<td>cumulative volume of gas evolved to time step ( j ) at temp. ( T )</td>
</tr>
<tr>
<td>( W_i )</td>
<td>initial sample weight</td>
</tr>
<tr>
<td>( W_m )</td>
<td>oxidized sample weight</td>
</tr>
<tr>
<td>( W_f )</td>
<td>reduced sample weight</td>
</tr>
<tr>
<td>( W_{\text{i}} )</td>
<td>initial dry sample weight</td>
</tr>
<tr>
<td>( W_{\text{TOT},i} )</td>
<td>total weight of element ( i )</td>
</tr>
<tr>
<td>( W_{\text{FeO}} )</td>
<td>total weight of FeO</td>
</tr>
<tr>
<td>( W_{\text{FeO},i} )</td>
<td>total weight of FeO in element ( i )</td>
</tr>
</tbody>
</table>
$W_m$  
width of element $m$

$X_{CO}$  
volume fraction of CO in gas at carbon gasification equilibrium

$X_{CO_2}$  
volume fraction of $CO_2$ in gas

$X_i$  
weight fraction of component $i$ in sample

$X'_{FeO}$  
modified weight fraction of FeO in sample (cf. equation 5-22a)

$X_{CO}$  
volume fraction of CO in gas at Fe/FeO equilibrium

$Y_i$  
volume fraction of component $i$ in sample

$z$  
density ratio defined in equation 5-22b

$Z$  
depth of slag bath

$\alpha$  
thermal diffusivity

$\beta$  
volumetric coefficient of thermal expansion

$Y_{Fe/g}$  
surface energy of solid Fe

$Y_{s/g}$  
surface energy of molten slag

$Y_{s/Fe}$  
interfacial energy between molten slag and solid Fe

$\delta$  
distance from inner surface of element $m$ to the moving boundary, present time step

$\delta^*$  
distance from inner surface of element $m$ to the moving boundary, next time step

$\Delta H_{rxn}$  
enthalpy of reaction

$\Delta H_{TR}$  
enthalpy of transformation

$\Delta r_{i,i-1}$  
distance between nodes in elements $i$ and $i-1$

$\Delta r_p$  
distance defined by equation 5-5c

$\Delta r_s$  
distance defined by equation 5-5b
\( \Delta t \) size of time step

\( \Delta T \) temperature difference defined by equation 5-5a

\( \Delta T_p \) temperature difference defined by equation 5-5c

\( \Delta T_s \) temperature difference defined by equation 5-5b

\( \Delta T_{TR} \) temperature range for occurrence of a phase transformation

\( \varepsilon \) energy dissipation per unit mass of fluid

\( \kappa \) specific reaction rate at Fe/FeO interface

\( \kappa_o \) pre-exponential rate constant for Fe/FeO interface reaction

\( \mu \) viscosity

\( \nu \) kinematic viscosity

\( \rho \) mass density

\( \rho_{\text{grain}} \) mean mass density of a single DRI grain

\( \rho_g \) molar density of gas

\( \rho_{\text{FeO}} \) molar concentration of oxygen in FeO

\( \sigma \) Stefan-Boltzmann constant

\( \tau \) tortuosity factor for the iron product layer on a DRI grain

\( \tau_o \) decay constant for transient forced convection (cf. equation 5-33)

\( \phi \) view factor for radiative transport (cf. equation 5.4b)

\( \phi \) modulus for numerical stability (cf. equation F-1)

\( \chi_{p,s} \) fraction of interfacial area between pellet and slag shell that is not in direct thermal contact

\( \chi_{p,b} \) fraction of interfacial area between pellet and thermocouple bead that is not in direct thermal contact
### Subscripts

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<td>b</td>
<td>bubble</td>
</tr>
<tr>
<td>d</td>
<td>diameter</td>
</tr>
<tr>
<td>i</td>
<td>element number or component</td>
</tr>
<tr>
<td>int</td>
<td>interface</td>
</tr>
<tr>
<td>int(+)</td>
<td>outer side of interface</td>
</tr>
<tr>
<td>int(-)</td>
<td>inner side of interface</td>
</tr>
<tr>
<td>ip</td>
<td>number of element to be penetrated by liquid slag in next time step</td>
</tr>
<tr>
<td>j</td>
<td>time element number</td>
</tr>
<tr>
<td>k</td>
<td>pellet surface element</td>
</tr>
<tr>
<td>L</td>
<td>liquid</td>
</tr>
<tr>
<td>m</td>
<td>element containing moving boundary</td>
</tr>
<tr>
<td>p</td>
<td>pellet</td>
</tr>
<tr>
<td>s</td>
<td>slag</td>
</tr>
<tr>
<td>ss</td>
<td>steady state</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>TR</td>
<td>transformation</td>
</tr>
</tbody>
</table>
## Dimensionless Groups

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Gr},d$</td>
<td>Grashof number based on particle diameter</td>
</tr>
<tr>
<td>Ko</td>
<td>Kolmogoroff number</td>
</tr>
<tr>
<td>$\text{Nu},b$</td>
<td>Nusselt number based on bubble diameter</td>
</tr>
<tr>
<td>$\text{Nu},d$</td>
<td>Nusselt number based on particle diameter</td>
</tr>
<tr>
<td>Pr</td>
<td>Prandtl number</td>
</tr>
<tr>
<td>$\text{Re},b$</td>
<td>Reynolds number based on bubble diameter</td>
</tr>
<tr>
<td>Sc</td>
<td>Schmidt number</td>
</tr>
<tr>
<td>$\text{Sh},d$</td>
<td>Sherwood number based on particle diameter</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

1.1 Background

Electric furnace steel production has undergone dramatic growth over the past two decades, amounting to 27 percent of the total steel production of the United States in 1982.\(^{(1)}\) Projections of the availability of scrap to feed these furnaces suggest that producers may be faced with shortages in scrap supply as a result of more efficient casting and forming operations.\(^{(3,4,5)}\) Having experienced such shortages in 1974,\(^{(3)}\) and faced with the prospects of future shortages, electric furnace steel producers have acquired an active interest in the utilization of direct reduced iron (DRI) as an alternate feed stock for the electric arc furnace. Because the cost of raw feed materials accounts for more than 75 percent of the total steel production costs in the operation of a typical electric arc furnace,\(^{(2)}\) the cost of scrap and the availability of alternative feed stocks for the electric arc furnace are key issues in the economics of electric furnace steel production.

The utilization of DRI as an electric furnace feedstock is not a new technology. Despite this fact, many of the factors that affect electric furnace operation with DRI are not well understood. Among those factors that are of importance are the factors that affect the rate of heat transfer to the pellets in the electric arc furnace and the factors that affect the melting time of an individual pellet.
The rate at which heat can be supplied to the pellets in the furnace is of primary importance to furnace operation. At steady state, the heat supplied by the arcs and by combustion reactions must be in balance with the heat supplied to the pellets for heating and melting and the heat losses from the furnace. For practical furnace operating temperatures, the rate at which heat is supplied to the pellet by convection from its melting environment may be the limiting step in the overall rate of heat transfer in the furnace. The factors that affect the rate of convective heat transfer to pellets in the furnace are, therefore, important in establishing the maximum rate of production of the furnace.

The melting time of an individual pellet also has an important influence on electric furnace operation. Nauman (6) has shown that the length of a transient that occurs in furnace operation, due to a change in the feed rate of pellets during continuous feeding, is approximately the melting time for an individual pellet. An understanding of the factors that affect the melting time of individual pellets is, therefore, important to the understanding and control of transients in furnace operation.

Industrial experience has shown that the differences in the physical and chemical characteristics between scrap and DRI are responsible for the differences in their melting behavior. The density of DRI is normally between that of the slag and the metal bath. For this reason, the melting of DRI usually takes place in the slag or at the slag/metal interface, as opposed to the metal bath. In addition, it is well established that upon charging the cold particle into a hot slag bath, a
solid shell of slag forms around the particle.\textsuperscript{(6,7)} In both cases, the slag may act as an appreciable barrier to the melting process. Industrial\textsuperscript{(8,9,10,11,12)} and laboratory\textsuperscript{(13,14)} experience has also shown that residual iron oxide and carbon within a DRI pellet may react upon heating to generate a substantial volume of gas, which is liberated from the pellet. The influence of this gas evolution on the rate of heat transfer in the furnace, and the melting time of a pellet in the furnace, is one of many important issues that make electric furnace practice with DRI different from the traditional electric furnace practice utilizing scrap.

1.2 The Structure and Properties of DRI

Direct reduced iron is a pelletized, briquetted or lump metal product that is produced by the direct reduction of iron ore in the solid state. Approximately 70 percent of the world's DRI production capacity is based upon gaseous reduction practices,\textsuperscript{(15)} using shaft furnace, retort, rotary kiln, or fluidized bed process. The balance use solid or liquid fuels and are almost exclusively based upon rotary kiln processes. Owing to the diversity of the currently operating direct reduction processes, the properties of DRI vary substantially from process to process. Virtually all commercially produced DRI contains unreduced iron oxide due to the incomplete reduction of iron ore. In addition to this residual oxygen, DRI also normally contains residual carbon and oxide gangue.

The extent of reduction of DRI is usually evaluated as percent metallization, which is defined as,
\[
\text{wt. \% Fe metallic} = \frac{\text{wt. \% Fe metallic}}{\text{wt. \% Fe total}} \times 100.
\] (1-1)

The percent metallization of commercial DRI typically lies between 85% and 98%. The carbon content of DRI can range from 0.1% to 2.5%, with carbon in the form of iron carbide or carbon soot. The amount of carbon present in DRI and its form depend primarily upon the method of production of the DRI product and the individual operating conditions of the reduction process. The amount of gangue present in DRI (as SiO\(_2\), Al\(_2\)O\(_3\), and CaO) may range from 3% to 12%. The gangue may be present from the iron ore, or from binder additions made before reduction to aid in agglomeration of the iron ore.

DRI typically has a highly porous, "sponge iron" structure, with a large internal surface area. The high porosity results in a low apparent density that normally ranges from 1.5 to 4.0 g/cm\(^3\). For briquetted DRI, mechanical densification of the porous structure results in a somewhat higher density, ranging from 5 to 6 g/cm\(^3\). A summary of some of the chemical and physical properties that are typically reported for commercially produced DRI is presented in Table 1.1.

The structure and composition of DRI are often difficult to characterize due to the heterogeneity of the material. Mean values of the composition and of the physical properties of large batches of material are often reported.\(^{(9,11,12,17)}\) The properties of individual pellets may vary substantially from these reported mean values. Sadrnezhaad\(^{(14)}\) observed large variations in both the structure and composition among individual pellets taken from the same production batch. Structural and compositional heterogeneity may also exist within a single pellet. In
Table 1.1
Properties of DRI

A. **Typical Composition of DRI**

<table>
<thead>
<tr>
<th>Component</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Metallization (% Fe&lt;sub&gt;met.&lt;/sub&gt;/% Fe&lt;sub&gt;tot.&lt;/sub&gt;)</td>
<td>85%-98%</td>
</tr>
<tr>
<td>% FeO (unreduced oxide)</td>
<td>3.0%-18.0%</td>
</tr>
<tr>
<td>% Carbon (C&lt;sub&gt;gr.&lt;/sub&gt; or Fe&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;gr.&lt;/sub&gt;)</td>
<td>0.10%-2.5%</td>
</tr>
<tr>
<td>% SiO&lt;sub&gt;2&lt;/sub&gt; (principal gangue)</td>
<td>1.0%-6.0%</td>
</tr>
<tr>
<td>% Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; (gangue)</td>
<td>0.3%-2.0%</td>
</tr>
<tr>
<td>% CaO (gangue + binder)</td>
<td>0.1%-2.0%</td>
</tr>
<tr>
<td>% MgO (gangue + binder)</td>
<td>0.1%-1.5%</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>0.002%-0.02%</td>
</tr>
<tr>
<td>% Phosphorus</td>
<td>approx. 0.02%</td>
</tr>
</tbody>
</table>

B. **Typical Physical Properties of DRI**

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (dia. or minimum dimension, mm)</td>
<td>1-30</td>
</tr>
<tr>
<td>Apparent Density (g/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>1.6-6.0</td>
</tr>
<tr>
<td>Relative Porosity</td>
<td>0.3-0.7</td>
</tr>
<tr>
<td>Specific Surface Area (m&lt;sup&gt;2&lt;/sup&gt;/g)</td>
<td>0.08-20</td>
</tr>
</tbody>
</table>
many instances, higher concentrations of iron oxide may be observed at the center of the pellet as is shown in Fig. 1.1 and Fig. 1.2. A high concentration of carbon at the surface of the pellet may also be observed in some instances. In still other cases, the carbon and oxygen within a pellet may be nearly uniformly distributed. These types of heterogeneity have made laboratory scale studies of the melting behavior of industrially produced DRI difficult to perform and interpret.

1.3 Industrial Experience with DRI in the Electric Arc Furnace

In addition to the more apparent factors that influence the choice of DRI or scrap as a feedstock for the electric arc furnace, such as cost and availability, other important factors have been recognized as a result of industrial experience with DRI.\(^{18}\) An important advantage that DRI has over scrap is its inherently low level of tramp elements (metallic impurities).\(^{8,11,12}\) Tramp element accumulation in recycled steel scrap can cause severe problems in the production of steels that require high standards of quality, such as grades used in rolling or deep drawing applications.\(^{11,12}\) DRI can help alleviate the problem by providing a source of iron with low levels of undesirable metallic elements and known purity. Another advantage is that DRI is easily transported and lends itself well to continuous feeding operations. The concept of continuous feeding has intrigued many producers.\(^{8,10,11,12,17}\) A decrease in energy consumption and an increase in production through a decrease in the required refining time have been obtained. There results an ability to operate at higher power levels without adverse effects on the furnace refractories.\(^{12,17}\) A
Figure 1.1 - Microstructure at the center of a Commercial DRI pellet. Optical @ 200X. The white areas are metallic iron, the light gray areas are wustite and dark gray areas are pores.

Figure 1.2 - Microstructure at the surface of the same pellet. Optical @ 200X. Note the virtual absence of wustite.
disadvantage in the use of DRI is its gangue content, which increases the energy requirements for heating. (12,16) Because the gangue is typically high in silica, lime additions are sometimes necessary to maintain slag basicity.

Much controversy still exists over the optimum composition, size, and physical characteristics of DRI that will result in the most efficient operation of the electric arc furnace. A number of advantages with the use of DRI possessing lower metallization (85%-90%), and with high levels of carbon (1%-2%) have been cited. (9,10,11) The carbon and oxygen in the direct reduced iron react upon heating resulting in an increase in metallization and the evolution of gases from DRI. The gas generated by the reaction can produce an actively boiling bath, and in some cases may generate a foamy slag in the furnace. The foamy slag has been credited with improving furnace operation by shielding the furnace lining from the arc radiation, (16) and by increasing the efficiency of the use of the arc energy. The presence of an actively boiling bath enhances bath agitation which in turn may enhance refining reactions and lower dissolved nitrogen and hydrogen levels in the bath. Bath agitation has also been credited with improving heat transfer and reducing temperature stratification in the bath, resulting in faster melting rates of the charge. (16,18) It must still be determined whether the improvements in furnace operating efficiency resulting from gas evolution can offset the energy required to support the gas generating reactions.

The optimum size of DRI feedstock for the electric arc furnace has not been investigated in detail by industrial users. The size of DRI
that has been established by producers has in many cases been dictated by available blast furnace pelletizing equipment or the needs of the reduction process rather than the needs of the electric arc furnace. The optimum size for electric furnace operation has yet to be determined.

The density of DRI that is desirable for use in the electric arc furnace is another area of controversy that must be resolved. A factor in favor of high density DRI is that a dense charge can penetrate rapidly to the slag metal interface where melting can proceed more rapidly. However, it has been argued that the rapid extraction of heat from the metal bath can result in temperature stratification within the metal bath due to heat transfer limitations from the arc to the bath. It is further argued that melting in the slag can occur very rapidly, and that melting in the slag layer has distinct refining advantages. On the other hand, the melting of a DRI charge in the slag requires close control to avoid the formation of pellet agglomerates in the slag which melt more slowly. It is apparent that much more information is needed about the factors that affect the heating and melting rate of DRI in the electric arc furnace before many of these questions can be answered.

1.4 Overview of the Research Program

The unique characteristics of DRI have prompted the development of a number of theoretically-based models for the prediction of the melting rate of DRI in the electric furnace environment. However, few experimental studies are available to verify the assumptions employed in the development of these models, or to test the accuracy of their pre-
dictions. Most of the models used to predict the heating and melting rates of DRI employ the assumption that the DRI pellet may be modeled as an inert sphere of low thermal conductivity. While such an assumption may be convenient from a computational standpoint, the employment of such an assumption sidesteps some important issues that relate directly to the uniqueness of the material. The purpose of this research program is therefore twofold. The first goal is to execute an experimental program that will be capable of providing reliable data on the heating rate, reactivity, and behavior of DRI when immersed in a hot steelmaking slag. Such a program will provide the information that is necessary for the development of the basic assumptions to be employed in a model of the heating and melting process. The results from the program will also provide a means of verifying some of the predictions made with a model of the melting process. The second goal is to develop a computer simulation of the heating and melting process for a single DRI pellet that incorporates the thermophysical properties of the material, phase transformations within the pellet, and the enthalpies associated with the reactions that occur in the pellet. By incorporating these factors into the model, a means of investigating the effects of variables such as the density of the pellet, the thermal conductivity of the pellet, the reactivity of the pellet, and the properties of the slag on the melting time and melting behavior of an individual pellet is available. Once the dependence of the melting time of an individual pellet on the properties of the pellet and the conditions of the melting environment is understood, the knowledge may ultimately be translated to the industrially important case of the continuous feeding of DRI in the electric arc furnace.
CHAPTER 2

LITERATURE SURVEY

A survey of the literature that relates to the present study on the melting of DRI in electric furnace slags is presented in this chapter in three parts. In the first section, literature on the melting of metallic particles in molten slag and molten metal is reviewed. The second section contains a review of literature that pertains to the kinetics of the gas generating reactions that occur in DRI upon heating. The final section is a review of literature that addresses the issue of heat transfer in a bubble agitated bath.

2.1 Melting Studies

Although only a few studies of the melting behavior of DRI in electric furnace slags have been performed, much experimental and theoretical information is available on the melting behavior of solid iron and DRI in molten iron. In some early work on scrap dissolution Pehlke et al., (19) studied the kinetics of dissolution of low carbon iron in pig iron melts and found that the dissolution process was controlled by the mass transport of carbon in the liquid. In their findings, Pehlke et al., reported the appearance of a solidified shell of iron on some of their samples during the initial period of immersion into the iron bath, indicating that heat transfer was also important during the initial stages of dissolution. Later work by Szekely et al., (20) showed that heat transfer could control the dissolution process when the carbon content of the melt was low and that mixed
control could occur when bath temperatures approach the melting temperature of the sample. Kim and Pehlke(21) later employed a numerical technique to predict the thickness of the solidified layer of iron on a cylindrical sample as a function of time, and demonstrated the detrimental effect that this frozen layer had upon the dissolution rate of iron.

Several studies have been reported that involve the heat transfer controlled dissolution of a single metal sphere in liquid iron. Guthrie, et al.,(22) studied the melting of aluminum spheres in liquid iron which involved both solid shell growth and subsurface melting of aluminum. An explicit finite difference technique was employed to solve the governing partial differential equations for heat transfer. Elrich et al.,(23,24) developed, and later tested, a model of the melting process for a porous iron sphere. The model included the formation of a dense iron shell. A sophisticated numerical procedure, which employed the Green's function technique, was used to solve the heat transfer problem. The same numerical approach was used by Seaton et al.,(25) to interpret data obtained from commercially produced pellets that were melted in an iron bath.

A more qualitative, but extensive series of studies of the melting behavior of synthetically produced DRI pellets has been carried out by Sato et al.(26,27,28) In these studies, the properties of DRI pellets were simulated by preparing mixtures of reduced iron powder, carbon, hematite, and various nonreducible oxides and pressing them to form cylindrical pellets. The pellets were dropped into a bath of molten iron, and the melting time was determined either through direct
observation or estimated by the termination of gas evolution from the pellet. Experiments were performed in iron melts of varying carbon content, and in melts in which a surface slag layer was present. The effects of a number of variables on the melting time of the synthetic pellets were reported.

To date, the only experimental works that directly involve the study of the heating and melting rates of metallic particles in slag systems are the studies of Nauman (13) and Sadrnezhaad (14). Nauman utilized solid spheres of nickel and copper to measure the heat transfer in the slag. The transient temperature rise at the center of an initially cold sphere was measured when it was immersed into a bath of molten slag. The effect of forced convection was investigated by spinning the sphere as it heated in the slag bath, or by bubbling gases through the slag bath while a sphere was suspended rigidly in the bath. The experimental results were interpreted with a computer model that utilized an explicit numerical scheme to solve the governing equations of heat transfer. Some experimental measurements and computed results using the model are shown in Fig. 2.1 for free convection and various types of forced convection. The results obtained by Nauman indicated that the rate of heat transfer was controlled primarily by the solid slag shell that formed and subsequently remelted. It was determined that an existing heat transfer correlation for a spinning sphere, that was originally developed from a low temperature study, adequately predicted the heat transfer coefficient for a spinning sphere in liquid slag (7). The applicability of low temperature heat transfer correlations to slag systems was therefore established. Nauman also
Figure 2.1 - Experimental and predicted rise in temperature at the center of a nickel sphere immersed in ferrous-silicate slag, according to Nauman (13), showing the effects of forced convection by bubbling and spinning.

Figure 2.2 - Comparison of heating rate predictions for a nickel sphere using a dendritic and a planar (sheared dendritic) S/L slag interface model with experiment, according to Nauman, et al. (29).
determined that the complex ferrous-silicate slags investigated in the study behaved as though they solidified and melted at their solidus temperatures, as demonstrated in Fig. 2.2. Because the conditions for solidification of the slag were such that dendritic solidification should have occurred, the observed behavior was attributed to the shearing off of the dendrites by the flowing slag.

Sadrnezhaad investigated the reactions that are responsible for the gas evolution from DRI and the effects that this gas evolution had on the heating rate of DRI in molten slag. The effect of gas evolution on heat transfer was investigated by studying the heating rate of a specially prepared inert sphere into which gas ports were machined. Gas was forced through these ports to simulate gas evolution from a reactive DRI particle. The results of this study demonstrated that local gas evolution had a significant influence on the thickness of the slag shell that initially formed on the sphere. The effect of gas evolution on the heating rate was somewhat less pronounced, as shown in Fig. 2.3. Some heating rate studies with commercial DRI pellets were also performed by Sadrnezhaad, as shown in Fig. 2.4. While the composition could not be determined for the pellets tested, comparisons were made of the heating rates of reactive pellets and pellets that were rendered nonreactive by a prior reduction treatment in hydrogen. The results of these tests indicated that the reactive pellets heated more slowly than the hydrogen treated pellets. Sadrnezhaad employed a computer model similar to Nauman's to interpret his results and to predict the melting rate of DRI under steelmaking conditions. The model included the effects of variable thermophysical properties, heats of
Figure 2.3 - Experimental and predicted heating rates for a nickel sphere with three active bubbling sites, according to Sadrnezhaad (14). Curves have been displaced by 10 and 20 seconds for clarity.

Figure 2.4 - Experimental and predicted heating rates for two different commercial DRI pellets according to Sadrnezhaad (14).
transformation and the enthalpy requirements for the gas producing reactions. Utilizing the predictions from the model in conjunction with experimental results, Sadrnezhaad concluded that the influence of gas evolution on the heating rate of DRI diminished as the rate of gas evolution increased, and that highly metallized pellets therefore heated more rapidly than reactive pellets. The thermal conductivity of the pellet and the solidus temperature of the slag were also judged to have a strong influence on the melting rate of DRI.

2.2 Reactions in DRI

In the production of DRI, most reduction processes are operated under conditions that result in the presence of residual levels of carbon and iron oxide in the final reduced product. For most types of commercial DRI produced, the residual oxide is in the form of wustite, which is retained from the high temperature reducing step by a quenching process that is employed to prevent the reoxidation of DRI when it is exposed to the atmosphere. Although carbon and wustite are not thermodynamically stable when they coexist in DRI, the kinetics for their mutual reaction at ambient temperatures are normally not favorable. The reaction kinetics become increasingly favorable at higher temperatures, leading to the following overall reaction,

\[
(2-X_{\text{CO}})\text{FeO}(s) + C(s) = (2-X_{\text{CO}})\text{Fe}(s) + (X_{\text{CO}})\text{CO}(g) + (1-X_{\text{CO}})\text{CO}_2
\]  

(2-1)

where \(X_{\text{CO}}\) is the volume fraction of CO in the product gas. This net reaction results in the mutual consumption of iron oxide and carbon in
the sample, and the formation of carbonaceous product gases that are liberated from DRI.

The reactions that occur in DRI are not unlike the reactions that occur in iron oxide-carbon mixtures during the latter stages of reduction. In both cases, a layer of metallic iron has been formed around individual wustite grains, and the carbon is not in direct contact with the wustite. The similarities in microstructure suggest that valuable information about the kinetics of the reactions in DRI might be obtained from kinetic studies of the reaction of iron oxide-carbon mixtures.

Studies of the nature of the reduction process have revealed that the reaction between carbon and iron oxide proceeds through the formation of gaseous intermediates, according to the following sequence of reactions, (31)

\[
\text{Fe}_0\text{O}_{x\ y}(s) + \text{CO}(g) = \text{Fe}_0\text{O}_{x\ y-1}(s) + \text{CO}_2(g) \tag{2-2}
\]

\[
\text{C}(s) + \text{CO}_2(g) = 2\text{CO}(g) \tag{2-3}
\]

The reaction kinetics of this gas-solids reaction has been studied extensively under isothermal conditions. A review of some early studies on the subject has been presented by Rao, (32) who studied the reaction of hematite with amorphous carbon. The results of his study suggested that the oxidation of carbon, reaction (2-3) was the rate limiting step in the temperature range of 850°C to 1087°C. Similar results were obtained by Fruehan (33) for the initial stages of reduction of hematite and wustite with several types of carbon. However, Fruehan noted that significant deviations from the equilibrium \( \text{CO}_2/\text{CO} \) ratio for
reaction (2-2) occurred during the latter stages of reduction. Because reaction (2-2) would be expected to remain at equilibrium if reaction (2-3) controlled the overall rate of reaction, Fruehan's results suggested that reaction (2-3) might not be rate controlling over the entire reduction period. The possibility of a change in the rate controlling mechanism is supported by other investigators (34,35,36) who have reported a continuous drift of the product gas composition away from Fe/FeO equilibria as reduction proceeded toward completion. Srinivasen and Laviri (37) found that the drift in product gas composition from Fe/FeO equilibria was accompanied by a continuous decrease in the apparent activation energy for the reduction rate. The authors suggested that the change in the temperature dependence of the apparent rate constant was a result of mixed control. The high activation energies that were observed during the initial stages of reduction (60 to 100 kcal/mole) (37,38,39) were associated with the carbon gasification reaction (2-3), while the lower activation energies that were observed during the latter stages of reduction (13 to 20 kcal/mole) (37,39,40) were associated with the reduction of FeO by CO.

The concept of mixed control has also been utilized by other investigators in the attempt to describe the kinetics of the iron oxide-carbon reaction. The gasification of carbon, reaction (2-3), has been generally accepted as one of the appropriate rate limiting steps by most investigators. However, the choice of the additional step (or steps) has not been agreed upon. Some investigators (37,39,41) support the idea that the reduction of FeO by CO may become kinetically influential at higher temperatures and at higher levels of reduction. The
lower activation energy associated with the gaseous reduction of FeO by CO, combined with the high activation energy associated with the gasification of carbon provides a means of explaining the apparent lowering of the activation energy with increasing temperature. The catalytic enhancement of the carbon gasification reaction by metallic Fe has also been cited as a possible cause for the observed temperature and composition dependence of the rate of reaction.(32) Other investigators(33,41,43) support the theory that bulk transport of the gaseous species within the pores of the sample, and penetration of gases from the surroundings into the pores of the sample, must be considered in conjunction with reaction (2-3). The applicability of combined gaseous diffusion-reaction control to gaseous reduction processes is well established,(31) and gaseous diffusion resistance at the oxide grain level has been shown to be significant.(44) Still other investigators(48) suggest that the observed change in the mechanism of reduction is brought about by physical changes in structure due to sintering of the iron product layer. The sintering results in a gradual closing of the pore structure so that toward the final stages of reduction, only a solid state diffusion mechanism can operate. This is supported by evidence in gaseous reduction studies.(32,46,47) It is clear that a comprehensive model of the kinetics of reaction of iron oxide-carbon mixtures that applies to the latter stages of reduction has yet to be developed.

An investigation of the reactivity of commercial DRI samples was recently performed by Sadrnezhaad.(14) Because the reaction conditions in DRI are further complicated by non-isothermal conditions,
Sadrnezhaad investigated the effects of heating rate on the rate of reaction in addition to performing isothermal reduction tests. The results of isothermal reactivity studies performed under an inert helium atmosphere indicated that the rate of reaction fell rapidly with time, suggesting that the displacement of CO and CO$_2$ in the pores of the sample by helium may have retarded the reduction rate, especially at lower temperatures. The results of gas composition measurements at various temperatures are summarized in Fig. 2.5. These results support the observations made in previous studies that the off-gas composition deviates significantly from Fe/FeO equilibria. The effects of heating rate on the reactivity of DRI were investigated by sealing a sample of commercial DRI powder in an iron capsule and heating the capsule at fixed rate. The volume of gas that was liberated from the sample during heating was measured by an integrating flowmeter. Because the sample was held in a sealed container, the effects of inert gas penetration could be avoided. The results of the constant heating rate tests provided some qualitative, but useful, information about the reactivity of DRI. First, the rates of reaction that were observed were significantly higher than those observed in isothermal tests, which implies that inert gas penetration had a significant influence on the rate of reaction in the isothermal tests. Second, multiple peaks in the rate of gas evolution were observed as a sample temperature increased as shown in Fig. 2.6. This indicated that more than one mechanism of reaction was occurring in DRI. Third, while the temperature and composition of DRI were found to influence the rate of gas evolution, the heating rate was observed to have little influence on the rate of gas
Figure 2.5 - Composition of the gas evolved from DRI as determined by Sadrnezhaad (14), plotted on the Fe-CO-CO$_2$ phase stability diagram at 1 atm. (99).
Figure 2.6 - Rate of gas evolution from commercial DRI powder at a heating rate of 250°C/min., as measured by Sadrnezhaad (14).
evolution. Furthermore, the total volume of gas that evolved was found to depend only on the composition of DRI. Finally, measurements of the average composition of the gases evolved from DRI in the constant heating rate studies were found to contain less than 6% CO₂ in all types of DRI tested (see Fig. 2.5). The percentage of CO₂ observed for these tests was lower than those reported previously for the isothermal tests, which further supports the fact that the carbon gasification reaction is not the sole rate limiting step for the reactions in DRI.

2.3 Heat Transfer in Bubble Agitated Fluids

The agitation of the slag bath by the evolution of gases from DRI has already been cited as a probable mechanism for improving heat transfer to DRI in electric arc furnace slags. However, the influence of gas agitation on heat transfer to a solid immersed in a liquid is difficult to determine quantitatively due to the complex turbulent flows that result. Because of the complexity of flow conditions, investigators have approached the problem by utilizing either dimensionless correlations derived from experimental heat transfer data or by utilizing simplified heat transfer models derived from studies of nucleate boiling. The first approach has been applied primarily to conditions in which a particle is freely suspended in an agitated bath. In this case, the agitation of the liquid by evolving gas affects the bath turbulence and ultimately influences both the motion of the particle and the heat transfer to the particle. The second approach has been applied to describe the heat transfer to a fixed surface while gas is evolved from the surface. In this case, bubble departure from the fixed surface has
been assumed to produce a convective pumping action that affects the heat transfer to the surface.

2.3.1 Freely Suspended Particles

The effect of gas agitation on mass transfer from freely suspended spheres in a recirculating vessel has been studied by Wright (50) and Woltz (51). Both investigators used dimensional analysis to relate the energy input per unit mass of fluid, $\epsilon$, to the mass transfer coefficient, $k$. Through the analogy between heat and mass transfer at low rates of mass transfer, Wright expressed the relationship between the heat transfer coefficient, $h$, and $\epsilon$, in the form,

$$\frac{h d}{Nu, d} = 0.167 \frac{Ko}{Pr^{1/3}}$$

where,

$$Nu, d = \frac{h d}{k L}$$

is the particle Nusselt number,

$$Pr = \frac{\nu L}{\alpha L}$$

is the fluid Prandtl number,

and,

$$Ko = \frac{\epsilon d^4}{\nu L^2}$$

is the Kolmogoroff number (Power number).

$\nu$ is the liquid kinematic viscosity

$\alpha$ is the liquid thermal diffusivity

The calculation of $\epsilon$ for a bubble stirred system was based on the work of Nakanishi, et al., (52) which related the work done by expanding bubbles to the energy dissipation per unit fluid mass,
\[ \varepsilon = \left(1.23 \times 10^5 Q T \right) \ln\left(1 + 9.679 \times 10^{-4} \rho_L Z\right) \]

where,

- \( \varepsilon \) is the power dissipation per unit fluid mass in \( \text{cm}^2/\text{s}^3 \)
- \( Q \) is the gas flow rate in \( \text{l/min STP} \)
- \( T \) is the bath temperature in \( \text{K} \)
- \( \rho_L \) is the fluid density in \( \text{g/cm}^3 \)
- \( Z \) is the bath depth in \( \text{cm} \)

and,

- \( m_L \) is the liquid mass in \( \text{g} \)

In using the Kolmogoroff number as one of the principal correlating groups, the investigators have employed certain assumptions about the nature of the turbulence and the mechanism of heat transport. According to Kolmogoroff's theory, large eddies that have been generated by a given means of bath agitation continuously decompose into smaller eddies by an inertial transfer of turbulent kinetic energy, until all of the kinetic energy is dissipated in the smallest eddies by viscous forces. As this breakdown occurs, directional information from the specific agitation process is gradually lost, so that these smaller eddies become statistically independent of the larger primary eddies. By employing the Kolmogoroff number, it is assumed that only the intermediately sized isotropic eddies that contain and dissipate little of the kinetic energy are responsible for heat (or mass) transfer to a particle suspended in the fluid. In this case, the rate of convective transfer will depend on the variables \( \varepsilon \) and \( \nu_L \).
convective transport, the use of the Kolmogoroff number is no longer generally valid, since the mode of bath agitation becomes important in correlating bath agitation to convective transport.

The application of Kolmogoroff's theory suggests that convective transport studies for impeller stirred systems should also correlate with equation (2-4). A comparison of the results of a number of investigations\(^{(50-57)}\) is presented in Fig. 2.7. The results from bubble stirred systems appear to fall within the range of results from impeller stirred systems. However, the overall agreement among different correlations is not very good, especially at lower levels of energy input (low \(K_o\)). This suggests that large primary eddies may have taken part in convective transport at least in some of the studies.

2.3.2 Fixed Surfaces

The effects of local gas bubbling on heat transfer from a fixed surface has received attention in the study of nucleate boiling. Rohsenow\(^{(58)}\) proposed a correlation that incorporated the bubble diameter as the characteristic dimension for the Reynolds number, \(\text{Re},b\), and the Nusselt number, \(\text{Nu},b\),

\[
\text{Nu},b = c \text{Re},b^{2/3} \text{Pr}^{-0.7}
\]

(2-6)

where,

\[
\text{Nu},b = \frac{\text{h}_b}{\text{k}_L} \quad \text{is the Nusselt number based on bubble diameter}
\]

\[
\text{Re},b = \frac{\text{G}_b}{\text{\mu}_L} \quad \text{is the Reynolds number based on bubble diameter}
\]

\[
\text{Pr} = \frac{\nu_L}{\alpha_L} \quad \text{is the Prandtl number for the fluid}
\]
Figure 2.7 - A comparison of some heat and mass transfer correlations for freely suspended spheres in agitated vessels.
c is a constant that depends on the properties of the surface and the fluid

d is the bubble diameter

G is the mass flow rate of the gas

L is the liquid viscosity

The correlation was based on the assumption that the detachment of gas bubbles was primarily responsible for heat transfer in nucleate boiling.

Mikic and Rohsenow (59) later developed a physical model based on the same assumption. A bubble was assumed to remove a portion of the thermal boundary layer each time it departed from the surface. Between bubble departures, the thermal boundary layer is assumed to reform by transient conduction. The sequence of events is depicted in Fig. 2.8. The model is essentially a surface renewal model in which the residence time of the fluid is controlled by the frequency of bubble departures. The area of influence is assumed to be equal to the equatorial area of the bubble. The expression for the heat transfer coefficient was,

\[ h = 2nd^2b(kL/\rho_Lc_Lf)^1/2 \]  

where,

n is the density of active bubbling sites

\( \rho_L \) is the liquid density

\( c_L \) is the liquid specific heat

f is the frequency of bubble departures from a site

This model was utilized by Sadrnezhaad to calculate the effects of gas evolution on heat transfer to a nickel sphere with three active gas bubbling ports (see Fig. 2.3). A comparison of the predictions of
Figure 2.8 - Thermal boundary layer removal by a departing bubble (58). (a) Formation of bubble and transient thermal boundary layer. (b) Bubble growth to critical diameter. (c) Bubble detachment and removal of boundary layer at bubble site. (d) Reformation of bubble and boundary layer.
equation 2-7 with some of the correlations described in Section 2.3.1 for freely suspended particles is shown in Fig. 2.9.

Some investigators have attempted to relate the convective heat or mass transfer coefficient for a solid surface that is rigidly suspended in a fluid to the gas flow rate for gas agitation or gas evolution. The empirical relationship is usually of the form,

\[ k = AQ^n \]  \hspace{1cm} (2-8a)  

or,

\[ h = A'Q^{n'} \]  \hspace{1cm} (2-8b)  

where \( A, A', n, \) and \( n' \) are empirical constants and \( Q \) is the gas flow rate. Sevinc and Elliott\(^{60}\) used an expression of this form to relate the mass transfer coefficient to the rate of gas evolution during the reduction of a \( \text{Cr}_2\text{O}_3 \) cylinder in an iron-carbon bath. From experiment they found that,

\[ k \propto Q^{0.84} \]  \hspace{1cm} (2-9)  

In a similar study, Sakuraya and Mori\(^{61,62}\) studied the reaction of oxygen in an iron cylinder with carbon in an iron-carbon melt. In this case, the investigators observed that,

\[ k \propto Q^{0.30} \]  \hspace{1cm} (2-10)  

In a different type of experiment, Lehner and Hsiao\(^{63}\) studied the dissolution of a graphite rod that was held in an argon stirred ladle that contained liquid steel. From their experiments they found that,
Figure 2.9 - Values of the heat transfer coefficient predicted by various models as a function of gas flow rate. The predictions are made for a 2.5 cm diameter sphere in a 2.5 kg bath of slag, using the properties of Slag B reported in Table 5.1.
best described the dependence of mass transfer on gas evolution rate. In still another study, Kutateladze\(^{(64)}\) forced gas through a microporous plate submerged in liquid to simulate the conditions of nucleate boiling. By investigating the effect of gas flow rate on heat transfer to such a plate in water and water-glycerol mixtures, Kutateladze observed that,

\[ h \propto Q^{2/3} \]  \hspace{1cm} (2-12)

at low flow rates, but that \( n \) decreased at higher gas flow rates. A summary of the power law relationships that were observed or implied in various investigations are presented in Table 2.1. For freely suspended particles, \( n \) ranges from 0.20 to 0.40 while for fixed surfaces \( n \) ranges from 0.30 to 0.85.
### Table 2.1

Experimentally Observed Relationships Between
The Convective Transport Coefficient and Gas Flow Rate

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Experimental Conditions</th>
<th>Observed Proportionality $\xi$</th>
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</thead>
<tbody>
<tr>
<td>Sevinc &amp; Elliott (60)</td>
<td>Gas Evolution - Fixed Surface</td>
<td>$k = Q^{0.84}$</td>
</tr>
<tr>
<td>Lehner &amp; Hsiao (63)</td>
<td>Gas Agitation - Fixed Surface</td>
<td>$k = Q^{0.29}$</td>
</tr>
<tr>
<td>Sakuraya &amp; Mori (61,62)</td>
<td>Gas Evolution - Fixed Surface</td>
<td>$k = Q^{0.30}$</td>
</tr>
<tr>
<td>Kutateladze (67)</td>
<td>Gas Evolution - Fixed Surface</td>
<td>$k = Q^{2/3} \rightarrow Q^{1/6}$</td>
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<tr>
<td>Rohsenow (58)</td>
<td>Gas Evolution - Fixed Surface</td>
<td>$k = Q^{2/3}$</td>
</tr>
<tr>
<td>Wright (50)</td>
<td>Gas Agitation - Freely Suspended</td>
<td>$k = Q^{1/4}$</td>
</tr>
<tr>
<td>Brian &amp; Hales *(56)</td>
<td>Gas Agitation - Freely Suspended</td>
<td>$h = Q^{1.4} \rightarrow Q^{1/6}$</td>
</tr>
<tr>
<td>Miller *(55)</td>
<td>Gas Agitation - Freely Suspended</td>
<td>$k = Q^{1/4}$</td>
</tr>
<tr>
<td>Levins &amp; Glastonbury *(53)</td>
<td>Gas Agitation - Freely Suspended</td>
<td>$k = Q^{207}$</td>
</tr>
<tr>
<td>Calderbank &amp; Moo-Young *(59)</td>
<td>Gas Agitation - Fixed/Freely Suspended</td>
<td>$k = Q^{1/4}$</td>
</tr>
</tbody>
</table>

* Implied by using $\epsilon = Q$ from Nakanichi, et al. (52)

$\xi$ h = heat transfer coefficient; k = mass transfer coefficient
CHAPTER 3

EXPERIMENTAL

A description of the work that was performed in the experimental program is presented in this chapter. The experimental work was executed in three phases: in the first phase, the potential reactivity of commercial and laboratory-prepared DRI powders was investigated by chemical analysis. The technique used to analyze the samples of DRI for oxygen, carbon, and total gangue content is described in section 3.1. In the second phase of the experimental program, single DRI pellets that were at room temperature, initially, were immersed into a bath of molten slag. The temperature of the pellet, and the volume of gas that was produced by the pellet, were measured as the pellet heated. The structure of the pellet and the frozen layer of slag that formed on the pellet was also investigated. A description of this phase of the program is presented in section 3.2. In the third phase of the experimental program, the reactivity of the carbon and oxygen in DRI was studied. These tests were performed by heating samples of DRI in the absence of slag under non-isothermal, but spatially uniform heating conditions. The experimental technique employed in this phase of the program is described in section 3.3.

3.1. Analysis of DRI

The DRI powders used in the experimental program were sampled and analyzed to determine the carbon, oxygen* and total gangue content of

* Oxygen in reducible form as iron oxides.
each powder lot. The procedures used to prepare these powder lots are described in section 3.2.1.

A two-step, gas phase reaction scheme was employed to perform the analyses. The essential features of the analysis scheme are outlined in Fig. 3.1. In the first step, a weighed sample of DRI powder was oxidized in O₂ for 6 hours at 1000 °C. During this step, metallic iron and its lower oxides were converted to hematite, and the carbon in the sample was oxidized to CO₂. The CO₂ that was liberated during the oxidation of the sample was collected by passing the exhaust gases through a collection tube that contained a chemical absorbent for CO₂. After the oxidation step was complete, the DRI sample was re-weighed and the weight gain of the CO₂ absorbent tube was determined. At this stage, the oxidized sample of DRI contained only Fe₂O₃ and gangue.

In the second step of the analysis procedure, the oxidized sample was reduced in H₂ for 12 hours at 1000 °C. This step reduced the Fe₂O₃ to metallic iron without reducing the gangue in the sample. The oxygen, carbon, and total gangue contents of the DRI sample were determined directly from the initial, oxidized and reduced DRI sample weights, and the weight gain of the CO₂ collection tube. A sample calculation is shown in Appendix A.

The apparatus for performing the analyses (shown in Fig. 3.2) incorporated several important features to ensure the accuracy of an analysis. The oxygen for the oxidation step was cleaned by passing the gas over a Pd-Asbestos catalyst at 450 °C to convert any hydrocarbons and CO in the gas to H₂O and CO₂. The H₂O and CO₂ were subsequently removed by passing the inlet gas through absorbent columns.
Figure 3.1 - Scheme used to analyze DRI powders for carbon, oxygen, and gangue content. $W_i$ is the initial sample weight, $W_m$ is the sample weight after complete oxidation, $W_r$ is the sample weight after complete reduction, and $W_{CO_2}$ and $W_{H_2O}$ are the weight gains of the $CO_2$ and $H_2O$ absorbent bulbs respectively during oxidation.
Figure 3.2 - Apparatus for the analysis of DRI powders.
containing CaSO₄, Ascarite®, Mg(ClO₄)₂, and P₂O₅. Because the accuracy of the carbon analysis depended on the assumption that all of the carbon that was oxidized from the sample in step 1 was completely converted to CO₂, the product gases were passed over a CuO catalyst at 750 °C. This ensured the complete conversion of any CO in the gas to CO₂. The collection tube contained Ascarite, CaSO₄, Mg(ClO₄)₂, and P₂O₅ absorbents, separated with pyrex wool. Because the CO₂ tube was capable of absorbing H₂O, the CO₂ collection tube was preceded by an H₂O collection tube containing CaSO₄, Mg(ClO₄)₂, and P₂O₅. These collection tubes were followed by a third blank tube that contained only pyrex wool. This tube served as a reference to determine the influence of daily changes of temperature and humidity on the weight of the collection tubes. Blank runs were employed periodically to determine changes in the weight of the silica boat used to hold the sample during the oxidation and reduction steps, and to determine the weight changes of the collection tubes in the absence of a sample. Appropriate corrections were employed to compensate for these effects (see Appendix A).

3.2. Heating Experiments in Molten Slag

This section contains a description of the procedures used to obtain experimental data for the study of the heating rates of single DRI pellets in molten slags. In these experiments, a specially prepared DRI pellet was immersed into a "semi-infinite" bath of molten slag. The pellet entered the bath at a predetermined temperature, and was held in

Ascarite® - Trademark of Arthur H. Thomas Co. for NaOH coated non-fiberous silicate.
the bath for the duration of a test. Two types of experiments were performed. In the first type of experiment, the temperature at a specified location within the pellet and the volume of gas that evolved from the pellet were recorded continuously with time. In the second type of experiment, a pellet was removed from the slag bath at a specified time to observe the structure of the pellet and the slag shell that existed at that time.

The influence of the properties of a pellet, and the conditions of the slag bath on the heating rate of a DRI pellet were studied by comparing temperature profiles obtained under different test conditions. The continuous temperature and gas volume measurements were also used in conjunction with structural observations to study the heat transfer process with the aid of a computer model.

3.2.1. Preparation of Materials

The variation in composition among individual pellets taken from commercial batches of DRI makes the use of single commercial pellets inherently difficult in an experimental testing program. The non-uniformity in the size and shape of commercial pellets, and the presence of cracks in many commercial pellets, adds to the difficulty of their use as a test material. Because of the problems associated with the use of commercial DRI, an important aspect of this experimental program was the development of techniques for producing single DRI pellets that possessed a homogeneous structure and a reproducible composition. Three different methods of pellet production were employed: 1) the re-agglomeration of crushed and blended commercial DRI pellets, 2) the reduction
of synthetic hematite pellets with a reducing gas to produce a sponge iron pellet, and 3) the re-agglomeration of sponge iron powder, produced by the reaction of a mixture of carbon powder and hematite powder.

3.2.1.1. Preparation of Pellets from Commercial DRI

Batches of DRI powder were prepared by crushing commercially produced DRI pellets. Typically, a batch of pellets from a single production lot was crushed to -35 mesh, USS, (-500 μ) by using a conventional jaw crusher. The -35 mesh fraction was separated after each pass through the crusher to minimize the generation of fines. The resulting powder was blended for a minimum of 8 hours to ensure the homogeneity of each batch, and each batch was stored in a sealed container to prevent reoxidation of the powder. Single spherical DRI pellets were produced from the powders by the following procedure: a sample of 50 grams of powder was carefully split from a batch of powder to obtain a representative sample. This powder sample was placed in a rubber bag which was then sealed and pressed to 14,000 psi (96.5 MPa) in an isostatic oil press. The resulting powder agglomerate, which was still moderately friable, was shaped into a sphere of desired weight (typically, 32 g) by rolling the powder agglomerate through a series of sized holes in a steel plate. Using this technique, the excess powder was shaved off of the agglomerate to produce a spherical pellet. The spherical pellet was subsequently re-pressed in a rubber bag using the isostatic press. The final pressing pressure varied from 20,000 psi (137 MPa) to 40,000 psi (275 MPa) depending on the final apparent density that was desired. The resulting pellets had excellent strength and a spherical shape, with a variation in diameter of less than ±0.1 mm.
The pellets produced by this procedure also had a homogeneous composition and pore structure. The apparent density of the pellet could normally be varied from 3.3 g/cm³ to 4.1 g/cm³ by changing the pressure used in the final pressing step. A listing of the physical properties of the pellets produced by this method is given in Table 3.1.

3.2.1.2. Preparation of DRI Pellets by the Gaseous Reduction of Hematite Pellets

Coarse hematite powder was prepared by first hand pelletizing a mixture of reagent grade hematite (Baker Chemical Co.) and distilled water. The green pellets were oven dried and then sintered for 72 hours at 1000 °C in air to produce small pellets that had 88% of the theoretical density of hematite. These pellets were then re-crushed using a roll crusher and a steel rod mill to produce -20 mesh USS (-850 μ) hematite powder.

Hematite spheres were prepared by blending 15 weight percent reagent grade hematite (to act as a binder) with the coarsened hematite powder, and then following the same isostatic pressing procedure used to produce DRI pellets from commercial powders.

The reduction of the hematite spheres with hydrogen or CO-CO₂ gas mixtures was performed in the apparatus shown in Fig. 3.3. The hematite pellets were held in a stainless steel container that was packed with tabular alumina (+10 mesh, USS). The alumina packing helped to produce a uniform flow of reducing gas around the pellets, and prevented the pellets from sintering to the walls of the canister, or to each other. The canister also provided a convenient means of removing the pellets from the furnace while protecting the pellets from oxidation with an
Table 3.1

The Physical Properties of Pellets Pressed from Commercial DRI

<table>
<thead>
<tr>
<th>Pellet ID#</th>
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<th>Pellet Diameter, cm</th>
<th>Pellet Apparent Density, g/cm³</th>
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<td>31.8</td>
<td>2.46</td>
<td>4.06</td>
</tr>
<tr>
<td>CD-8-24</td>
<td>-35</td>
<td>40</td>
<td>26.9</td>
<td>2.34</td>
<td>4.03</td>
</tr>
<tr>
<td>CD-8-25</td>
<td>-35</td>
<td>40</td>
<td>21.9</td>
<td>2.18</td>
<td>4.01</td>
</tr>
<tr>
<td>CD-8-26</td>
<td>-35</td>
<td>40</td>
<td>14.8</td>
<td>1.92</td>
<td>3.96</td>
</tr>
<tr>
<td>CD-8-28</td>
<td>-35</td>
<td>40</td>
<td>31.8</td>
<td>2.22</td>
<td>4.17</td>
</tr>
<tr>
<td>CD-8-29</td>
<td>-35</td>
<td>40</td>
<td>32.0</td>
<td>2.49</td>
<td>3.95</td>
</tr>
<tr>
<td>CD-9A-1</td>
<td>-18 + 50*</td>
<td>40</td>
<td>31.6</td>
<td>2.54</td>
<td>3.66</td>
</tr>
<tr>
<td>CD-9B-1</td>
<td>-50*</td>
<td>20</td>
<td>31.9</td>
<td>2.64</td>
<td>3.30</td>
</tr>
<tr>
<td>CD-9B-1</td>
<td>-50</td>
<td>40</td>
<td>32.0</td>
<td>2.51</td>
<td>3.84</td>
</tr>
</tbody>
</table>

*Batch CD-9 was split into a +50 mesh batch and a -50 mesh batch.
Figure 3.3 - Furnace assembly for the reduction of hematite pellets with reducing gases.
inert gas during cooling. The pellets produced by this method had a slightly larger variation in diameter (±0.5 mm) than the pressed pellets described in section 3.2.1.1., but lower densities could be achieved (2.0 - 3.4 g/cm³). A summary of the physical properties of the pellets produced by this method is given in Table 3.2.

3.2.1.3. Preparation of Pellets from Reduced Hematite-Carbon Mixtures

A mixture of carbon and hematite powders was prepared by blending 15 weight % high purity carbon (Amorphous, -325 mesh, Ultra Carbon Co.) with the coarsened hematite powder described in section B for 8 hours. The blended powder mixture was placed into the same type of container shown in Fig. 3.3. The canister was lowered into a sealed furnace that was continuously flushed with argon and was held at 1100 °C. No gas was forced into the canister during the reduction of the powder mixture. The weight of the canister and the reacting powder mixture was checked periodically. When the desired weight loss had been achieved, argon flow through the canister was initiated. The flow of argon was continued as the canister was removed from the furnace and as the canister cooled.

Once the sample was cooled, the metallized product was removed from the canister. Because the product was removed as a singed agglomerate that had an easily compactable structure, the agglomerate was quenched in liquid nitrogen prior to crushing. The nitrogen quenched agglomerate was fractured and crushed to -18 mesh, USS (-1000 μ) using a jaw crusher and a steel mortar and pestel. Pellets were produced from this powder by using the same procedure that was used to pelletize commercial DRI
Table 3.2
Laboratory Reduced Pellets and Special Pellets Used in Testing

(a) Gas Reduced Hematite Pellets

<table>
<thead>
<tr>
<th>Pellet ID</th>
<th>Red. Atm.</th>
<th>Red. Temp. °C</th>
<th>Red. Time, min</th>
<th>Gas Flowrate l/min</th>
<th>Weight, g</th>
<th>Dia., cm</th>
<th>App. Density, g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR-1B-1</td>
<td>H₂</td>
<td>890</td>
<td>85</td>
<td>5.0</td>
<td>15.9</td>
<td>2.48</td>
<td>2.03</td>
</tr>
<tr>
<td>LR-2D-1</td>
<td>CO-1%CO₂</td>
<td>1100</td>
<td>122</td>
<td>4.1</td>
<td>19.3</td>
<td>2.64</td>
<td>2.02</td>
</tr>
<tr>
<td>IR-2J-1</td>
<td>H₂</td>
<td>900</td>
<td>120</td>
<td>3.0</td>
<td>14.6</td>
<td>2.03</td>
<td>3.37</td>
</tr>
</tbody>
</table>

(b) Carbon Reduced Hematite-Pressed Pellets

<table>
<thead>
<tr>
<th>Pellet ID</th>
<th>C/Fe₂O₃ Ration</th>
<th>Red. Temp°C</th>
<th>Red. Time, min</th>
<th>Powder Mesh Size, USS</th>
<th>Weight, g</th>
<th>Dia., cm</th>
<th>App. Density, g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR-3A-1*</td>
<td>0.176</td>
<td>1100</td>
<td>135</td>
<td>-18 +50</td>
<td>31.8</td>
<td>2.36</td>
<td>4.61</td>
</tr>
<tr>
<td>LR-3A-2</td>
<td>0.176</td>
<td>1100</td>
<td>135</td>
<td>-50</td>
<td>32.1</td>
<td>2.47</td>
<td>4.09</td>
</tr>
</tbody>
</table>

(c) Special Pellets

<table>
<thead>
<tr>
<th>Pellet ID</th>
<th>Description of Pellet</th>
<th>Weight, g</th>
<th>Dia., cm</th>
<th>App. Density, g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD-8 comm.</td>
<td>Commercial Pellet from Batch CD-8 before crushing</td>
<td>6.71</td>
<td>~1.7</td>
<td>~2.6</td>
</tr>
<tr>
<td>SP-4</td>
<td>Solid Ferrovac-E pure iron sphere</td>
<td>63.0</td>
<td>2.48</td>
<td>7.92</td>
</tr>
<tr>
<td>SB-1</td>
<td>Heat Treated Fe Alloy Ball Bearing</td>
<td>66.7</td>
<td>2.54</td>
<td>7.77</td>
</tr>
<tr>
<td>HR1-8-1</td>
<td>H₂ Treated, type CD-8 Powder-Pressed Pellet</td>
<td>32.1</td>
<td>2.32</td>
<td>4.88</td>
</tr>
</tbody>
</table>

* Coarse and fine material separated from the same reduction batch
powders. The pellets produced by this process were similar in structure to the pellets produced from commercial powders. A listing of the physical properties of the pellets produced by this method is given in Table 3.2.

3.2.1.4. Preparation of Slags

Synthetic electric furnace slags were prepared by the same procedure utilized by Nauman (15) and Sadrnezhaad. (14) The powdered materials, shown in Appendix B, were mixed to produce the desired composition. The FeO composition was achieved by adding equimolar amounts of hematite and iron to the powder mixture. Agglomerates within the powder mixture were broken up by sifting the powders through a -35 mesh, USS (-500 μ) screen, and the powder mixture was blended for 24 hours. The powder mixture was then fused in an iron crucible under an inert argon atmosphere. Slag fusion was performed in the same furnace that was used for the pellet heating experiments (cf. Fig. 3.7). The compositions of the slags used in the pellet heating experiments are presented in Table 3.3.

3.2.1.5. Mounting the Pellets for Testing

The technique that was used to mount an individual DRI pellet depended on the type of experiment to be performed with the pellet. Two types of tests were performed. In the first type of experiment, the temperature within a pellet (normally the center) was measured while the pellet was immersed and held in a slag bath. In the second type of experiment, a pellet was immersed and held in a slag bath for a
Table 3.3

Slag Compositions

<table>
<thead>
<tr>
<th>Slag</th>
<th>Wt. % CaO</th>
<th>Wt. % FeO</th>
<th>Wt. % SiO₂</th>
<th>Wt. % Al₂O₃</th>
<th>Wt. % MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30.0</td>
<td>20.0</td>
<td>30.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>B</td>
<td>37.2</td>
<td>20.0</td>
<td>24.8</td>
<td>10.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>

*Composition as prepared by mixing of powders
specified period of time and was then withdrawn so that the thickness of the slag shell and the structure of the pellet could be observed.

Pellets that were to be used for temperature measurements were prepared by first drilling a 1/8" (3.2 mm) diameter hole into the pellet that extended to a point 2.5 mm short of the center. A 1/16" (1.6 mm) diameter hole was drilled for the remainder of the distance to the center of the pellet. The pellets were bored on a lathe to center the hole accurately. Care was taken to avoid heating the pellet. The fines that were generated during the boring process were collected. A thermocouple was inserted into the hole so that the bead sat in the small well at the center of the pellet. The fines from the boring process were added to cover the bead and fill the small diameter boring and then a special tool was used (cf. Fig. 3.4) to peen the thermocouple bead into place. The thermocouple wire was sheathed by an alumina or mullite support tube. The lower end of the support tube was wrapped with molybdenum foil before it was slid into the pellet, to prevent the wetting of the ceramic support tube by the slag. The complete pellet support assembly is shown in Fig. 3.5.

Pellets to be used for immersion and withdrawal test in molten slags were mounted on a 1/16" (1.6 mm) diameter steel rod by drilling a hole completely through the pellet and passing the rod through the hole. The end of the rod was bent to secure the pellet.

3.2.2. The Experimental System

The experimental system that was used to perform heating experiments with DRI pellets in molten slags is shown in Fig. 3.6. The
Figure 3.4 - Technique for inserting a thermocouple into a pellet.
Figure 3.5 - Pellet support assembly for temperature measurement.
Figure 3.6 - The experimental system used for DRI pellet heating experiments in molten slags.
equipment was designed to allow both the temperature within a pellet, and the volume of gas that evolved from a pellet to be measured continuously while the DRI pellet was heated in the slag bath. The equipment used in the experimental set-up consisted of:

(a) a sealed furnace that was powered by a 10KHz., 50KW Tocco induction generator (see Fig. 3.7);
(b) a spirometer (W.E. Collins, Inc., Survey Model), with an 8 liter capacity for the measurement of gas volume;
(c) a microcomputer (Apple II, 48K) equipped with a 12 bit A/D converter to record, store, and manipulate data from the thermocouple and the spirometer;
(d) pen recorders to provide an additional hard copy of the raw temperature and volume data;
(e) and a control system to provide an accurate way of recording starting times, marking the times of visually observed events, and to ensure that all recording systems were chronologically synchronized.

3.2.2.1. The Furnace

The furnace that was used to contain and heat the slag is shown in Fig. 3.7. The slag bath was held in an iron crucible (10 cm id., 14 cm od., 30.5 cm deep) that also acted as as susceptor for induction heating. Only the lower half of the crucible was filled with slag. The
Figure 3.7 - The furnace used for pellet heating experiments in molten slags.
upper half was fitted with a heat shield to minimize heat loss from the
top of the bath. The additional space in the crucible was provided to
accommodate the formation of a foamy slag, which resulted in an expan-
sion of the slag volume to 2-3 times its original volume.

The crucible assembly was fitted inside a 23 cm dia. silica tube. The ends of the tube were sealed with water cooled brass caps to provide a gas-tight seal. The inside of the tube surrounding the crucible was packed with ceramic fiber insulation to minimize heat losses and to limit the convective "pumping" of the gases in the furnace. Two exit lines for the exhaust gases were extended to the interior of the crucible to minimize back pressure. A gas inlet at the bottom of the furnace allowed the system to be flushed with argon during the fusion of a slag mixture and between experiments. A fitting at the top of the furnace allowed the pellet mounting assembly (cf. Fig. 3.5) to be inserted and removed easily. A viewing port was also positioned at the top of the furnace so that the condition of the slag could be viewed during an experiment.

3.2.2.2. The Volume Measurement System

The spirometer that was used to measure the volume of gas generated by a reacting DRI particle consisted of a low mass bell that had a water seal. The gas entering the unit caused the bell to be displaced upwardly. The displacement of the bell was recorded directly onto chart paper that was calibrated to indicate the volume of gas within the bell. The displacement was also monitored with a linear potentiometer that was attached to the unit to generate a voltage signal
that varied linearly with the displacement of the bell. This signal was supplied to the computer.

The spirometer was connected to the furnace assembly as shown in Fig. 3.6. The gas that exited from the furnace was passed through a water cooled heat exchanger prior to entering the spirometer to cool the gas to a constant temperature. The heat exchange system helped to impose a steady temperature profile throughout the sealed gas collection system. The steady temperature distribution was necessary to make accurate measurements of the volume of gas evolved during a test. The temperature of the gas inside the spirometer was measured by a thermometer that was attached directly to the unit. A manometer was also attached to the system to monitor the gas pressure.

Preliminary testing of the gas volume measurement system was performed to evaluate its performance. Blank volumes of CO, CO₂, and Ar were held in the spirometer to establish that the absorption of these gases by the water in the sealing system was negligible. Tests with the furnace at operating temperature were also performed. The results of gas volume measurements for two tests performed using non-reactive pellets, and a third test using a reactive pellet are shown in Fig. 3.8. For the inert spheres, a nearly constant increase in volume with time was observed, even though no gas was evolved. However, the magnitude of the volume drift was different for the two inert pellets. A nearly constant increase in volume with time was also observed for the reactive pellet once the active evolution of gas had ended. The drift in volume that occurred in all of the tests was probably a result of changes in the internal temperature of the furnace assembly with time. During all
of these tests, the gas pressure within the system never increased by more than 1 mm H₂O relative to atmospheric pressure, indicating that pressure effects could be neglected.

In order to correct the gas volume measurements for individual volume drifts, the following procedure was adopted: the data from the last 100 seconds of an experiment, that fell within the nearly level region of the reaction volume profile (cf. Fig. 3.8), were used to determine the volume drift for the experiment by performing a linear regression analysis. The slope determined from the least squares fit was used to represent the drift for the experiment. This rate was subtracted from the measured gas volume to give the true reaction volume profile for that experiment. The procedure was easily performed on the computer, which was also used to calculate the rate of gas evolution versus time from the gas volume data. The procedure used to calculate the STP gas volumes and gas evolution rates from the raw data is outlined in Appendix C.

Some typical correction factors that were calculated from the linear regression analysis procedure and used to correct the gas volume measurements are presented in Table 3.4. The drift corrections vary from a low of about 10 cm³/min STP to a high of about 40 cm³/min STP in all tests, except those in which slag foaming occurred. When slag foaming occurred, the foam filled the upper regions of the furnace assembly and often blocked the gas exit lines. The expansion of the slag into the upper regions of the furnace also disturbed the temperature distribution within the furnace, producing large errors in the gas volume that was measured by the spirometer. Because of this, the volume
Figure 3.8 - Uncorrected gas volumes measured for a single reactive pellet and two different inert pellets, showing a nearly constant volume drift with time. The linear regression line, used to correct for the observed volume drift, is also shown.
Table 3.4

Typical Volume Drift Corrections Employed in DRI Pellet Heating Tests in Molten Slag

<table>
<thead>
<tr>
<th>Run #</th>
<th>Pellet ID #</th>
<th>Drift Correction, cm³/min STP *</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>SB-1-1</td>
<td>11.4</td>
</tr>
<tr>
<td>23</td>
<td>CD-8-20</td>
<td>18.6</td>
</tr>
<tr>
<td>23</td>
<td>CD-8-23</td>
<td>30.1</td>
</tr>
<tr>
<td>25</td>
<td>CD-8-25</td>
<td>23.6</td>
</tr>
<tr>
<td>25</td>
<td>CD-7-26</td>
<td>13.0</td>
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<tr>
<td>27</td>
<td>CD-7-18</td>
<td>35.7</td>
</tr>
<tr>
<td>27</td>
<td>CD-7-28</td>
<td>25.3</td>
</tr>
<tr>
<td>27</td>
<td>CD-8-26</td>
<td>33.2</td>
</tr>
<tr>
<td>27</td>
<td>SP-4</td>
<td>25.1</td>
</tr>
<tr>
<td>27</td>
<td>HR1-8</td>
<td>30.2</td>
</tr>
<tr>
<td>28</td>
<td>CD-9A-2</td>
<td>11.7</td>
</tr>
<tr>
<td>28</td>
<td>CD-8-28</td>
<td>14.8</td>
</tr>
<tr>
<td>28</td>
<td>CD-9B-1</td>
<td>13.7</td>
</tr>
<tr>
<td>28</td>
<td>LR-25-1</td>
<td>15.6</td>
</tr>
</tbody>
</table>

* excluding tests in which slag foaming occurred

* calculated from linear regression procedure described in Appendix C
measurements made in the presence of a foaming slag were considered unreliable and were not included in the results. The reproducibility of the gas volume measurements made in the absence of slag foam formation is demonstrated in Chapter 4 (cf. Fig. 4.48).

3.2.2.3. Pellet Temperature Measurement

The measurement of changes in the temperature within any solid is subject to error due to the lag in the response of the temperature sensing element, and due to contamination of the temperature sensing element. When a thermocouple is protected from contamination with a protective sheath, the response time of the temperature sensing element is increased. On the other hand, if the thermocouple is placed in direct contact with the solid, the thermocouple may eventually become contaminated, and the temperature versus emf. relationship for the thermocouple altered. In the present study, direct contact between the thermocouple bead and the pellet was employed because it was judged that the effects of contamination on the temperature versus emf. relationship of a thermocouple would be small during the relatively short duration of a test (typically, 4 minutes or less). In this way, lags associated with the presence of a sheath on the temperature sensing element could be avoided.

The procedure that was used to attach a thermocouple to a pellet has been discussed previously in section 3.2.1 (cf. Fig. 3.4 and Fig. 3.5). Some details of the temperature recording system are given in Fig. 3.6. The signal from a thermocouple was supplied directly to an X-Y plotter that recorded the thermocouple output on graph paper, and
generated an amplified voltage signal that was proportional to the thermocouple emf. The amplified signal was supplied to the computer.

Several precautions were employed to minimize the error in the measurement of the temperature within a DRI pellet as it was heated in molten slag. Electrical noise from the induction system was minimized by shielding thermocouple wires and connectors, where possible, and by positioning the pellet and the thermocouple support tube concentrically within the induction coil. The crucible assembly was also grounded to minimize electrical "leakage" from the induction susceptor to the pellet (cf. Fig. 3.7). A preliminary test was also performed to investigate the influence of the induction field on temperature measurement during a pellet heating test in molten slag, by turning the induction field off momentarily. The test indicated that the induction field did not influence the output of the thermocouple.

The uncertainty in the starting time of test was minimized by employing a foot activated switch that was pressed as a pellet entered the slag to automatically record the start of the test. The experimental system was designed so that a pellet could be placed in the sealed furnace and then lowered into the slag rapidly without heating the pellet appreciably prior to its entry into the bath.

The reproducibility of the temperature measurements was investigated by duplicating experimental conditions with different pellets and comparing the recorded temperature profiles for each pellet. The effects of thermocouple contamination were investigated in a similar manner by using two different types of thermocouples. The results of these tests are presented in Fig. 3.9. The three temperature profiles
Figure 3.9 - Temperature measurements from four different, but identically prepared pressed DRI pellets in slag B. Type CD-7 powder, 2.5 cm pellet diameter.
obtained using Chromel-Alumel® (ASTM Type K) thermocouples are in good agreement. The measured temperatures agree to within 15 °C below 1300 °C, indicating that the reproducibility of the experiments is quite good. The agreement between the W-Re\* type thermocouple and the Chromel-Alumel thermocouples is not as good. Differences in temperature as large as 40 °C are observed below 1300 °C. The larger discrepancy in the temperatures that was obtained with the two types of thermocouples suggest that contamination may have occurred in at least one of the two types of thermocouples tested.

Several observations suggest that the W-Re type thermocouples may have been affected by contaminants from the pellets. The plots of thermocouple emf. versus time that were generated from the W-Re type thermocouples were not as "smooth" as the plots from the Chromel-Alumel thermocouples. The emf. increased in small jumps when the W-Re type thermocouples were used. In contrast, the emf increased smoothly with the Chromel-Alumel thermocouples. In addition, thermal arrests that were observed in the temperature profiles were recorded more clearly with Chromel-Alumel thermocouples than with W-Re type thermocouples. Another factor to be considered was the relatively small diameter of the W-Re wire. The W-Re wire was 0.127 mm in diameter, while the Chromel-Alumel wire was 0.330 mm in diameter. The fineness of the W-Re wire could have increased its susceptibility to the contamination.

Because of the superior performance of the Chromel-Alumel thermocouples over the Tungsten-Rhenium type thermocouples under the present

\* Tungsten 3% Rhenium vs. Tungsten 25% Rhenium.
testing conditions, Chromel-Alumel thermocouples were employed in all of the tests that are discussed, subsequently. Clearly, the issue of contamination has not been completely resolved. Observations suggest that the discrepancy between the two types of thermocouples is largely a result of contamination of the W-Re type thermocouple by the pellet. However, in the worst case, the measured temperature profiles will be systematically low by about 40 °C at long times after immersion. In comparison, previous tests \(^{(13)}\) that have employed various forms of thermocouple protection exhibited considerably larger random errors in temperature that were in the range of 50 °C to 100 °C. These errors were attributed largely to the uncertainties in the position of the thermocouple, and the contact between the thermocouple and the pellet. Both of these uncertainties are more rigidly controlled in the present tests.

3.2.2.4. Slag Bath Temperature Measurement

The temperature of the slag bath was measured by sighting an optical pyrometer (Leeds and Northrop, disappearing filament type) down a steel tube through which argon gas was bubbled. The tube was immersed approximately 10 cm into the slag, and the end was allowed to heat to the temperature of the bath. Once the end had heated, an optical reading was taken by sighting on the inside of the bubbles that formed at the end of the tube, as shown in Fig. 3.10. The bubbling also proved to be a convenient way to stir the bath to maintain a uniform slag bath temperature in the crucible between tests.

An immersion thermocouple (Type B) was used to independently compare the temperature obtained in the slag by the optical method with
Figure 3.10 - Technique used for the optical measurement of the slag bath temperature.
the temperature measured by the immersion thermocouple. The tempera-
tures agreed to within 3 °C at 1400 °C without an emissivity correction.
Apparently, the bubble acts as a black body cavity--possessing an
apparent emissivity that is close to unity even though the true emissiv-
ity of the slag is about 0.7.

An immersion probe was also used in some tests to estimate the
solidus and liquidus temperatures of slag B (see Fig. 3.11), by observ-
ing and recording the thermal arrests in a small sample of slag on the
tip of the probe as it heated. The testing procedure involved first
dipping the probe tip into the slag bath and quickly removing it to
obtain a frozen slag sample on the probe tip. The tip of the probe with
the slag sample was then re-immersed into the slag bath, and the temper-
ature was recorded as a function of time as the slag sample melted from
the probe in the slag bath. The procedure was repeated several times,
and the arrest temperatures were estimated from the thermal arrests
observed in the heating curves, as shown in Fig. 3.12.

3.2.3. Experimental Procedure

The slag in the system was melted under an argon atmosphere.
Prior to a test, slag level was adjusted by adding slag powder to
achieve a slag depth of 15 cm. The slag was held for a minimum of 2
hours after any additions were made, to ensure the homogeneity of the
bath. Optical readings of the bath temperature were taken, and the
furnace power was adjusted until the temperature of the bath had sta-
bilized at the desired temperature. Once the desired temperature of the
slag bath had been achieved, the optical sight tube was removed and the
**Figure 3.11** - Detail of the tip of the immersion thermocouple used for slag dip sampling and slag solidus and liquidus temperature determinations.

**Figure 3.12** - Heating curves for dip-sampled slag B showing the thermal arrests for the solidus and liquidus temperatures of the slag.
furnace assembly was sealed. Approximately 1 liter of argon was purged into the sealed system to test for leaks. If no gas leaks were observed, the data acquisition software on the computer was initiated, the pellet assembly was fitted into the furnace cap, and the system was resealed. The pellet was then lowered into the slag by sliding the support tube through a compression fitting on the furnace cap plug (cf. Fig. 3.5). When the pellet entered the slag bath, a foot switch was activated (cf. Fig. 3.6) to start the recorders and to signal the starting time of the test to the computer. The pellet assembly was marked so that the pellet could be quickly positioned 8 cm below the surface of the slag. The reactivity of the pellet and the condition of the slag were subjectively evaluated during the test by direct visual observation of the surface of the slag. After a predetermined data acquisition time (typically, 4 minutes), the pellet was removed and saved for macroscopic and microscopic examination. After the test, the argon purging was resumed and the optical sight tube was re-installed. The same procedure was repeated for the next test. A number of tests could normally be performed while the slag was molten. The slag level was checked periodically between experiments so that small additions of slag could be made when necessary. Because the bath temperature was normally at 1400 °C, the slag level was also carefully watched to detect any signs of crucible failure. Normally, three days of testing could be achieved with a single iron crucible before failure occurred. Failure normally occurred by grain growth and subsequent intergranular failure of the crucible.
3.3. DRI Reactivity Tests

The reactivities of several of the DRI powders that were used in the pellet heating experiments described in section 3.2 were studied by heating a sample of DRI in a sealed reaction chamber and simultaneously measuring the temperature of the sample and the volume of gas that evolved from the sample as a function of time. The experimental technique that was employed was similar to the technique employed by Sadrnezhaad (14) in his study of the reactivity of commercial DRI powders (cf. section 2.2).

3.3.1. Sample Preparation

Cylindrical specimens were prepared from commercial DRI powders as follows: a sample of approximately 12 grams of powder was split from a powder batch, and placed into a 1.25 cm dia. cylindrical rubber die that held a thermocouple at the center of the powder charge, as shown in Fig. 3.13. The die was pressed to 40,000 psi in an isostatic oil press. The resulting cylindrical DRI sample was approximately 3 cm in length and 1.2 cm in diameter. The leads from the imbedded thermocouple were welded to wires of the same type (Chromel-Alumel, Type K) and sheathed with mullite tubing.

3.3.2. Experimental System and Procedure

The reaction chamber that was used to heat the DRI sample and to collect the evolving gases is shown in Fig. 3.14. An alumina tube with a closed end was centered inside a cylindrical graphite susceptor using bubble grain alumina as a packing material. The open end of the tube was sealed with a brass cap that was water cooled. The gas exit line
Figure 3.13 - Isostatic press mold used to prepare a cylindrical DRI pellet with an imbedded thermocouple for DRI reactivity tests.
Figure 3.14 - The heated reaction chamber used for the DRI reactivity experiments.
from the reaction tube was connected to the heat exchange and volume measurement systems described in section 3.2. (cf. Fig. 3.6.). The cylindrical DRI sample with the imbedded thermocouple was placed inside the reaction capsule, and the excess volume within the capsule was packed loosely with ceramic fiber insulation to minimize convective "pumping" problems. Prior to a test, the reaction chamber was evacuated with a mechanical vacuum pump and backfilled with argon. The sample was heated at approximately 100 °C/min, by increasing the power to the induction coil.

A constant heating rate was not achievable in practice. The temperature of the sample, and the volume of gas that evolved, were recorded continuously with time on mechanical recorder and by the computer, as described in section 3.2. A preliminary blank test indicated that no blank volume corrections were needed for the experimental system. A typical volume and temperature trace for an experiment is shown in Fig. 3.15. Gas evolution rates were calculated for these tests as described in Appendix B.
Figure 3.15 - Experimentally measured temperature and gas volume profiles obtained by heating a cylindrical DRI sample in the absence of slag.
CHAPTER 4
EXPERIMENTAL RESULTS

The results from the three segments of the experimental program are summarized in this chapter. The results of the chemical analyses that were performed on the direct reduced iron used in the experimental program are presented in section 4.1. Information from a study of the microstructures of several DRI pellets has also been included in this section. Results from experiments in which pellets were heated in molten slags are presented and discussed in section 4.2. Observations from an experimental study of the reactivity of DRI in the absence of slag are presented in section 4.3.

4.1. Composition and Structure of DRI

The oxygen, carbon, and total gangue content of all of the types of DRI employed in this study are reported in this section. Microstructural examinations were also performed on some selected types of DRI pellets to determine the physical form of the reactive oxygen and carbon within these pellets. These examinations also provided qualitative information about the structure of the pellets, which was useful in the interpretation of some of the results reported in section 4.2.

4.1.1. Chemical Analysis of DRI

The oxygen, carbon, and total gangue content of the lots of DRI powder used in the experimental program are presented in Table 4.1. The FeO content and percent of metallization for these powder lots, which
Table 4.1
Chemical Analysis of DRI

<table>
<thead>
<tr>
<th>Sample/Lot</th>
<th>Wt. % C</th>
<th>Wt. % O</th>
<th>Wt. % Gangue</th>
<th>Wt. % FeO*</th>
<th>% Met.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD-7**</td>
<td>2.37</td>
<td>3.09</td>
<td>6.75</td>
<td>14.64</td>
<td>87.72</td>
</tr>
<tr>
<td>CD-8**</td>
<td>1.98</td>
<td>1.96</td>
<td>5.74</td>
<td>9.30</td>
<td>92.43</td>
</tr>
<tr>
<td>CD9A**</td>
<td>2.15</td>
<td>3.25</td>
<td>6.37</td>
<td>15.41</td>
<td>87.13</td>
</tr>
<tr>
<td>CD-9B**</td>
<td>2.53</td>
<td>3.50</td>
<td>6.27</td>
<td>16.57</td>
<td>86.09</td>
</tr>
<tr>
<td>HRI-8°</td>
<td>0.06</td>
<td>0.65</td>
<td>7.31</td>
<td>2.94</td>
<td>97.51</td>
</tr>
<tr>
<td>LR-3A-1#</td>
<td>1.08</td>
<td>1.62</td>
<td>0</td>
<td>7.29</td>
<td>94.17</td>
</tr>
<tr>
<td>LR-3A-2#</td>
<td>4.01</td>
<td>5.37</td>
<td>0</td>
<td>24.12</td>
<td>79.40</td>
</tr>
<tr>
<td>LR-1B**°°</td>
<td>0</td>
<td>1.44</td>
<td>0</td>
<td>6.45</td>
<td>94.91</td>
</tr>
<tr>
<td>LR-2D°°</td>
<td>0</td>
<td>3.13</td>
<td>0</td>
<td>14.08</td>
<td>88.70</td>
</tr>
<tr>
<td>LR-2J°°</td>
<td>0</td>
<td>0.06</td>
<td>0</td>
<td>0.26</td>
<td>99.80</td>
</tr>
</tbody>
</table>

* Assuming all oxygen present as FeO

** Crushed, Repressed Commercial DRI Pellets

° Crushed, H₂ Heat Treated, Repressed Commercial DRI

# Repressed, Carbon Reduced Hematite Powder

°° Gas Reduced Hematite Pellets
were also included in Table 4.1, were calculated by assuming that all of the reactive oxygen in the sample was present as FeO*. The weight percentage of carbon and oxygen in each sample is plotted in Fig. 4.1 to show the range of concentrations studied in the research program, and to indicate which of these reactants limits total volume of gas that can theoretically be evolved from each type of material by the overall reaction,

\[(1-X_{\text{CO}_2})_0 \text{(in DRI)} + C \text{(in DRI)} = (1-X_{\text{CO}_2})\text{CO}_2(g) + (X_{\text{CO}_2})\text{CO}_2(g)\]  

Also identified in the figure are lines of balanced consumption of C and O, according to reaction 4-1, as a function of the CO2 content of the product gas.

The compositions of the DRI materials presented in this section were used to evaluate the relative completeness of the reactions that occurred within DRI pellets during immersion in molten slags (section 4.2.). The compositions were also used as a starting point for predicting the rate of reaction of carbon and oxygen in DRI using a kinetic model (cf. Chapter 6).

4.1.2. Microstructure of DRI

The microstructures of three types of DRI pellets, that were examined prior to testing, are compared in this section. The microstructures of two pellets, that were prepared from type CD-7 and type

* The assumption that the reactive oxygen in the samples is present as wustite is supported by microstructural evidence, which is presented in section 4.1.2. All subsequent calculations are based on stoichiometric FeO.
Figure 4.1 - Compositions of DRI used in this study. The lines identify the amount of oxygen that can be theoretically removed from a sample for a given carbon content and product gas composition, according to reaction (4-1).
CD-8 powders by isostatic pressing, are presented in Fig. 4.2 and Fig. 4.3, respectively. The structures of the two pellets are similar. Both pellets have a porous structure that is composed primarily of metallic iron. Unreduced wustite can also be seen within the metallic structure of both pellets. The wustite is present as isolated "islands" that are completely enveloped within a shell of dense iron. None of the wustite appears to be directly exposed to the pores in the pellet.

The pore structures observed in the type CD-7 and type CD-8 pressed pellets, shown in Fig. 4.2 and Fig. 4.3, respectively, differ very little from the pore structures observed in commercial pellets (cf. Fig. 1.2). With the exception of distributing the wustite more uniformly, and decreasing the porosity of the DRI slightly, the crushing and re-pressing procedure, that was used to produce the DRI pellets for the experimental program, appears to have had very little effect on the structure of the material. Preservation of the microstructural features of the DRI is desirable because gross alterations in the microstructure could ultimately lead to an alteration in the kinetics of the reaction of carbon and wustite in the material.

The type CD-7 and type CD-8 pellets were etched with a 1 percent Nital solution to test for the presence of iron carbide in the material. (The etchant preferentially darkens Fe₃C to make it visible.) The test indicated that the type CD-7 sample contained iron carbide. In contrast, no iron carbide could be detected in the type CD-8 sample. Because both samples contain carbon (cf. Table 4.1), the carbon in the type CD-8 sample is apparently present as soot, which would be difficult to detect by optical inspection of the microstructure. On the other
Figure 4.2 - Microstructure of a type CD-7 pellet prepared by pressing. SEM @ 500X.

Figure 4.3 - Microstructure of a type CD-8 pellet prepared by pressing. SEM @ 500X.
hand, a substantial portion of the carbon in the type CD-7 sample is in the form of Fe₃C. The iron carbide in the type CD-7 sample is shown in Fig. 4.4.

The microstructure of a type LR-2J pellet, which was prepared by reducing a hematite sphere with H₂ to produce a sponge iron (DRI) sphere, is shown in Fig. 4.5. The microstructure of this pellet is markedly different from the microstructures of the pressed DRI pellets discussed previously (cf. Fig. 4.1 and Fig. 4.2). Regions of high density, that appear to correspond to the original grains of hematite in the pellet prior to reduction, are clearly visible. The regions of high density are surrounded by regions of relatively low density. The pore structure within the pellet is also segregated. Figure 4.6 shows a band of high porosity that exists in the region adjacent to the surface of the pellet. This band of porous iron surrounds the core of the pellet, which has a much lower porosity. It is interesting to note that although the apparent density of the type LR-2J pellet was determined by direct measurement to be lower than the apparent density of the type CD-7 pellet (3.4 g/cm³ and 3.9 g/cm³, respectively), Fig. 4.6 indicates that the type LR-2J pellet has a central core that is less porous than the type CD-7 pellet. It should also be noted that no wustite was observed within the type LR-2J pellet. This observation is in good agreement with the composition of the pellet reported in Table 4.1, which indicates that the pellet was almost completely reduced to metallic iron.

The three-dimensional structures of a pressed (type CD-7) pellet and a lab-reduced (type LR-2J) pellet are compared in Figs. 4.7-4.10.
Figure 4.4 - Type CD-7 pellet etched with a 1% Nital Solution to reveal the presence of Fe\(_3\)C. Optical @ 500X.

Figure 4.5 - Microstructure of pellet LR-2J prepared by the gaseous reduction of Fe\(_2\)O\(_3\) in H\(_2\). SEM @ 500X.
Figure 4.6 - Pellet LR-2J structure near the surface of the pellet showing heterogeneity in pore structure. Optical @ 65X.
The fractured surface of the type CD-7 pellet is shown in Fig. 4.7, and the corresponding polished cross-section of the same pellet is shown in Fig. 4.8. The fractured surface of the type LR-2J pellet, and the corresponding polished cross-section are shown in Fig. 4.9 and Fig. 4.10, respectively. The fractured surface of the type CD-7 pressed pellet reveals a relatively loosely connected iron matrix. The individual grains of DRI are not sintered together. In contrast, the fractured surface of the type LR-2J pellet reveals a highly sintered iron matrix. There is evidence of torn connecting filaments of iron on the fractured surface. The differences in the structures of the pressed, type CD-7, pellet and the hydrogen-reduced, type LR-2J, pellet demonstrate the kinds of structural differences that can be encountered in DRI. These structural differences ultimately influence the thermophysical properties of the material. The structure has a strong influence on the thermal conductivity of a porous material.

4.2. Experiments in Molten Slag

The results obtained from testing in molten slag are divided into two groups: the first group of results were obtained by immersing a pellet into the slag bath for a specified period of time and then removing it. Using this procedure, the structures and morphologies of the solid slag shell and the pellet were studied. The results of this investigation are presented in section 4.2.1. The second group of results were obtained by measuring the temperature within a pellet and the volume of gas that evolved from the pellet as the pellet was introduced and held in a bath of molten slag. Using this procedure, the
Figure 4.7 - Fracture surface from a type CD-7 pressed pellet showing the 3-dimensional pellet structure. SEM @ 2000X.

Figure 4.8 - Corresponding polished cross-section from a type CD-7 pressed pellet. SEM @ 2000X.
Figure 4.9 - Fracture surface from a type LR-2J hydrogen reduced hematite pellet. SEM @ 2000X.

Figure 4.10 - Corresponding polished cross-section of a type LR-2J pellet. SEM @ 2000X.
temperature profiles and gas evolution profiles for various types of pellets under different heating conditions could be studied and compared. The results of this investigation are presented in section 4.2.2.

4.2.1. Results from Immersion and Withdraw Tests

Tests with a number of types of DRI in both slag A and slag B (cf. Table 3.3) indicate that two conditions of slag/pellet contact exist that are common to all of the experimental conditions encountered in this study: (1) a non-wetting period that exists while a solid shell of slag surrounds the pellet, and (2) a wetting period that commences once the solid shell remelts, and that ultimately results in the penetration of molten slag into the pores of the pellet. While the formation of a slag shell on DRI during the initial stages of heating is well documented, (6,7,13,14) the penetration of slag into DRI during the latter stages of heating has not been reported prior to this study.

4.2.1.1. Structure and Morphology of the Slag Shell

Samples of the slag shells were obtained for type CD-7 and type CD-8 pellets in slags A and B using the immersion and withdrawal method. The slag shells that were present on 32g type CD-7 pellets after 5, 15, 30, and 120 seconds of immersion in slag B at 1400 °C are shown in Figs. 4.11, 4.12, 4.13, and 4.14, respectively. The slag shells that formed on 32g type CD-8 pellets after 15s and 60s of immersion in slag B at 1400 °C are shown in Figs. 4.15 and 4.16, respectively. The shells that are shown in these figures were removed from the pellet after a test, reassembled, mounted in epoxy, and then sectioned
Figure 4.11 - Slag shell formed on a 32g type CD-7 pressed pellet. 5 s immersion. Slag B at 1400 °C. Scale is in cm.

Figure 4.12 - Slag shell formed on a 32g type CD-7 pressed pellet. 15 s immersion. Slag B at 1400 °C. Scale is in cm. The arrow shows the position of the gas channel.
Figure 4.13 - Slag shell formed on a 32g type CD-7 pressed pellet. 30 s immersion in Slag B at 1400 °C. Scale is in cm. The arrow shows the position of the gas channel.

Figure 4.14 - Slag shell formed on a 32g type CD-7 pressed pellet. 120 s immersion in Slag B at 1400 °C. Scale is in cm.
Figure 4.15 - Slag shell formed on a 32g type CD-8 pressed pellet 15 s immersion in Slag B at 1400 °C. Scale is in cm. The arrow shows the position of the gas channel.

Figure 4.16 - Slag shell formed on a 32g type CD-8 pressed pellet. 60 s immersion in Slag B at 1400 °C. Scale is in cm.
along the original vertical mounting axis, to reveal a cross-sectional view of the slag shell.

Figures 4.11-4.14 reveal some interesting aspects of the slag shell formation and growth process. After 5 seconds of immersion, a solid shell of slag had already formed to an appreciable thickness, except in one small area where no shell had formed. The region, where the shell had not yet formed, coincided with a region of active gas evolution from the pellet. It was observed that a considerable amount of gas evolved from this area when the pellet was removed from the slag bath. After 15 seconds, the slag shell had completely enveloped the pellet, and gas escaped from the enclosed pellet through three or four small channels in the shell. The gas exited through these small openings at high velocity, producing 3 or 4 actively bubbling sites on the pellet. One of these gas channels through the slag shell can be seen in Figs. 4.12 and 4.13. After 30 seconds, the thickness of the shell had increased considerably, and gas was still being evolved through the passageways in the shell. After 120 seconds, the gas evolution had essentially ceased. No passageways through the slag shell could be found. Apparently, the passageways in the shell collapsed and healed once the gas evolution from the pellet ended.

The mean thickness of the slag shell that was observed on 32g pellets as a function of immersion time in slag B at a 1400 °C bath temperature is shown for type CD-7 and type CD-8 pellets in Fig. 4.17 and Fig. 4.18, respectively. In addition to showing the total thickness of the slag shell that was observed after a test, the distance to the base of a ring of bubbles seen just below the surface of the slag
Figure 4.17 - Experimentally measured slag shell thicknesses on 32g type CD-7 pellets immersed in Slag B at 1400 °C.

Figure 4.18 - Experimentally measured slag shell thicknesses on 32g type CD-8 pellets immersed in Slag B at 1400 °C.
shell (cf. Figures 4.11-4.16) is also shown. This ring of bubbles marks the surface of the slag that existed when the pellet was in the slag bath. The additional slag that is observed on the shell is liquid slag that was retained and solidified upon removal of the pellet from the slag bath. The presence of an adhering layer of liquid slag is supported by microstructural evidence, presented in Figures 4.19 and 4.20, which shows that the slag shell has a dendritic structure, with dendrite tips that extend just beyond the line of gas bubbles within the shell. A fine dendritic structure exists beyond the line of bubbles. This region corresponds to the liquid slag that was retained upon removal of the pellet from the slag bath. The thickness of this retained slag layer is also in qualitative agreement with theoretical estimates of the retained slag thickness calculated in Appendix D.

A micrograph of the structure of the slag in the vicinity of a channel that passed through the shell, and through which gas was evolved, is shown in Figure 4.21. Small droplets of metallic iron can be seen in the region adjacent to the channel. These droplets of metallic iron were probably formed by the reduction of FeO in the slag by the gases evolved from the pellet. The observation, that the gases evolved from DRI are reducing to the FeO in the slag, supports earlier studies (14) that indicate that the gases that are evolved from DRI during heating consist predominantly of CO with about 5 percent CO₂ (cf. Figure 2.5). The microstructure of a solid shell of slag that was formed on a pellet during immersion in slag A is shown in Figure 4.22. The slag has a dendritic structure with large primary dendrite arms and
Figure 4.19 - Microstructure of a solid slag shell at the outer surface that bordered the molten slag bath. Note the gas bubbles and dendrite tips below the apparent surface. Slag B at 1400 °C. Optical @ 50X.

Figure 4.20 - Microstructure of a solid slag shell at the interior surface that bordered the pellet. Slag B at 1400 °C. Optical @ 50X.
Figure 4.21 - Cross-section of a channel that passed through the slag shell, permitting gas to escape. Note the small metallic iron droplets in the shell adjacent to the channel. Slag B. Optical @ 50X.

Figure 4.22 - Microstructure of solid slag shell formed on a pellet immersed into Slag A at 1350 °C. Optical @ 50X.
no secondary dendrites. In contrast, slag B has a dendritic structure that contains both primary and secondary dendrites (cf. Figure 4.19).

4.2.1.2. Slag Penetration

When a pellet was held in the slag bath for relatively long times (greater than 3 minutes) a thin layer of slag adhered to the pellet upon removal of the pellet from the bath. In contrast to the slag shells that were obtained for short immersion times (cf. Figures 4.11-4.16), which could be easily removed from the pellet upon cooling, the layer of slag that was present on a pellet after long immersion times could not be removed. The slag appeared to be bonded to the pellet. In order to investigate this "bonding" phenomenon, the microstructures of a number of pellets were investigated. Because the "bonding" phenomenon appeared only after the complete remelting of the solid shell of slag that initially formed on a pellet, the pellets were held in the slag bath for a sufficient span of time to ensure the complete remelting of the solid slag shell.

The macrostructure, and corresponding microstructure, of a commercial DRI pellet (type CD-8, before crushing) that was immersed and held in slag B for 300 seconds is shown in Figures 4.23 and 4.24, respectively. The single, most important observation to be made from these figures is that the pellet pore structure has been completely filled with slag. Slag is observed in the smallest pores of the pellet, and is present throughout the entire pore structure. The composition of the slag phase within the pore structure of the pellet was investigated by electron beam microanalysis to identify the components that make up the
Figure 4.23 - Macroscopic cross-section of a commercial DRI pellet (type CD-8) after immersion in Slag B for 300 s. Scale is in cm.

Figure 4.24 - Microstructure of the pellet shown above (Fig. 4.23) showing slag phase within the pores of the pellet. Optical @ 50X.
slag. The results of the microprobe analysis, which are presented in Figures 4.25 and 4.26, indicate that the composition of the slag found within the pores of the pellet is the same as the composition of the slag bath (cf. Table 3.3). This is strong evidence that the slag was drawn into the pellet pore structure from the slag bath, and that the slag was not formed from the gangue materials within the DRI pellet.

Slag penetration is also documented for a type LR-2J pellet in Figures 4.27-4.30. Because this pellet was almost completely metallized, and contained no gangue (cf. Table 4.1), this test indicates that the presence of gangue in DRI is not a prerequisite for slag penetration. Apparently, upon the disappearance of the solid slag shell, the molten slag wets the sponge iron and is drawn into the pores of the pellet by capillary forces. This mechanism of slag penetration is also supported by calculations in Appendix E.

Evidence of slag penetration is also shown for other types of pellets in Figures 4.31-3.34. In all cases examined, penetration of slag into the pores was complete. The penetration apparently occurs very rapidly once wetting conditions are favorable. The pellet shown in Figure 4.32 was completely impregnated with slag after 180 seconds, even though Figure 4.17 indicates that a solid shell of slag was present on the pellet for well over 120 seconds.

4.2.1.3. Changes in Pellet Structure

As a DRI pellet is heated in a bath of molten slag, structural changes occur within the pellet as a result of reactions within the pellet, sintering of the porous iron structure of the pellet, and slag
Figure 4.25 - Microstructure of the slag phase present within the commercial DRI pellet shown in Fig. 4.24. SEM @ 2000X.

Figure 4.26 - Energy dispersive X-ray analysis of the slag phase shown in Fig. 4.25. The sample was coated with Au prior to analysis.
Figure 4.27 - Microstructure of a type LR-2J pellet after immersion in Slag B for 180 s showing penetration of slag and the adhering slag layer on the surface. Optical @ 65X.

Figure 4.28 - Microstructure of adhering layer of slag in Fig. 4.27. SEM @ 1000X.
Figure 4.29 - Microstructure of the interior of a type LR-2J pellet after immersion in Slag B for 180 s. White areas are the iron grains of the pellet. SEM @ 1000X.

Figure 4.30 - X-ray map for calcium corresponding to the micrograph in Fig. 4.29, showing regions within the pellet structure that the slag has penetrated. SEM @ 1000X.
Figure 4.31 - Microstructure of a type CD-9B pellet after immersion in Slag B for 240 s. Optical @ 100X.

Figure 4.32 - Microstructure of a type CD-7 pellet after immersion in Slag B for 180 s. Optical @ 200X.
Figure 4.33 - Microstructure of pellet HR1-8 after immersion in Slag B for 320 s. Optical @ 200X.

Figure 4.34 - Microstructure of pellet HR1-8 (cf. Fig. 4.33) at 500X.
penetration into the pores of the pellet. These changes also affect the dimensions of the pellet, as shown in Figures 4.35 and 4.36. The decrease in the diameter of the pellet appears to be a result of the sintering of the porous iron structure during heating. Information on the densification of a number of pellets has already been presented in section 4.2.1.3. The change in the diameter of a number of pellets that were immersed in molten slag for different times are summarized in Figures 4.37 and 4.38. The results in these figures indicate that reactive pellets exhibit a considerable decrease in pellet diameter upon heating. Similar changes in diameter are observed for reactive pressed pellets and reactive commercial pellets (cf. Figure 3.8) during immersion. On the other hand, non-reactive pellets, such as type LR-1B, LR-2D, and HR1-8 pellets, exhibit essentially no change in diameter during immersion. The structural stability of these pellets may, in part, be due to the highly interconnected structures observed in these pellets.

4.2.2. Pellet Heating Tests in Molten Slags

The results of measurements of the temperature and gas volume for a number of different DRI pellets are presented in this section. The I.D. numbers of the pellets have been included on each set of experimental results so that the properties of a particular pellet may be readily obtained. The physical properties of each pellet are summarized in Tables 3.1 and 3.2, and the chemical compositions are summarized in Table 4.1. The compositions of the two types of slags used in the experiments are presented in Table 3.3.
Figure 4.35 - Pellet CD-7-24 prior to testing, mounted for temperature measurement at the center.

Figure 4.36 - Pellet CD-7-24 after immersion in Slag B at 1400 °C for 250 seconds, showing a decrease in pellet diameter due to sintering.
Figure 4.37 - Shrinkage of 32g type CD-7 pellets after immersion in Slag B at 1400 °C.
Figure 4.38 - Shrinkage of commercial and laboratory produced DRI pellets after immersion in Slag B at 1400 °C.
For the experimental results that follow, the rate at which the temperature at the center of a pellet increases with time is used to provide a semi-quantitative means of evaluating the heating rate of the pellet. Similarly, the time-dependent rate of gas evolution from a pellet is used to provide a semi-quantitative means of evaluating the reactivity of the carbon and oxygen in the pellet.

4.2.2.1. Preliminary Testing with Solid Iron Spheres

Two preliminary heating experiments in molten slag were performed with solid iron spheres. The first sphere of iron tested was machined from a bar of high purity iron (Ferrovac E). This test was performed to obtain measurements on a pellet that possessed well characterized thermo-physical properties. This simplified test served as a logical starting point in the evaluation of the performance of the computer model of the heating and melting process (cf. Chapter 6). The second test was performed with an annealed ball bearing that contained complex alloy carbides. This test was performed simply to demonstrate the effect of the purity of the iron on the measured heating rate. In both tests, no gas evolution occurred. The heat transfer in the slag was therefore dominated by natural convection in these tests.

The heating rate of a 2.5 cm diameter, high purity, iron sphere in slag B at a 1400 °C bath temperature is presented in Fig. 4.39. This figure shows the sensitivity of the technique of temperature measurement. The thermal effects of the Curie (magnetic) transforma-

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* See Appendix B.
Figure 4.39 - Heating rate of a 2.5 cm dia., high purity iron sphere in Slag B at 1400 °C. The heat affects of the α to γ phase transformation and the magnetic (Curie) transformation are clearly visible.

Figure 4.40 - Heating rate of a 2.5 cm dia. annealed iron sphere containing alloy carbides in Slag B at 1400 °C.
tion, and the alpha-gamma phase transformation in the iron sphere are clearly visible, even though the enthalpy changes of these transformations are relatively small, 21.8 cal/g (91.1 kJ/kg) and 3.8 cal/g (15.9 kJ/kg), respectively. The absence of a lag at the beginning of the measured temperature profile, and the agreement between the observed transformation temperatures and the reported equilibrium transformation temperatures for pure iron, (67) are good indications that lags associated with the temperature measurement system are small.

The heating rate of a 2.5 cm diameter annealed ball bearing that was immersed in slag B at a 1400 °C bath temperature is presented in Figure 4.40. Although the exact composition of the sphere was not known, microstructural examination revealed the presence of alloy carbides (probably containing iron and chromium) in a ferritic matrix. The large heat effect in the temperature profile of Figure 4.40 is apparently due to the solution of these carbides. The solution of carbides of both iron and chromium in γ iron is endothermic, (68)

\[ \text{Fe}_3\text{C}(s) = 3\text{Fe}(\gamma) + \text{C}(\text{in } \gamma \text{ Fe}), \quad \Delta H^\circ_{1000K} = 9.47 \text{ kcal/mole (4-2)} \]

\[ \text{Cr}_7\text{C}_3(s) = 7\text{Cr}(\text{in } \gamma \text{ Fe}) + 3\text{C}(\text{in } \gamma \text{ Fe}), \quad \Delta H^\circ_{1000K} = 115.55 \text{ kcal/mole (4-3)} \]

The results from this test demonstrate the influence that alloying elements such as these can have on the heating rate of metallic particles of iron.

4.2.2.2. Surface and Center Temperatures in Reactive DRI Pellets

The temperatures at the surface and at the center of two 32g DRI pellets (type CD-7 and type CD-8) are presented along with their
corresponding gas evolution profiles in Figures 4.41-4.44. At the onset of heating, an appreciable difference between the temperature at the surface and the center in both types of pellets is established. The large temperature differences indicate that substantial temperature gradients exist within both pellets for almost two minutes after the initial immersion of the pellet. Measurements of the thickness of the solid shell of slag that formed on comparable pellets (cf. Figures 4.17 and 4.18) indicate that a solid shell of slag is present on both pellets during this time. Because the temperature at the pellet/slag shell interface is well below the solidus temperature of the slag during the initial stages of heating, a substantial temperature gradient must also exist within the slag shell. The existence of substantial temperature gradients within the pellet and the slag shell, implies that both the pellet and the slag shell contribute a substantial resistance to the overall heating process. Because the slag shell and the pellet are both important in determining the heat flow into the pellet, simplifying assumptions that neglect the resistance to heat flow in one domain (the slag shell or the pellet) cannot be employed in a model of the pellet heating process.

Later in the heating process, when the temperatures in the pellets' had reached the 700 °C - 1100 °C temperature range, arrests in the temperature profiles of both pellets are observed. The arrests in the temperature profiles do not appear to be directly associated with any equilibrium transformations in the iron-carbon-oxygen system, but instead appear to coincide with the observed maximum rates of gas evolution from the pellets. In addition, the arrests that were observed
Figure 4.41 - Measured heating rate at the surface and center of a 32g type CD-7 pellet immersed in Slag B at 1400 °C.

Figure 4.42 - Measured gas evolution from a 32g type CD-7 pellet immersed in Slag B at 1400 °C.
Figure 4.43 - Measured heating rate at the surface and center of a 32g type CD-8 pellet immersed in Slag B at 1400 °C.

Figure 4.44 - Measured gas evolution from a 32g type CD-8 pellet immersed in Slag B at 1400 °C.
in the surface temperature profiles do not coincide with the arrests that were observed in the center temperature profiles for each pellet. These observations suggest that the perturbations observed in the temperature profiles of these pellets are a result of the enthalpy requirements for the reaction of FeO and carbon within the pellets, and that kinetic factors control the rate at which this reaction occurs.

Still later in the heating process, when the temperature approaches the solidus temperature of the slag, a rapid rise in the heating rate is observed. This increase is presumably the result of the penetration of slag into the pores of the pellet, which has already been discussed in section 4.2.1. The enthalpy carried by the superheated slag as it is drawn into the pellet pore structure results in a rapid rise in the temperature of the pellet during this stage of the heating process.

Once the penetration of slag is complete, bulk enthalpy transport into the pellet by the slag also ceases and the heating of the pellet, which is now slag filled, is continued once again by a conductive heating process. It is to be noted in both of these tests that the evolution of gas from the pellets had essentially ceased before the solid slag shell had completely remelted (cf. Figures 4.17 and 4.18). Thus, slag penetration had no influence on the evolution of gas in these tests.

4.2.2.3. Effect of the Weight of Reactive DRI Pellets

The effects of weight on the heating rate and reactivity of type CD-7 and type CD-8 in slag B at a 1400 °C bath temperature are summarized in Figures 4.45-4.50. In both types of pellets, the heating
Figure 4.45 - Effect of pellet size on the heating rate of type CD-7 pellets in Slag B.

Figure 4.46 - Effect of pellet size on the volume of gas evolved from type CD-7 pellets during heating in Slag B. Refer to Fig. 4.45 for key.
Figure 4.47 - Effect of pellet size on the rate of gas evolution from type CD-7 pellets during heating in Slag B. Refer to Fig. 4.45 for key.

Figure 4.48 - Gas volume evolved per unit pellet mass for different sized type CD-7 pellets heated in Slag B. Refer to Fig. 4.45 for key.
Figure 4.49 - Effect of pellet size on the heating rate of type CD-8 pellets in Slag B.

Figure 4.50 - Effect of pellet size on gas volume and the rate of gas evolution from type CD-8 pellets heated in Slag B. Refer to Fig. 4.49 for key.
rate of a pellet decreases as its weight (and size) is increased. The volume of gas that is evolved from a pellet (cf. Figures 4.47 and 4.50) increases as the weight of the pellet is increased. The maximum in the rate of gas evolution is also observed to occur at later times for larger pellets. While the total volume of gas that is evolved from a pellet increases as the weight of a pellet increases, the volume of gas evolved per unit pellet mass (i.e., cm$^3$ gas/g pellet) is shown to be independent of the weight (size) of the pellet in Figure 4.48. The normalized gas volume shown in this figure indicates that the carbon and oxygen in these pellets had reacted completely, and also attests to the accuracy of the gas volume measurements. The results presented in Table 4.2 show that the reactions in DRI proceeded to completion for all of the conditions in which the gas volume could be measured. Tests in which the slag foamed are excluded from these measurements, because accurate gas volume measurements could not be made during foaming.* Thus, the results for foaming conditions are inconclusive. It should be noted, however, that gas generation was observed to proceed for some time after the onset of slag foaming and it is therefore likely that the reactions proceeded to completion under foaming conditions, as well.

4.2.2.4. Effect of Pellet Density

The effects of pellet density on the heating rate and reactivity of type CD-7, type CD-8, and type CD-9B pellets are summarized in Figures 4.51-5.60. The density of these pellets was varied by changing

* Slag foaming generally resulted in the expansion of the slag to such large volumes that gas exit lines were clogged, and the temperature distribution in the furnace assembly was altered drastically (cf. Appendix B).
Table 4.2

A Comparison of Experimentally Determined Normalized Gas Volumes with Predicted Gas Volumes Based on the Concentration of the Limiting Reactant

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Limiting Reactant</th>
<th>Predicted</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD-7</td>
<td>oxygen</td>
<td>41.2°</td>
<td>41</td>
</tr>
<tr>
<td>CD-8</td>
<td>oxygen</td>
<td>26.1°</td>
<td>29</td>
</tr>
<tr>
<td>CD-9A</td>
<td>carbon</td>
<td>40.1</td>
<td>40</td>
</tr>
<tr>
<td>CD-9B</td>
<td>oxygen</td>
<td>46.7°</td>
<td>47</td>
</tr>
<tr>
<td>LR-3A-1</td>
<td>carbon</td>
<td>20.2</td>
<td>19</td>
</tr>
<tr>
<td>HR1-8</td>
<td>carbon</td>
<td>1.1</td>
<td>2</td>
</tr>
</tbody>
</table>

* Excluding slag foaming conditions, see text

# Gas volumes measured from pellet heating tests in molten slag

° Assuming 5% CO$_2$ in the product gas
Figure 4.51 - Effect of pellet density on the heating rate of type CD-7 pellets in Slag B.

Figure 4.52 - Effect of pellet density on the reactivity of type CD-7 pellets heated in Slag B. Refer to key in Fig. 4.51.
Figure 4.53 - Effect of pellet density on the relative volume of gas evolved from type CD-7 pellets heated in Slag B. Refer to key in Fig. 4.51.
Figure 4.54 - Effect of pellet density on the heating rate of type CD-8 pellets in Slag B at 1400 °C.

Figure 4.55 - Effect of pellet density on the reactivity of type CD-8 pellets heated in Slag B. Refer to key in Fig. 4.54.
Figure 4.56 - Effect of pellet density on the relative volume of gas evolved from type CD-8 pellets heated in Slag B. Refer to key in Fig. 4.54.
Figure 4.57 - Effect of pellet density on the heating rate of type CD-9B pellets in Slag B.

Figure 4.58 - Effect of pellet density on the reactivity of type CD-9B pellets heated in Slag B. Refer to key in Fig. 4.57.
Figure 4.59 - Effect of pellet density on the reactive volume of gas evolved from type CD-7 pellets heated in Slag B. Refer to key in Fig. 4.57.
Figure 4.60 - Effect of pellet density on the heating rate of type CD-7 pellets in Slag A at 1400 °C, which was subject to slag foaming.
the final isostatic pressing pressure during the preparation of the pellets, as described in section 3.2.1. It was observed in all of the tests that the heating rate of a pellet increased as its apparent density increased. The effect was more pronounced for the type CD-9B pellets, which were produced from more finely screened DRI powders (−50 mesh, USS) than the type CD-7 and CD-8 pellets (−35 mesh, USS).

The change in the heating rate, that was induced by changing the apparent density of a pressed pellet, was probably brought about, indirectly, by a change in the thermal conductivity of the pellet. Increasing the final pressing pressure of the powder during pellet production not only results in an increase in the apparent density, but also results in better contact between the grains of DRI within the pellet. This ultimately leads to a higher thermal conductivity.

Changes in the apparent density of the pellets appear to have very little influence on the total volume of gas that is evolved during an immersion test (cf. Figures 4.53, 4.56, and 4.59). However, slightly higher rates of gas evolution are observed from pellets with greater apparent densities. The effect of apparent density on the gas evolution rate is, once again, more pronounced in the type CD-9B pellets. Because the observed increases in gas evolution rate appear to be closely related to the observed increases in heating rate, the increase in the gas evolution rate probably results from the increased heating rate of the higher density pellets.

The effects of apparent density on the heating rate of type CD-8 pellets in slag A, under conditions of slag foaming, are shown in Fig. 4.60. The effects on the heating rate are the same as those observed in
the absence of foaming. However, the onset of slag foam formation appears earlier in the heating process for the lower density pellet.

4.2.2.5. **Effect of Slag Type**

The effects of the type of slag used in the pellet heating experiments is demonstrated in Fig. 4.61. The figure compares the heating rates of two, type CD-7, pellets in different slags at 1400 °C. The two slags contained the same components (cf. Table 3.3), but slag A had a lower basisity \((\text{CaO}/\text{SiO}_2 = 1.0)\) than slag B \((\text{CaO}/\text{SiO}_2 = 1.5)\). The solidus and liquidus temperatures were also lower for slag A than for slag B (cf. Fig. 4.61). It is evident from Fig. 4.61 that the pellet heating test performed in slag A resulted, ultimately, in the formation of a foamy slag, while no foaming was observed in the test performed with slag B. However, slag A did not form a slag foam until almost 50 seconds after the initial immersion of the pellet into the slag, even though gas was being evolved from the pellet at a substantial rate during this period. During the initial testing period, large gas bubbles (approx. 1cm dia.) rose through the slag bath. Then, after approximately 50 seconds, smaller gas bubbles became entrapped in the slag, and slag A began expanding in volume. The slag remained in the expanded, foamy state until the evolution of gas from the pellet had ceased (after approx. 100 seconds) and then the foam collapsed back to its original dense state. In the test performed in slag B, the gas evolving from the pellet rose through the slag as large bubbles in the same manner that was observed in the initial portion of the test in slag A. However, no transition to a foamy slag condition was observed in slag B.
Figure 4.61 - Comparison of the heating rates of type CD-7 pellets in type A and type B slag baths at 1400 °C.

Figure 4.62 - Heating rate of type CD-7 and type CD-8 pellets in Slag A at 1400 °C.
A rapid rise in the heating rate is observed in the test performed in slag A (cf. Fig. 4.61) at the onset of slag foam formation, resulting in a substantially shorter heating time for the pellet used in that test. A similar rise in the heating rate is observed for both type CD-7 pellets and type CD-8 pellets when they are heated in slag A at a bath temperature of 1400 °C, as shown in Fig. 4.62. However, foaming was not always observed in slag A. Figures. 4.63 and 4.64 demonstrate that the generation of foam in slag A is avoided by lowering the bath temperature to 1350 °C. These figures also demonstrate that the observed enhancement of the heating rate is related to the occurrence of slag foaming in some manner. Slag foam generation is also observed to be affected by the properties of the pellet, as shown in Fig. 4.60. This figure demonstrates that the time at which foam formation is first observed is dependent upon the apparent density of the pellet.

A number of observations, that were made from pellet heating tests in which slag foam was formed, have led to the formulation of a mechanism that explains the occurrence of slag foam formation: the observations suggest that foaming occurs if gas is evolved from the pellet when the pellet is wetted by molten slag. Because the liquid slag cannot wet the pellet until after the frozen slag shell has completely remelted (cf. section 4.2.1), foaming would occur if gas was still being evolved from a pellet after the shell had remelted. By this mechanism, the "incubation period" that is observed in a test, before the onset of foam formation, is the time in which a frozen slag shell still exists on the pellet. Foaming occurs after the shell is melted away. The rise in
Figure 4.63 - Heating rate of a type CD-8 pellet in Slag A at 1350 °C. No foaming of slag was observed in this test.

Figure 4.64 - Heating rate of a type CD-8 pellet in Slag A at 1400 °C. Foaming of the slag was induced by increasing the bath temperature in this test.
the heating rate, that is observed after the onset of foaming, would therefore be explained by the penetration of slag into the pellet.

4.2.2.6. Effect of Preheating the Pellet

The effects of preheating a pellet prior to immersion into the slag were investigated by holding a pellet above the slag bath to allow it to heat, and then immersing it into the slag. Although this procedure did not heat the pellet uniformly, some interesting results were obtained from the tests. The effects of small amounts of preheat on a type CD-7 and a type CD-8 pellet are shown in Figures 4.65 and 4.66. The preheat causes the temperature profiles to be displaced to higher temperatures at a given time, without producing an appreciable change in the shape of the profiles early in the heating process. Later in the heating process, when the temperature in the pellet approaches the solidus temperature of the slag, the heating rate increases sharply due to the melting away of the slag shell and penetration of the slag into the pellet. The melting of the slag shell occurs more rapidly in the preheated pellets because the preheating results in the formation of a thinner shell of slag on the pellet, initially.

The effects of greater amounts of preheat on a type CD-7 pellet are demonstrated in Fig. 4.67. In this case, the preheating was sufficiently great to cause the solid slag shell to melt away before gas evolution from the pellet had ceased, resulting in foam formation. This test was one of only two tests using slag B in which slag foaming was observed. The observation, that foam formation can be induced by preheating a
Figure 4.65 - The effect of preheating on the heating rate of a type CD-7 pellet in Slag B at 1400 °C.

Figure 4.66 - Effect of pellet preheating on the heating rate of a type CD-8 pellet in Slag B at 1400 °C.
Figure 4.67 - Effect of greater preheat on the heating rate of a type CD-7 pellet in Slag B at 1400 °C, showing the onset of foam generation in the slag.
pellet, provides additional support for the proposed mechanism of slag foam formation mentioned in the previous section.

4.2.2.7. Effect of Differences in the Reactivity of Pressed Pellets

The heating rates and reactivities of the different types of pressed DRI pellets employed in this study are compared in this section, by comparing the measured center temperature profiles and the measured gas evolution rate profiles of the pellets. Results for pellets that were pressed from crushed commercial DRI (types CD-7, CD-8, CD-9A, and CD-9B), are compared in Figures 4.68 and 4.69. Results for pellets that were pressed from sponge iron powder that was produced in the laboratory (cf. section 3.2.1.3) by reacting a mixture of carbon and hematite powders (types LR-2J-1 and LR-2J-2), are compared in Figures 4.70 and 4.71.

It is generally observed from these tests, that more reactive pellets heat more slowly than less reactive pellets of comparable structure. This suggests that the improvements in convective heat transfer produced by increased agitation of the slag bath are small in comparison to the increased thermal requirements of the gas producing reactions.

Differences in the reactivities of pellets prepared from commercial DRI, and DRI produced in the laboratory are also reflected in the temperature profiles. The reactivity of the type LR-3A pellets (cf. Fig. 4.71) was, initially, very low in comparison to the reactivity of other pellets (cf. Fig. 4.69). The time delay, that is evident in the gas evolution rate profiles shown in Fig. 4.71, was unique to the type
Figure 4.68 - A comparison of the heating rates of various types of pressed pellets in Slag B at 1400 °C.

Figure 4.69 - A comparison of the reactivities of the various types of pressed pellets presented in Fig. 4.68.
Figure 4.70 - The heating rates of type LR-3A pellets in Slag B.

Figure 4.71 - Reactivities of the type LR-3A pellets in Fig. 4.70. The gas evolution rate profile shown for pellet (2) is excessively large due to foaming of the slag. Note the time delay before the onset of gas evolution.
LR-3A pellets. The delay indicates that the kinetics of the reaction of carbon and oxygen in these pellets are less favorable, and that higher temperatures are therefore necessary to promote the reaction. The effects from the thermal requirements of the reactions in the pellet are, therefore, observed at higher temperatures in the temperature profiles, as shown in Fig. 4.70.

The high concentrations of carbon and oxygen in the LR-3A-2 pellet (cf. Table 4.1) ultimately led to the evolution of a large volume of gas at a substantial rate, late in the heating process (cf. Fig. 4.71). The large rate of gas evolution resulted in the generation of a foamy slag in this test. The generation of foam in this test suggests that extremely large rates of gas evolution from a pellet increases the melting rate of the slag shell.

4.2.2.8. Effect of Reactivity and Structure

The heating rates and reactivities of a non-reactive type LR-2J pellet, that was prepared by the gaseous reduction of a hematite sphere (cf. section 3.2.1.2), and two repressed commercial DRI pellets of comparable size are compared in Figures. 4.72 and 4.73. A similar comparison with a non-reactive type LR-2D pellet is presented in Fig. 4.74. In both cases, the non-reactive pellets had a higher heating rate than reactive, pressed pellets of comparable weight. The higher heating rates of the type LR-2D and LR-2J pellets is most likely a combined influence of structure and reactivity. The microstructural examinations that were performed previously (cf. section 4.1.2), indicated that the structure of the gas-reduced pellets was highly interconnected compared
Figure 4.72 - Comparison of the heating rates of pressed commercial DRI pellets, a type LR-2J pellet in Slag B at 1400 °C.

Figure 4.73 - Reactivities of the pellets described in Fig. 4.72.
Figure 4.74 - Comparison of the heating rates of pressed typed CD-7 pellets with a type LR-2D pellet in Slag B at 1400 °C.
to the pressed pellets, which had a loosely connected structure. A more highly connected structure possesses a higher thermal conductivity, which ultimately leads to a faster heating rate. In addition, a less reactive pellet has a smaller thermal requirement, and therefore may also heat more quickly.

The effects of the presence of reactive components (carbon and oxygen) on the heating rate of a pressed DRI pellet was also investigated by comparing the heating rate of a pellet prepared from H₂ heat treated type CD-8 powder (type HR1-8) with the heating rate of a pellet prepared from untreated type CD-8 powder. The results of this comparison are summarized in Figures 4.75 and 4.76. The less reactive H₂ treated pellet was observed to heat more rapidly than the untreated pellet. Also, the removal of most of the reactive oxygen and carbon from the sample virtually eliminated the perturbations from the temperature profile, indicating that the perturbations observed in the temperature profiles result from the thermal effects of the gas producing reactions. Because the heat treatment of the type CD-8 powder may have ultimately influenced the thermal conductivity of the type HR1-8 pellet, the observed increase in the heating rate is probably the combined effect of an increased thermal conductivity and a reduced thermal requirement.

4.3. Reactivity of Uniformly Heated DRI in the Absence of Slag

The reactivities of samples of DRI that were heated uniformly from room temperature to approximately 1300 °C are reported in this section. Tests were performed with type CD-7, type CD-8, and type CD-9A samples.
Figure 4.75 - The effects of removal of reactive components from a type CD-8 pellet, by heat treatment in H₂, on the heating rate in Slag B at 1400 °C.

Figure 4.76 - Reactivity of the pellets described in Fig. 4.75.
Selected results from these tests are presented in the form of plots of evolved gas volume versus time and gas evolution rate versus time in Figures 4.77-4.82. The temperatures identified on the gas evolution rate profiles of each sample mark the boundaries of the following thermodynamic domains: (1) at 530 °C and above, wustite becomes stable, thermodynamically; wustite is metastable below this temperature; (2) at 680 °C and above, the CO/CO₂ ratio for the carbon gasification reaction (cf. Equation 2-3) becomes sufficiently large to reduce wustite to metallic iron; thus, wustite can be reduced by carbon through gaseous intermediates (CO and CO₂) above this temperature; and (3) the 727 °C temperature identifies the eutectoid temperature of the iron-carbon system.

In all three types of sample, two peaks in the rate of gas evolution were observed as the temperature of the samples was increased. This observation is consistent with observations made by Sadrnezhaad (14) in similar test (cf. Fig. 2.6). The observation suggests that more than one reaction mechanism is in operation over the range of temperature studies. The smaller peak, that is observed at lower temperatures, appears to coincide with the temperature at which the reduction of wustite and carbon can proceed via gaseous intermediates (i.e., 680 °C). The size of this peak appears to be unaffected by the composition of the sample. On the other hand, the larger peak that is observed at higher temperatures, is influenced strongly by the composition of the sample. The size of this peak increases with the concentration of the limiting reactant (carbon or oxygen, cf. Table 4.1).
Figure 4.77 - Temperature and gas volume profiles for a heated type CD-7 sample.

Figure 4.78 - Temperature and gas evolution rate for a heated type CD-7 sample.
Figure 4.79 - Temperature and gas volume profiles for a heated type CD-8 sample.

Figure 4.80 - Temperature and gas evolution rate for a heated type CD-8 sample.
Figure 4.81 - Temperature and gas volume profiles for a heated type CD-9A sample.

Figure 4.82 - Temperature and gas evolution rate for a heated type CD-9A sample.
The region between the two peaks in reaction rate appears to fall in the vicinity of the iron-carbon eutectoid temperature. The separation of the peaks was most pronounced in the type CD-8 sample, and not as pronounced in the type CD-7 and type CD-9A samples. The reactivity in the region between the two peaks, for the type CD-7 and type CD-9A samples, was higher than the reactivity of the type CD-8 sample in the same region. The reactivity in the region between the primary peaks may be related to the presence of Fe₃C in the samples. Both type CD-7 and type CD-9A powders were observed to contain Fe₃C, while no Fe₃C was observed in the type CD-8 powders.
CHAPTER 5

MODEL DEVELOPMENT

An explicit finite difference technique was developed to simulate the heating and melting of a DRI pellet immersed in a molten electric furnace slag. The finite difference model employs the properties of the DRI pellet and the slag to predict the following time dependent quantities for different conditions in the melting environment: (1) the temperature at various radial positions within the pellet and the slag shell, (2) the thickness of the slag shell, (3) the diameter of the pellet during melting, and (4) the volume of gas that is evolved from the pellet. The total melting time for the slag shell and the pellet are also predicted by the model. The finite difference equations that are used to describe the heating and melting process are presented in section 5.1. The approaches used to model the kinetics of the gas producing reactions in DRI are presented in section 5.2. Section 5.3 contains a description of the procedures employed to estimate the value of the convective heat transfer coefficient in the slag bath. Finally, the physical and thermophysical properties of the DRI pellet and the slag are estimated in section 5.4.

5.1. The Finite Difference Model

The development of a comprehensive model of the heating and melting process for DRI pellets requires an understanding of the individual events that make up the process. Results from the experimental investigations of the DRI heating process in molten slags (cf. Chapter
4) indicate that there are several stages of the DRI heating and melting process that must be considered when formulating a model. The sequence of events that describes the heating and melting process is presented in Fig. 5.1, and a description of the stages of the process follows. In the first stage of the process, a layer of slag freezes on the pellet, grows, and then melts away. During this stage, heat transfer within the pellet and the slag shell occurs by conduction. The gas evolution, which occurs due to reactions within the pellet, affects the heating process by influencing the convective heat transfer from the slag bath, and by introducing additional heat requirements within the pellet arising from the enthalpy demands of the reactions. In the second stage of the heating process, molten slag is drawn into the pores of the pellet. As the slag is drawn into the pellet, heating occurs by bulk enthalpy transport and by conduction. If gas evolution continues into this stage, the convection of heat from the slag bath may be affected by the generation of a foamy slag. The third stage of the process begins when slag penetration is complete. During this stage, heat transfer within the pellet occurs, once again, by conduction. However, the thermal properties of the pellet have now been altered by the presence of liquid slag in the pores of the pellet. The final stage of the process involves the melting of the pellet. During this stage of the process, the molten iron is assumed to be completely ablated.

In the sequence of events that is presented in Fig. 5.1, the heating and melting process has been assumed to occur entirely within the slag layer of the electric furnace. This assumption may not be true under certain conditions. Pellets that are more dense than the molten
Figure 5.1 - Steps in the heating and melting of a DRI pellet in molten slag (a) before immersion into slag. After immersion: (b) initial formation of the slag shell, (c) fully developed shell, (d) shell almost completely melted, (e) partial penetration of molten slag into pellet, (f) complete slag penetration, (g) melting of pellet, and ablation of liquid iron.
slag may sink through the slag layer to the slag-metal interface. Similarly, pellets that are less dense, initially, may densify during the initial stages of heating and melting in the slag, causing the pellets to drop to the slag-metal interface during the latter stages of heating or melting. In some cases, slag penetration may also contribute to a sufficient increase in density to cause the pellet to drop to the slag-metal interface. In other cases, the formation of a foamy slag, with a low apparent density, may result in the passage of the pellet to the interface.

In the present treatment of the heating and melting process for a pellet, the model is developed based on the assumption that the heating and melting process occurs in the slag. The model may also be applied to a pellet that passes to the slag-metal interface if it is assumed that there is a sufficient residence time for the pellet in the slag to allow the solid slag shell to form, completely, before the pellet reaches the interface. In this case, the change in the magnitude of the heat transfer coefficient must be considered when the pellet reaches the slag-metal interface. It is also assumed that the melting process at the interface is controlled by heat transfer.

In the sections that follow, the finite difference model of the heating and melting process for a single, spherical DRI pellet in molten slag will be described. The computer program that was used for the simulation is presented in Appendix F, along with a listing of variables, a description of the program, and a brief discussion of the stability requirements of the numerical technique.
5.1.1. Heat Conduction by Finite Differences

The transient conduction of heat into a sphere can be represented by equations that are developed from a heat balance on spherical shell elements of finite thickness. In this formulation, the pellet is divided into \( k \) spherical shell elements, as shown in Fig. 5.2. The size of element 1, which represents the thermocouple bead at the center of the pellet, is chosen to agree with the diameter of the bead. The remainder of the elements in the pellet are of equal thickness. Additional elements are also provided to accommodate the slag shell, which resides in elements \( k + 1 \) to \( m \). Element \( m \) contains the moving solid/liquid interface of the slag shell (or the pellet, during melting). The exact position of the interface within element \( m \) is given by \( \delta \), which is the distance from the inner wall of element \( m \) to the solid/liquid interface. During solidification and melting, the interface is free to move within the element. When the interface passes from one element to the next, the number of elements in the slag shell is increased or decreased by 1, for solidification or melting, respectively.

In the development of the finite difference equations for conductive heat transfer, each element is assumed to be isothermal. The temperature of each element is associated with a node, that is positioned at the center of each element. During a finite time, \( \Delta t \), heat flows into element \( i \) from element \( i + 1 \), and heat flows out of element \( i \) to element \( i - 1 \). Heat may also be generated or consumed within the element by reactions. The net change in the heat content of element \( i \) produces a change in the temperature of the element during the finite
Figure 5.2 - Spherical shell elements used in the finite difference model. Element 1 is the thermocouple bead, element i is an arbitrary interior element in the pellet (or slag), element k is the element at the surface of the pellet, and element m is the element that contains the moving boundary. $\delta$ is the distance from the inner wall of element m, to the surface of the slag shell.
period of time. In forward difference form, this heat balance is written,

\[ v_i \rho_i C_i \frac{T_i^* - T_i}{\Delta t} = k_{i+\frac{1}{2}} A_{i+\frac{1}{2}} \frac{T_{i+1} - T_i}{\Delta r_{i+1,i}} - k_{i-\frac{1}{2}} A_{i-\frac{1}{2}} \frac{T_i - T_{i-1}}{\Delta r_{i,i-1}} + q_i v_i \]  

(5-1)

With some rearrangement, the temperature of element \( i \) after a finite time can be written,

\[ T_i^* = T_i + M_{i}^{(i)} (T_{i+1} - T_i) - M_{i-1}^{(i)} (T_{i} - T_{i-1}) + Q_i, \]  

(5-2a)

where,

\[ M_{i}^{(i)} = \frac{k_{i+\frac{1}{2}} A_{i+\frac{1}{2}} \Delta t}{\rho_i C_i v_i \Delta r_{i+1,i}}, \]  

(5-2b)

\[ M_{i-1}^{(i)} = \frac{k_{i-\frac{1}{2}} A_{i-\frac{1}{2}} \Delta t}{\rho_i C_i v_i \Delta r_{i,i-1}}, \]  

(5-2c)

\[ Q_i = \frac{q_i \Delta t}{\rho_i C_i}, \]  

(5-2d)

and where,

- \( T_i^* \) is the temperature of element \( i \) at time \( t + \Delta t \)
- \( T_i \) is the temperature of element \( i \) at time \( t \)
- \( T_{i-1} \) is the temperature of element \( i-1 \) at time \( t \)
- \( T_{i+1} \) is the temperature of element \( i+1 \) at time \( t \)
- \( v_i \) is the volume of element \( i \)
- \( A_{i+\frac{1}{2}} \) is the outer surface area of element \( i \)
- \( A_{i-\frac{1}{2}} \) is the inner surface of element \( i \)
- \( \Delta r_{i+1,i} \) is the distance between the node in element \( i \) and the node in element \( i+1 \)
\[ \Delta r_{i,i-1} \text{ is the distance between the node in element } i \text{ and the node in element } i-1. \]

\[ \Delta t \text{ is the time step} \]

\[ k_{i+1} \] is the effective thermal conductivity evaluated at \( (T_i + T_{i+1})/2 \)

\[ k_{i-1} \] is the effective thermal conductivity evaluated at \( (T_i + T_{i-1})/2 \)

\[ \rho_i \] is the apparent density of element \( i \).

\[ C_i \] is the effective specific heat of element \( i \)

\[ q_i \] is the volumetric rate of heat generation in element \( i \).

The nodes used to calculate the temperature of element \( i \) at time step \( j+1 \) are shown in Fig. 5.3. It is to be noted that the thermal conductivities used in the calculation are evaluated at a temperature that is between the temperatures of adjacent nodes, and not at the temperature of an individual node. This ensures that a heat balance is maintained between adjacent elements.

The explicit form of equation 5-2 allows the new temperature distribution within the pellet and the slag shell to be calculated directly from the old temperature distribution, except in the vicinity of any bounding surfaces where specific boundary conditions must be satisfied. The procedures used to satisfy these boundary conditions are discussed in the sections that follow.

5.1.2. Pellet-Slag Shell Interface

The transfer of heat from the solid shell of slag to the pellet, at the pellet-slag shell interface, can occur by conduction in areas where the pellet and the slag shell are in direct thermal contact, and
Figure 5.3 - Temperature nodes used in the finite difference heat transfer calculation for an interior element in the pellet or slag shell. The temperature of element $i$ at time step $j + 1$ ($T_{i,j+1}$) is calculated from the temperature of elements $i-1$, $i$, and $i+1$ at the $j$th time step ($T_{i-1,j}$, $T_{i,j}$, and $T_{i+1,j}$).

Figure 5.4 - Placement of the temperature nodes near the interface between the slag shell and the pellet. The temperature (or temperatures) at nodal point int. are chosen so that the boundary conditions at the interface are satisfied.
by radiation in areas that are not in direct thermal contact. For both

types of heat transfer, a heat balance must be established across the

interface. Because equation 5-2 is incapable of satisfying this re-

quired condition in its present form, an extra node, with no thermal

mass,* is positioned at the interface, as shown in Fig. 5.4. This

node is used to satisfy the boundary conditions at the interface by

assigning a temperature (or temperatures) to the interfacial node that

satisfies the boundary conditions.

For the regions at the pellet-slag shell interface that are in good

thermal contact, a heat balance at the interface yields,

\[
\frac{k}{\Delta r_{\text{int},k}} \frac{T_{\text{int}} - T_k}{k} = \frac{k}{\Delta r_{\text{int},k+1}} \frac{T_{k+1} - T_{\text{int}}}{k+1}
\]

Similarly, a heat balance for the regions of the interface that are in

poor thermal contact yields,

\[
\frac{k}{\Delta r_{\text{int},k}} \frac{T_{\text{int}(-)} - T_k}{k} = \frac{k}{\Delta r_{\text{int},k+1}} \frac{T_{k+1} - T_{\text{int}(+)} = \phi \sigma (T_{\text{int}(+)} - T_{\text{int}(-)})}{\Delta r_{k+1,\text{int}}}
\]

where

\[
\phi = \frac{1}{(1/E_p^p) + (1/E_s^s) - 1}
\]

and

\( \sigma \) is the Stefan-Boltzmann constant

\( E_p \) is the emissivity of the pellet

\( E_s \) is the emissivity of the slag.

The finite difference representation of the temperature gradients

in the vicinity of the interface, for both boundary conditions, are

shown in Fig. 5.5. Note that for convective transport across the

* I.e., the node has no mass or heat capacity associated with it.
Figure 5.5 - Finite difference representation of the temperature profile at the pellet/sludge shell interface. The solid lines represent the temperature profile for radiative heat transport across the interface (i.e., no thermal contact). The dashed lines represent the temperature profile for conductive heat transport across the interface (i.e., complete thermal contact).
interface, a single temperature $T_{\text{int}}$ can be assigned to the interfacial node to satisfy condition 5-3. On the other hand, two temperatures, $T_{\text{int}(+)}$ and $T_{\text{int}(-)}$, at the interface are necessary to satisfy condition 5-4, because of the discontinuity in the temperature profile. However, because the temperatures associated with elements $k$ and $k+1$ are determined by the total change in heat content within these elements (by conduction and radiation), the temperatures at nodes $k$ and $k+1$ are single valued.* The following variables may therefore be defined (cf. Fig. 5.5),

$$\Delta T = T_{\text{int}(+)} - T_{\text{int}(-)}$$  \hspace{1cm} (5-5a)

$$\Delta T_s = T_{\text{int}(+)} - T_{\text{int}}$$  \hspace{1cm} (5-5b)

$$\Delta T_p = T_{\text{int}} - T_{\text{int}(-)}$$  \hspace{1cm} (5-5c)

Employing these variables in equations 5.3 and 5.4, the set of finite difference equations that predict the temperature of elements $k$ and $k+1$ after a finite time, $\Delta t$, may be expressed as,

$$T_{k}^{*} = T_{k} + M_{k}^{(k)} (T_{\text{int}} - \chi_{p,s} \Delta T_{p} - T_{k}) - M_{k}^{(k+1)} (T_{k} - T_{k-1}) + Q_{k}$$  \hspace{1cm} (5-6)

$$T_{k+1}^{*} = T_{k+1} + M_{k+1}^{(k+1)} (T_{k+2} - T_{k+1}) - M_{k}^{(k+1)} (T_{k+1} - T_{\text{int}} - \chi_{p,s} \Delta T_{s})$$  \hspace{1cm} (5-7)

where,

$$\Delta T_s = \frac{k_{s} \Delta r_{s} \Delta T}{k_{s} \Delta r_{s} + k_{k+1} \Delta r_{p}}$$  \hspace{1cm} (5-8)

$$\Delta T_p = \frac{k_{k+1} \Delta r_{p} \Delta T}{k_{k} \Delta r_{s} + k_{k+1} \Delta r_{p}}$$  \hspace{1cm} (5-9)

* This condition is also necessary to maintain spherical symmetry of the temperature field in the pellet.
\[ \Delta T = \frac{T_{k+1} - T_k}{1 + \left[ \frac{\Delta r_s}{k_{k+1}} + \frac{\Delta r_p}{k_k} \right] \cdot 4\pi T^3_{\text{int}}} \quad (5-10) \]

and
\[ T_{\text{int}} = \frac{k_{k+1} \Delta r_p T_{k+1} + k_k \Delta r_s T_k}{k_k \Delta r_s + k_{k+1} \Delta r_p} \quad (5-11) \]

where \( \chi_{p,s} \) denotes the fraction of the total interfacial area at the pellet-slag shell interface that is not in direct thermal contact. The variables \( M_x \), \( Q_x \), and \( Q_p \) are defined in the same manner discussed in section 5.1.1.

5.1.3. Pellet-Thermocouple Interface

The boundary conditions for the interface between the thermocouple bead and the pellet are the same as the boundary conditions for the pellet-slag shell interface (cf. section 5.1.2.). As discussed earlier, the thermocouple bead is treated as an isothermal, spherical element at the center of the pellet. The arrangement of the temperature nodes near the interface is shown in Fig. 5.6. The finite difference equations that are used to predict the temperature at elements 1 and 2, and that satisfy the boundary conditions at the interface are,

\[ T_1^* = T_1 + M_1 (T_{\text{int}} - \chi_{p,b} \Delta T_b - T_1) \quad (5-12) \]

\[ T_2^* = T_2 + M_2 (T_3 - T_2) - M_1 (T_2 - T_{\text{int}} - \chi_{p,b} \Delta T_p) + Q_2 \quad (5-13) \]

where \( M_x \), \( Q_x \), and \( \Delta T_x \) are defined in the same manner presented previously, and \( \chi_{p,b} \) is the fraction of the total interfacial area between the pellet and the thermocouple bead that is not in direct thermal contact.
Figure 5.6 - Placement of the temperature nodes near the pellet/thermocouple interface.

Figure 5.7 - Placement of the temperature nodes near the surface of the pellet when the pellet is exposed directly to the molten slag. The temperature at nodal point int. is chosen to satisfy the convective boundary condition at the surface of the pellet.
5.1.4. Heating Pellet Surface

After the solid shell of slag on the pellet melts away, heat is transferred to the surface of the pellet by convection in the slag bath. When the temperature at the surface of the pellet is below the melting temperature of the pellet, and liquid slag is not being drawn into the pellet, a heat balance at the surface of the pellet yields,

\[ k_r \frac{T_{\text{int}} - T_k}{\Delta r_{\text{int},k}} = h(T_\infty - T_{\text{int}}) \]  

(5-14)

This equation can be rearranged as follows to define the temperature of the extra node at the interface, \( T_{\text{int}} \),

\[ T_{\text{int}} = \frac{h\Delta r_{\text{int},k}T_\infty + k_r T_k}{k_k + h\Delta r_{\text{int},k}} \]  

(5-15)

where \( h \) is the heat transfer coefficient, and \( T_\infty \) is the temperature of the slag bath. The arrangement of the temperature nodes near the surface of the pellet is shown in Fig. 5.7. The finite difference equation that satisfied the boundary conditions at the surface of the pellet, and predicts the temperature of element \( k \) after a finite time \( \Delta t \) is,

\[ T_k^* = T_k + M^{(k)}_k(T_{\text{int}} - T_k) - M^{(k)}_{k-1}(T_k - T_{k-1}) + Q_k \]  

(5-16)

5.1.5. Solidifying or Melting Surfaces

The movements of the solid-liquid interface of the slag during freezing or melting, and the movement of the surface of the pellet
during melting, are described by the following heat balance at the moving boundary,

\[ h(T_\infty - T_{M,\psi}) - k_{m-\frac{1}{2}} \frac{T_{M} - T_{m-1}}{\Delta r_{\delta,m-1}} = \rho_{m} L_{\psi} \frac{R - R}{\Delta t} \]  \hspace{1cm} (5-17)

where,

- \( T_{M,\psi} \) is the melting temperature of the pellet (\( \psi = p \)) or the slag shell (\( \psi = s \))
- \( L_{\psi} \) is the latent heat of fusion of the pellet (\( \psi = p \)) or the slag shell (\( \psi = s \))
- \( R^* \) is the distance from the center of the pellet to the melting or freezing interface at time \( t + \Delta t \)
- \( R \) is the distance from the center of the pellet to the melting or freezing interface at time \( t \).

This equation, when rearranged, gives the position of the solid liquid interface after a finite time \( \Delta t \),

\[ R^* = R + N_+ (T_\infty - T_{M}) - N_- (T_{M} - T_{m-1}) \]  \hspace{1cm} (5-18a)

where

\[ N_+ = \frac{h \Delta t}{\rho_{m} L_{\psi}} \]  \hspace{1cm} (5-18b)

\[ N_- = \frac{k_{m-\frac{1}{2}} \Delta t}{\rho_{m} \Delta r_{\delta,m-1} L_{\psi}} \]  \hspace{1cm} (5-18c)

The placement of the temperature nodes near the moving boundary is shown in Fig. 5.8. The relative position of the interface within element \( m \) is given by \( \delta \), which is the distance from the inner wall of element \( m \) to the interface, at time \( t \). The distance at time \( t + \Delta t \) is given by \( \delta^* \), thus \( R^* - R = (\delta^* - \delta) \) and equation 5-18a may be written as,
Figure 5.8 - Placement of the temperature nodes near a moving boundary. $\delta^* - \delta$ indicates the distance that the interface moves (within element m) during a single time step. The temperature of the surface element is fixed at its melting temperature.

Figure 5.9 - Node placement when the interface crosses into a new element. Because an additional spatial element has been added at time step $j + 1$, the temperature of nodal point $m + 1$, at time step $j + 1$, is undefined. Note that element $m$ is always defined as the element that contains the moving boundary.
\[
\delta^* = \delta + N_+(T_\infty - T_m) - N_-(T_m - T_{m-1}),
\]

(5-19)

when the interface remains within element \(m\). If the thickness, \(\delta^*\), falls outside of the range, \(0 < \delta^* < W_m\) (where \(W_m\) is the width of element \(m\)), then the number of spatial elements is increased or decreased by 1 element.

A potential dilemma arises when the number of elements is increased (solidification). In this case, the number of elements at time step \(j+1\) exceeds the number of elements at time step \(j\), so that there is one more unknown than there are equations. This leads to an indeterminant temperature at element \(m-1\) at time step \(j+1\), as shown in Fig. 5.9. This dilemma is overcome by fitting the temperatures of elements \(m-3\), \(m-2\), and \(m\) at time step \(j+1\) to a second order polynomial in \(r\),

\[
T^* = a + br + cr^2
\]

(5-20a)

and then using this equation to estimate \(T^*_m-1\),

\[
T^*_m-1 = a + br_{m-1} + cr^2_{m-1}
\]

(5-20b)

A similar interpolation procedure was used by Kim and Pehlke. (21)

5.1.6. Penetration of Molten Slag

As discussed previously, the penetration of liquid slag into the pores of a DRI pellet results in the bulk transport of heat into the pellet during penetration, and an alteration of the thermophysical properties of the pellet after penetration. In the present treatment of slag penetration into DRI, two assumptions are employed: (1) the rate
of slag penetration into the pellet is limited by heat transfer, and (2) local thermal equilibrium is achieved between the molten slag and the solids in the pellet.

Assumption (1) is supported by experimental evidence from this study (cf. section 4.2.1.2) which indicates that slag penetration occurs very rapidly after the melting of the slag shell, when thermal gradients in the pellet are small. For larger temperature gradients in the pellet, the slag would only be expected to penetrate a short distance beyond the position of the slag solidus isotherm before freezing, and penetration would therefore be limited by heat transfer.

Assumption (2) is supported by the size and thermal conductivity of the solids within the pellet, and the size of the pores in the pellet. The small size of the metallic "grains" and the pores in the pellet (\(10\mu\) dia.), and the relatively high thermal conductivity of solids, promote a rapid exchange of heat between the molten slag and the solids in DRI.

In the numerical procedure that is used to calculate the heating rate of a pellet during slag penetration, the contributions of slag penetration and thermal conduction to the heating of a spatial element are calculated separately during the same time step. First, the change in the temperature of the element due to slag penetration is determined by performing a heat balance on the solids in the element and the molten slag that enters the element. Then, the change in the temperature of the element due to thermal conduction is determined by the procedures described previously.* The total change in the temperature of the

* The thermophysical properties of the elements that contain molten slag are altered accordingly.
element during the time period, \( \Delta t \), is the sum of the temperature changes due to slag penetration and thermal conduction.

Slag penetration into an element is allowed to occur if the slag can fill the pores in the element completely without freezing. The new temperature of the element that has just been filled with slag, \( T_{ip}^* \), is determined by a heat balance between the solids in the element at temperature \( T_{ip} \), and the slag that penetrates the pores of the element from its neighboring element at temperature \( T_{ip+1} \),

\[
T_{ip}^* = \frac{P_1 T_{ip+1} + P_2 T_{ip}}{P_1 + P_2} \tag{5-20a}
\]

where

\[
P_1 = m_{s,ip} C_s = V_{ip} e_{ip} \rho_{s} C_s \tag{5-20b}
\]

\[
P_2 = m_{p,ip} C_{p,ip} \tag{5-20c}
\]

and

- \( m_{s,ip} \) is the mass of slag entering element \( ip \)
- \( m_{p,ip} \) is the mass of solids in element \( ip \)
- \( C_s \) is the specific heat of the slag
- \( C_{p,ip} \) is the specific heat of the solids in element \( ip \)
- \( V_{ip} \) is the volume of element \( ip \)
- \( e_{ip} \) is the porosity of element \( ip \).

A similar heat balance is performed on the spatial elements in the pellet that lie outside of element, \( ip \), as shown in Fig. 5.10. In this case, the slag that already is in element \( i \) is partially displaced by slag entering from element \( i+1 \). The heat balance on element \( i \) yields,
Figure 5.10 - Details of slag penetration into an element. (a) shows the configuration of an element before the slag penetrates into element, ip, and (b) shows the contributions of the various components to the heat balance on an element after the penetration of slag into element ip.
\[ T_i^* = \frac{P_{i-1}T_{i-1} + (P_3 + P_4)T_i}{P_{i-1} + P_3 + P_4} \quad (5-21a) \]

where

\[ P_3 = m_{p,i} \cdot C \quad (5-21b) \]

\[ P_4 = m_{s,i}^{(rem)} \cdot C_s = (V_{i e_i} - V_{i p_i}) \cdot p \cdot s \cdot C_s \quad (5-21c) \]

and

\[ m_{p,i} \] is the mass of solids in element \( i \)

\[ m_{s,i}^{(rem)} \] is the mass of slag that originally filled the element that was not displaced by new slag

\[ V_{i e_i} \] is the volume of element \( i \)

\[ e_i \] is the porosity of element \( i \).

Using this procedure, molten slag enters and leaves an element by plug flow during a finite time interval. The new temperature is calculated by assuming complete mixing of the slag that remains in the element and the slag that enters the element.

5.2. Reaction Kinetic Models

The kinetics of the reaction of carbon and oxygen in DRI are modeled in this section using information from literature (cf. section 2.2), and information obtained from this study (cf. Chapter 4). The models developed in this section are evaluated in Chapter 6, using gas evolution rate data obtained from the experiments described in section 3.3. The models that best represent the reaction kinetics have been utilized in the computer simulate of the DRI pellet heating and melting process. The requirements for the model that are essential to its performance in the computer simulation are that it predict, adequately:

1. the temperature dependence of the rate of reaction,
2. the
compositional dependence of the rate of reaction, and (3) the composi-
tion of the gases evolved.

5.2.1. Selection of Possible Rate Limiting Steps

Results from previous studies of the reaction of carbon and oxygen in DRI, and of the reaction of mixtures of carbon and iron oxide during the latter stages of reduction, have provided some information about the mechanism of reaction in DRI. These works have shown that the composition of the gases evolved during reaction are high in CO, and close to the carbon gasification equilibrium composition (cf. Fig. 2.5). This indicates that the kinetics of carbon gasification are sufficiently rapid in comparison to other steps in the overall reaction process that the equilibrium for reaction 2-3 controls the composition of the gases evolved from DRI. Thus, carbon gasification can be eliminated as a possible rate controlling step.

The microstructure of DRI also provides some clues to the nature of the reaction kinetics. Examinations of the microstructure (cf. 4.2.1) have revealed that the oxygen in DRI, which is present as wustite, is isolated within individual grains that are surrounded by metallic iron. This metallic layer prevents the direct contact of carbon and wustite, and ultimately may act as a barrier for the reaction of carbon and oxygen by solid state and gaseous exchange mechanisms. The microstructural examinations also provide a basis for the formulation of a structural model of DRI. The simplified structure, that is used as a basis for the formulation of the kinetic models that follow, is shown in Fig. 5.11. In this simplified representation, individual grains of DRI are
Figure 5.11 - Idealized structure of individual grains within a DRI pellet. This structure is used as a basis for the development of several models of the kinetics of reaction of carbon and wustite in DRI.
assumed to be spherical. The spherical grains consist of a central core of wustite, and an outer shell of metallic iron. Carbon is assumed to be confined to the outer surface of the grain, where it is exposed to the macroporous region through which the gases escape. Thus, the carbon controls the composition of the gases in this region.

To develop a simple kinetic model for use in the computer simulation, it is necessary to relate the average radius of an individual grain of DRI, $R_o$, and the average radius of an individual wustite core, $R$, to the concentration of FeO in a sample of DRI. This is done by defining a modified weight fraction of FeO that is based on the initial weight of the sample, as follows,

$$X'_{FeO} = \frac{W_{FeO}}{W_{TOT,i}} = \frac{1}{z} \frac{R^3}{R_o^3} \quad (5-22a)$$

$$z = \frac{\rho_{grain,i}}{\rho_{FeO}} \quad (5-22b)$$

and

$$X'_{FeO}$$

is the modified weight fraction of FeO

$$W_{FeO}$$

is the weight of FeO in the sample (or element) at any time

$$W_{TOT,i}$$

is the initial weight of the DRI sample (or element)

$$\rho_{grain,i}$$

is the initial apparent density of a grain

$$\rho_{FeO}$$

is the density of FeO.

This form is convenient, because it allows the rate of gas evolution to be determined, readily, in terms of two time dependent variables, $X'_{FeO}$, and $X'_{CO}$. Based a molar balance for reaction 2-1,
\[
\frac{dV}{dt} = -22400 \frac{W_{TOT,i}}{M_{FeO}(2-X_{CO})} \frac{dX'_FeO}{dt} \tag{5-23}
\]

where \( \frac{dV}{dt} \) is the rate of gas evolution from the sample (or element)

and \( M_{FeO} \) is the molecular weight of FeO.

The volumetric rate of heat consumption for the reaction is therefore given by,

\[
q = \frac{W_{TOT,i} \Delta H_{Rxn}}{M_{FeO} v} \frac{dX'_FeO}{dt} \tag{5-24}
\]

where \( \Delta H_{Rxn} \) is the enthalpy for reaction 2-1 per mole of FeO consumed (cf. section 5.3.2.4),

and \( v \) is the volume of the sample (or element).

These equations are used with different forms of the kinetic expression (cf. sections 5.2.2-5.2.4)

\[
\frac{dX'_FeO}{dt} = f(X'_{FeO(t)}, T(t)) \tag{5-25}
\]

to evaluate the rate of gas evolution and the volumetric rate of heat consumption for DRI. For the reactivity experiments described in section 3.3, the expressions were applied to the entire uniformly heated sample. For the computer simulation described in this chapter, the above expressions were applied to individual isothermal elements of the pellet. In both applications, the composition of the gas evolved is assumed to be governed by the carbon gasification reaction. Thus, the
temperature dependence of $X_{CO}$ is determined by the equilibrium for reaction 2-3 (cf. section 5.3.2.4).

In the sections that follow, three rate controlling mechanisms will be proposed and formulated: (1) control by countercurrent gaseous diffusion of CO and CO$_2$ through a microporous iron product layer, (2) control by the solid state diffusion of oxygen through a dense iron product layer, and (3) control by the kinetics of the reduction of wustite at the wustite-iron interface.

5.2.2. Gas Phase Diffusion Control

The reaction of carbon and wustite may proceed through gaseous intermediates, according to reactions 2-2 and 2-3, if the layer of metallic iron that surrounds the individual grains of wustite in DRI is sufficiently porous. For the case in which equimolar counterdiffusion of CO and CO$_2$ through the porous iron product layer is the rate limiting step, the equilibrium for reaction 2-2 fixes the gas composition at $r=\bar{R}$, and the equilibrium for reaction 2-3 fixes the gas composition at $r=R_0$. If quasi-steady diffusion is assumed, the rate of movement of the Fe/FeO interface is given by,

$$
\frac{dR}{dt} = -D_{eff} \frac{\bar{\rho}_g}{R_0 \bar{\rho}_{FeO}} \left( \frac{R}{R_0} \right)^{-1} \left( \frac{R}{R_0} \right) X_{CO}^I - X_{CO}^l
$$

(5-23)

where

- $D_{eff}$ is the effective binary diffusion coefficient for CO and CO$_2$,
- $\bar{\rho}_g$ is the molar density of the gas,
- $X_{CO}^I$ is the mole fraction of CO in the gas at Fe/FeO equilibrium,
\[ X_{CO} \] is the mole fraction of CO in the gas for the carbon gasification equilibrium, and \[ X_{FeO} \] is the molar concentration of oxygen in FeO.

In terms of the modified weight fraction of FeO that was defined earlier, the equation may be written as,

\[
\frac{dX'_{FeO}}{dt} = -3D_{eff} \rho_{g} (X_{CO} - X_{CO}^{I}) \frac{z^{1/3}X_{CO}^{1/3}}{1-z^{1/3}X_{CO}^{1/3}} \]

\[ (5-24a) \]

The temperature dependence of the rate of reaction is controlled in this case by the temperature dependence of \( D_{eff}, \rho_{g}, X_{CO}, \) and \( X_{CO}^{I} \) where, \((71,72)\)

\[
D_{eff} = \frac{e_{m}}{\tau(1/D_{CO-CO_{2}} + 1/D_{k})} \]

\[ (5-24B) \]

\[
D_{CO-CO_{2}} = 1.19 \times 10^{-5} T^{1.67} \text{ [cm}^{2}/\text{s }] \]

\[ (5-24c) \]

\[
D_{k} = 1143 \bar{r}_{g} T^{1/2} \text{ [cm}^{2}/\text{s }] \]

\[ (5-24d) \]

and \( e_{m} \) is the micro-porosity of the iron product layer, \( \tau \) is the tortuosity factor for the iron product layer, \( D_{CO-CO_{2}} \) is the binary molecular diffusion coefficient, \( D_{k} \) is the Knudsen diffusion coefficient, and \( \bar{r}_{g} \) is the mean pore radius in the iron product layer.

The temperature dependence of \( \rho_{g} \) is given by

\[
\tilde{\rho}_{g} = \frac{P}{RT} \]

\[ (5-24c) \]
where $P$ is the pressure of the gas, and $R'$ is the gas constant.

The temperature dependence of $X_{CO}^I$ is given by equation 5-43 (cf. section 5.3.2.4.). The temperature dependence of $X_{CO}^I$ is given by,

\[ X_{CO}^I = \frac{1}{1 + K} \]  

(5-24d)

where 

\[ \ln K^I = \frac{2119.39 - 2.5695}{T} \]  

(5-24e)

5.1.3. Solid State Oxygen Diffusion Control

If the metallic iron layer surrounding the wustite is dense, the reaction of wustite and carbon can only proceed by the solid state diffusion of oxygen through the iron product layer. If the diffusion of oxygen is taken as the rate limiting step in the reaction process, and quasi-steady diffusion is assumed, the rate of movement of the Fe/FeO interface in a grain is given by,

\[ \frac{dR}{dt} = \frac{D_o \tilde{c}_o}{R_o^2} \left( \frac{R}{R_o} \right)^2 \left( \frac{R}{R_o} \right)^{-1} \]  

(5-25)

where $D_o$ is the diffusivity of oxygen in metallic iron, and $\tilde{c}_o$ is the molar concentration of oxygen in iron at saturation.

In terms of the modified weight fraction of FeO,

\[ \frac{dX_{FeO}'}{dt} = \frac{-3D_o \tilde{c}_o}{R_o^2} \left( \frac{R}{R_o} \right)^{2/3} \frac{z^{1/3} X_{FeO}^{1/3}}{1 - z^{1/3} X_{FeO}^{1/3}} \]  

(5-26a)
In this case, the temperature dependence of the rate of reaction is governed by the temperature dependence of $D_o$ and $\tilde{C}_o$. Kohl and Engell\(^{(46)}\) have estimated the temperature dependence of the product $\tilde{C}_oD_o$ to be,

$$D_o\tilde{C}_o = 85.7 \exp \frac{-62000}{RT} \text{ moles O} \cdot \text{cm sec}$$

(5-26b)

### 5.2.4. Interfacial Reaction Control

If the rate of reaction at the Fe/FeO interface is rate limiting, the rate of movement of the Fe/FeO interface may be written in the generalized form,

$$\frac{dR}{dt} = -\kappa \frac{\partial}{\partial \tilde{X}_{FeO}}$$

(5-27)

where $\kappa$ is the rate of reaction per unit interfacial area $\text{moles O} \cdot \text{cm}^2 \cdot \text{sec}$.

In terms of the modified weight fraction of FeO,

$$\frac{dX'_{FeO}}{dt} = -\frac{3kz}{R_o\tilde{X}_{FeO}}^{2/3} X_t^{2/3} \text{ FeO}$$

(5-28a)

The temperature dependence of the rate of reaction is governed by the temperature dependence of $\kappa$, which is assumed to follow a simple Arrhenius expression,

$$\kappa = \kappa_o \exp \frac{-Q}{RT}$$

(5-28b)

where $\kappa_o$ is the pre-exponential constant, and $Q$ is the activation energy for the interfacial reaction.
5.3. **Estimating the Convective Heat Transfer Coefficient**

In this section, the techniques that are used in the model to predict the value of the convective heat transfer coefficient for a DRI pellet in molten slag will be presented. Natural convection and forced convection are considered as the primary modes of heat transfer. In the present analysis, steady state heat transfer is assumed to be governed by either natural convection, or a constant forced convection condition, maintained by a constant rate of gas evolution in the electric furnace. The effects of transient forced convection, caused by local gas evolution from within a pellet, are also considered. Transient entry effects, from the initial plunging of the pellet into the slag bath, are neglected in accordance with calculations made by Sadrnezhaad\(^{(14)}\) which indicate that these effects are small.

5.3.1. **Natural Convection**

The heat transfer coefficient for a sphere under conditions of natural convection can be estimated from the following dimensionless correlation,\(^{(73)}\)

\[
Nu, d = 2.0 + 0.06 \frac{Gr, d^{1/4}}{Pr^{1/3}}
\]  

where,

- \(Nu, d\) is the particle Nusselt number
- \(Pr\) is the fluid Prandtl number
- \(Gr, d\) is the Grashof number
- \(\beta\) is the volumetric thermal expansion coefficient for the fluid
\( g \) is the gravitational constant

and \( T_s \) is the surface temperature of the sphere.

The natural convection is induced by a local increase in the density of the slag near the surface of the pellet. As the pellet is heated in the slag it cools the layer of liquid slag adjacent to its surface, increasing the density of the slag layer. The difference between the density of the layer of slag adjacent to the pellet and the density of the slag bath induces a flow in the slag bath that passes downward across the surface of the pellet. This flow in turn reduces the thickness of the thermal boundary layer and enhances the rate of heat transfer to the pellet.

The above correlation applies to a sphere that is suspended rigidly in a fluid under conditions in which laminar flow prevails. Laminar flow is assured if,

\[
\frac{Gr}{d^{1/4}} \frac{Pr^{1/3}}{Pr^{1/3}} < 200.
\]

For the slags and pellets employed in this study, the value of the natural convection heat transfer coefficient ranges from 0.003 cal/cm² s °C to 0.005 cal/cm² s °C.

5.3.2. Forced Convection by Bubble Agitation in the Slag Bath

Agitation of the slag in the electric furnace results from carbon boil and from gases evolved from reactive DRI pellets that reside in the slag as they are heated and melted. The evolution of gases from these sources is assumed to be constant with time, so that agitation of the slag bath depends on the total rate of gas evolution from the
furnace. The heat transfer coefficient for an individual pellet that is suspended freely in this slag is calculated based upon the constant rate of gas evolution from the furnace using the correlation proposed by Wright,

\[ \text{Nu}_d = 0.167 \left( \frac{K}{\delta} \right)^{1/4} \text{Pr}^{1/3} \]  

(5-30)

This correlation has been discussed previously in section 2.3.1. Because the correlation predicts that the heat transfer coefficient is independent of particle diameter, a computer calculation that is based on a constant value of \( h \) can be used to describe a variety of furnace conditions, using equation 5-30.

5.3.3. Forced Convection by Local Gas Evolution

The effect of local gas evolution from a pellet on heat transfer is estimated by using an equation of the form,

\[ h = BQ^{1/4} \]  

(5-31)

where \( B \) is a constant and \( Q \) is the rate of gas evolution from the pellet. The value of 1/4 for the exponent of \( Q \) is based, in part, on the values of the exponents reported by previous investigators (cf. section 2.3.1), and, in part, on observations made in experiments that indicate that moderate changes in \( Q \) have a relatively small effect on the heating rate of a pellet (cf. section 4.2.2). The value of the constant, \( B \), is estimated by fitting the model predictions to experimental results, using \( h \) as an adjustable parameter (cf. Chapter 6).
This procedure gives,

\[ h = 8.6 \times 10^{-3} Q^{1/4} \]  \hspace{1cm} (5-32)

where \( Q \) is in units of \([\text{cm}^3/\text{s STP}]\) and \( h \) is in units of \([\text{cal/cm}^2 \text{ s K}]\).

It is recognized that equation 5-32 by itself does not adequately represent the convective conditions during the transient evolution of gases from the pellet. This is evident by noting that enhanced heat transfer, that results from the non-steady evolution of gas from a pellet, persists for a period of time after the evolution of gas from the pellet has ceased. This continued enhancement of the heat transfer process is a result of the time required for the turbulence to decay, and the recirculating flows in the bath to dampen. Such flows have been found to decay exponentially with time,\(^{(74)}\) when the turbulence is homogenous and isotropic. In the present treatment, the value of the heat transfer coefficient is assumed to decay in a similar manner. Thus,

\[ h = h_{\text{max}} \exp \left( \frac{-(t_{\text{max}} - t)}{\tau_0} \right) \]  \hspace{1cm} (5-33)

where \( h_{\text{max}} \) is the value of the heat transfer coefficient when the rate of gas evolution from the pellet is at a maximum.

\( t_{\text{max}} \) is the time at which the maximum is observed,

and \( \tau_0 \) is a constant that characterizes the rate of decay of the transient heat transfer.

The value of \( h \) used in the model was evaluated by calculating the heat transfer coefficients predicted by equations 5-32 and 5-33, and using the larger of the two coefficients.
The value of $T_o$ is estimated from experimental observations of the melting rate of the slag shell in section 4.2.1. The melting rate gives an indication of the magnitude of the heat transfer coefficient during the melting period, if the temperature gradients in the pellet and the slag shell are small,

$$\rho_s L_s \frac{dR}{dt} = h(T_\infty - T_{MS}) - k_s \frac{dT}{dr}$$

Thus,

$$h = \frac{\rho_s L_s}{dR} \frac{dT}{dt}$$

This analysis indicates that the value of $h$ changes very little during the melting period, well after gas evolution has already ceased. From this observation, $T_o$ was estimated to be approximately 180 seconds.

5.4. **Estimation of the Properties of the Pellet and the Slag**

The physical and thermophysical properties of a DRI pellet and the slag are utilized in the computer simulation to predict the heating and melting rate of a pellet in a bath of molten slag. A precise knowledge of these properties is necessary to predict the heating and melting rate, reliably, since the choice of these properties influences the calculated rate of heat transfer in the system. In many cases, however, a precise knowledge of a property of the system is not available, and the property must be estimated from data that are available. The values of the properties that are used in the model, and the techniques that are used to estimate some of these properties, are presented in the sections that follow.
5.4.1. Properties of the Slags

The properties of the slags that are used in this study are summarized in Table 5.1. The densities are estimated from the density of a similar slag that is reported by Nauman. The thermal diffusivities of the liquid and solid slags employed in this study are estimated from measurements that were performed by Fine, et al. The viscosities of the slags were estimated from values for similar slags reported by Elliott, et al. The volumetric coefficient of thermal expansion for the liquid slags is estimated from the data of Lee and Gaskell.

The specific heats, and the heats of fusion, of the solid and liquid slags are estimated from the properties for the pure components using Kopp's rule,

\[ C_s = \sum X_i C_i \]  \hfill (5-35a)

\[ L_s = \sum X_i C_i \]  \hfill (5-35b)

where \( X_i \) is the weight fraction of the component.

The properties of the pure components used in this estimation are summarized in Table 5.2.

The thermal conductivity and the kinematic viscosity for the slags are calculated from the following relationships,

\[ k_s = \alpha_s \rho_s C_s \]  \hfill (5-36)

\[ \nu_s = \mu_s / \rho_s \]  \hfill (5-37)
Table 5.1

Thermal Properties of Slag *

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol, Units</th>
<th>Slag A °</th>
<th></th>
<th>Slag B °</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>( \rho_s ), g/cm³</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>( c_s ), cal/g°C</td>
<td>0.25</td>
<td>0.29</td>
<td>0.24</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>( k_s ), cal/cm s°C</td>
<td>2.9</td>
<td>3.4</td>
<td>2.8</td>
</tr>
<tr>
<td>Viscosity</td>
<td>( \mu_s ), poise</td>
<td>---</td>
<td>5.0</td>
<td>---</td>
</tr>
<tr>
<td>Volumetric Thermal Expansion Coefficient</td>
<td>( \beta ), cm³/cm³°C \times 10³</td>
<td>---</td>
<td>1.5</td>
<td>---</td>
</tr>
<tr>
<td>Kinematic Viscosity</td>
<td>( \nu_s ), cm²/s</td>
<td>---</td>
<td>1.7</td>
<td>---</td>
</tr>
<tr>
<td>Thermal Diffusivity</td>
<td>( \alpha_s ), cm²/s \times 10³</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Heat of Fusion</td>
<td>( L_s ), cal/g</td>
<td>---</td>
<td>-205.0</td>
<td>---</td>
</tr>
<tr>
<td>Solidus Temperature</td>
<td>( T_{MS} ), °C</td>
<td>1230.0</td>
<td>---</td>
<td>1287.0</td>
</tr>
<tr>
<td>Liquidus</td>
<td>( T_{ML} ), °C</td>
<td>---</td>
<td>1310.0</td>
<td>---</td>
</tr>
<tr>
<td>Prandtl Number</td>
<td>Pr, 1</td>
<td>---</td>
<td>425.0</td>
<td>---</td>
</tr>
</tbody>
</table>

* See text for appropriate references.

° Cf. Table 3.3.
Table 5.2

Specific Heats and Heats of Fusion of Slag Components

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C_i$ (77) cal/g K</th>
<th>$L_i$ (68) cal/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>0.292</td>
<td>252</td>
</tr>
<tr>
<td>CaO</td>
<td>0.229</td>
<td>339</td>
</tr>
<tr>
<td>FeO</td>
<td>0.197</td>
<td>103</td>
</tr>
<tr>
<td>MgO</td>
<td>0.303</td>
<td>459</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.278</td>
<td>43</td>
</tr>
</tbody>
</table>
The solidus and liquidus temperatures for slag A are estimated from DTA measurements performed on similar slags by Nauman.\(^{(13)}\) The solidus and liquidus temperatures for slag B are taken from measurements performed in this study, which are described in section 3.2.2.4 (cf. Figs. 3.11 and 3.12).

5.4.2. Properties of a DRI Pellet

The physical and thermophysical properties of a DRI pellet are difficult to estimate, due to the complex structure of the pellet and the thermophysical changes that occur in the pellet during heating. The techniques that are used to estimate the properties of a DRI pellet are discussed in the sections that follow.

5.4.2.1. Composition and Porosity

The initial composition of a pellet is supplied in wt. % as input to the program. The volume fraction of each component, \(Y_i\), in the pellet is determined from the formula,

\[
Y_i = X_i \left( \frac{\rho_p}{\rho_i} \right) \quad (5-38a)
\]

where \(\rho_p\) is the apparent density of the pellet, \(\rho_i\) is the density of component \(i\), and \(X_i\) is the weight fraction of component \(i\).

The porosity of the pellet is calculated from,

\[
e = 1 - \sum \limits_i Y_i \quad (5-38b)
\]
As the reaction of carbon and oxygen in the pellet proceeds, the composition, mass, and porosity of each element are altered, accordingly, to maintain a constant overall particle diameter. The consumption of FeO is governed by the reaction kinetics in section 5.2, and the consumption of carbon is calculated from a molar balance, based on reaction 2-1.

5.4.2.2. Thermal Conductivity

The effective thermal conductivity of a porous DRI pellet plays an important role in determining the heating rate of the pellet. Unfortunately, the techniques that are available to predict the effective thermal conductivity of a porous material from a knowledge of the porosity, composition, and structure are subject to considerable error. This is evident from Fig. 5-12, which shows the range of effects of porosity on the effective thermal conductivity that is calculated from upper and lower bound predictions for porous metallic iron at room temperature. The predictions from several intermediate models are also presented in Fig. 5.12. These models are summarized in Appendix G.

A limited amount of experimental data on the thermal conductivity of DRI is available from the literature. (78, 79) The results from these studies are summarized in Fig. 5.13. They indicate that the thermal conductivity of DRI ranges from about 0.003 to 0.012 cal/cm s °C below 700 °C. Above 700 °C, the thermal conductivities reported by Gudenau, et al., (78) increase with increasing temperature. This rise in thermal conductivity was attributed to sintering, which resulted in the formation of "bridges" between individual grains of DRI. Because the experimental technique required that the sample be held at the
Figure 5.12 - The effects of porosity on the effective thermal conductivity of porous iron, as predicted by various models: (1) Series conduction (upper bound); (2) Parallel conduction (lower bound); (3) Maxwell-Eucken model, (a) continuous solid phase, (b) continuous gas phase; (4) Geometric mean model; (5) Koh and Fortini model (empirical). See Appendix G for the appropriate references and model formulations.
Figure 5.13 - The thermal conductivity of DRI as determined by experimental measurements. The increase in the effective thermal conductivity of DRI at high temperatures was attributed to the sintering of the pressed samples. The thermal conductivity of solid iron is shown for comparison.
measurement temperature for a period of time before a measurement could be made, the thermal conductivities that are reported above about 700 °C are representative of highly sintered DRI.

Because of the difficulty in predicting the effective thermal conductivity of DRI, the value of this property was estimated by varying the value of the thermal conductivity to force the low temperature portions of the experimental and predicted temperature profiles into agreement (cf. section 6.2). The thermal conductivities obtained by this procedure are presented in Table 5.3. These thermal conductivities are in good agreement the thermal conductivities reported in Fig. 5.13 by Beer(79) and Gudenu, et al.(78)

For predictions of the thermal conductivity of pellets outside of the range of study, the empirical equation of Koh and Fortini(80) (cf. Appendix G) was used in the following form to represent the thermal conductivity of individual commercial pellets,

\[ \kappa_{\text{eff}} = \frac{\kappa_M (1 - e)}{(1 + 11e^2)} \]  

(5-39)

with \( \kappa_M = 0.093 \text{ cal/cm s °C} \).

The predictions of the effects of porosity on the thermal conductivity of commercial DRI from equation 5-39, and the experimental data that are available for commercial DRI pellets and pressed DRI powders are shown in Fig. 5.14.

The thermal conductivity of a pellet that was filled with liquid slag was estimated from the geometric mean formula(81) in the following form,
Table 5.3

Estimated Mean Thermal Conductivity of Pellets Used in This Study

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation Technique</th>
<th>Porosity</th>
<th>Mean Thermal Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR-2J</td>
<td>H₂ Reduced</td>
<td>0.57</td>
<td>0.009</td>
</tr>
<tr>
<td>LR-1B</td>
<td>H₂ Reduced</td>
<td>0.74</td>
<td>0.0045</td>
</tr>
<tr>
<td>HR1-8</td>
<td>Pressed</td>
<td>0.32</td>
<td>0.009</td>
</tr>
<tr>
<td>CD-8</td>
<td>Pressed</td>
<td>0.40</td>
<td>0.006</td>
</tr>
<tr>
<td>CD-7</td>
<td>Pressed</td>
<td>0.41</td>
<td>0.006</td>
</tr>
</tbody>
</table>

* Values of thermal conductivity determined by fitting theoretically predicted temperature profiles to experimentally obtained temperature profiles, using the thermal conductivity as an adjustable parameter. (Cf. Chapter 6.)
Figure 5.14 - Effect of porosity on the effective thermal conductivity of pressed DRI and DRI pellets. The dashed line represents equation 5-39.
\[ k_{\text{eff}} = k_M (1-e) k_s^e \]  \hspace{1cm} (5-40)

where \( k_M \) is defined from equation (5-39), and \( k_s \) is the thermal conductivity of the liquid slag.

It is to be noted that the contributions of radiative heat transport across the pores in the sample has been neglected in the estimation of the thermal conductivity of DRI. The magnitude of the contribution by radiation to the effective thermal conductivity of a porous solid can be estimated from the following equation for the effective thermal conductivity of a pore, including conductive and radiative terms,

\[ k_{\text{pore,eff}} = k_{\text{gas}} + k_{\text{rad}} \]  \hspace{1cm} (5-41a)

\[ k_{\text{rad}} = 3\sigma d e^{-3} \]  \hspace{1cm} (5-41b)

where

\( k_{\text{gas}} \) is the thermal conductivity of the gas in the pore,

\( k_{\text{rad}} \) is the effective radiation conductivity of the pore,

\( \sigma \) is the Stefan-Boltzmann constant,

and

\( d_e \) is the mean pore diameter

For a sample with 10\( \mu \) diameter pores that is below the solidus temperature of the slag the radiation contribution is an order of magnitude smaller that the gas conduction contribution to the overall effective thermal conductivity of a pore. The radiation effects on the overall effective thermal conductivity of the pellet have therefore been neglected in the present analysis.
5.4.2.3. Specific Heat

The effective specific heat of DRI was evaluated from the specific heats of the components found in DRI, using Kopp's rule. The specific heats of these components are reported in Table 5.4. The thermal requirements for phase transformations, and for the dissolution of iron carbide and carbon in γ-Fe, are also included in the effective specific heat of DRI by assuming that the thermal effects for these processes occur within a known temperature range, $\Delta T_{TR}$ about a transformation temperature, $T_{TR}$. The effective specific heat is expressed in the form,

$$C_{TR, \text{eff}} = \frac{\Delta H_{TR}}{(\pi^2/4)\Delta T_{TR}} \exp \left( \frac{-(T - T_{TR})^2}{(\Delta T_{TR}/4)} \right)$$  (5-42)

Using this form to represent the heat of transformation, the thermal requirement may be distributed over a narrow range of temperatures, as shown in Fig. 5.15. In this figure, the area under the $C_{TR, \text{eff}}$ vs. temperature curve is equal to the heat of transformation. The transformations and reactions that have been included in the calculation of the total effective specific heat of DRI are summarized in Table 5.5, along with the corresponding enthalpy requirements and the range of temperatures within which the thermal effects are assumed to occur.

5.4.2.4. Reaction Enthalpy

Several net reactions are possible in DRI, depending on the form of the carbon that is present and the temperature. Below the eutectoid temperature of the iron-carbon system (1000 K), the carbon
Table 5.4

Specific Heat of Components in DRI\(^{(68)}\)

<table>
<thead>
<tr>
<th>Component</th>
<th>Temp. Range, K</th>
<th>Relationship, cal/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha) Fe* (\text{including Curie Trans.})</td>
<td>280 - 800</td>
<td>(8.55 \times 10^{-2} + 5.96 \times 10^{-5}T + 4.45 \times 10^{-8}T^2)</td>
</tr>
<tr>
<td></td>
<td>800 - 1000</td>
<td>(9.78 \times 10^{-1} - 2.10 \times 10^{-3}T + 1.36 \times 10^{-6}T^2)</td>
</tr>
<tr>
<td></td>
<td>1000 - 1020</td>
<td>(-9.58 \times 10^{-1} + 1.19 \times 10^{-3}T)</td>
</tr>
<tr>
<td></td>
<td>1020 - 1042</td>
<td>(-4.4417 + 4.61 \times 10^{-3}T)</td>
</tr>
<tr>
<td></td>
<td>1042 - 1060</td>
<td>(8.3289 - 7.65 \times 10^{-3}T)</td>
</tr>
<tr>
<td></td>
<td>1060 - 1185</td>
<td>(3.6380 - 5.80 \times 10^{-3}T + 2.43 \times 10^{-6}T^2)</td>
</tr>
<tr>
<td>(\gamma) Fe</td>
<td>1000 - 1768</td>
<td>(1.02 \times 10^{-1} + 3.58 \times 10^{-5}T)</td>
</tr>
<tr>
<td>(\delta) Fe</td>
<td>1667 - 1811</td>
<td>(1.05 \times 10^{-1} + 4.29 \times 10^{-5}T)</td>
</tr>
<tr>
<td>FeO</td>
<td>298 - 1200</td>
<td>(1.69 \times 10^{-1} + 4.29 \times 10^{-5}T - 9.7 \times 10^{-1}T^{-2})</td>
</tr>
<tr>
<td>Gangue **</td>
<td>298 - 1800</td>
<td>(2.27 \times 10^{-1} + 6.13 \times 10^{-5}T - 5.74 \times 10^{-3}T^{-2})</td>
</tr>
<tr>
<td>(\text{Fe}_3)C</td>
<td>298 - 463</td>
<td>(1.09 \times 10^{-1} + 1.11 \times 10^{-4}T)</td>
</tr>
<tr>
<td></td>
<td>463 - 1500</td>
<td>(1.43 \times 10^{-1} + 1.67 \times 10^{-5}T)</td>
</tr>
<tr>
<td>C</td>
<td>298 - 1100</td>
<td>(2.17 \times 10^{-3} + 7.75 \times 10^{-4}T - 2.95 \times 10^{3}T^{-2} - 3.46 \times 10^{-7}T^2)</td>
</tr>
<tr>
<td></td>
<td>1100 - 4000</td>
<td>(4.87 \times 10^{-1} + 8.66 \times 10^{-6}T - 6.3 \times 10^{4}T^{-2})</td>
</tr>
</tbody>
</table>

* Relationships for \(\alpha\) Fe were calculated from the tabular data of reference (77) using second order polynomials.

** 90% SiO\(_2\) - 10% Al\(_2\)O\(_3\) assumed.
Figure 5.15 - Representation of a heat of transformation as an effective specific heat according to equation 5-42.
Table 5.5

Heats of Transformation and Reaction $^{(49,77,82)}$
Included in the Effective Specific Heat of DRI

<table>
<thead>
<tr>
<th>Transformation or Reaction</th>
<th>$\Delta H_{TR}$, cal/mole</th>
<th>$T_{TR}$, K</th>
<th>$\Delta T_{TR}$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha \rightarrow \gamma_{Fe}$</td>
<td>160</td>
<td>1000</td>
<td>20</td>
</tr>
<tr>
<td>$\gamma \rightarrow \delta_{Fe}$</td>
<td>200</td>
<td>1668</td>
<td>20</td>
</tr>
<tr>
<td>Fe$<em>3$C $\rightarrow$ 3Fe$</em>\gamma$ + C(.77 w/o in $\gamma_{Fe}$)</td>
<td>10,220</td>
<td>1050</td>
<td>100</td>
</tr>
<tr>
<td>C$<em>{gr}$ $\rightarrow$ C(.77 w/o in $\gamma</em>{Fe}$)</td>
<td>12,480</td>
<td>1050</td>
<td>100</td>
</tr>
</tbody>
</table>
that reacts with FeO may be present as solid carbon, or as Fe\textsubscript{3}C. Above the eutectoid temperature, the carbon that reacts with FeO may, again, be present as solid carbon, or may be present as dissolved carbon in γ Fe. Each of these net reactions has a different overall enthalpy requirement. The net reactions, and their overall enthalpy requirements are summarized in Table 5.6. The temperature dependence of the overall enthalpy requirements is assumed to arise primarily from the change in the composition of the product gas with temperature. As discussed previously (cf. section 5.2.1) the composition of the product gas is fixed by the equilibrium for the carbon gasification reaction, equation 2-3. In the present model, the equilibrium CO content of the gas is calculated from the following analytical expression for the equilibrium of reaction 2-3,\textsuperscript{(83)}

$$X_{CO} = \frac{(K^2 + 4K)^{1/2} - K}{2}$$ \hspace{1cm} (5-43a)

$$\log_{10}K = 3.2673 - 8.82069 \times 10^3 - 1.208714 \times 10^{-3}T + 1.53734 \times 10^{-7}T^2 + 2.295483\log_{10}T$$ \hspace{1cm} (5-43b)

The enthalpies of the appropriate reactions in Table 5.6, that are calculated using the equilibrium CO content of the gas calculated from equation 5-43, are included in the heating and melting model for a DRI pellet through equation 5-24 (cf. section 5.2.1).

5.4.2.5. **Melting Temperature**

The melting temperature of DRI is calculated from the final carbon content of the pellet after the completion of the reactions, based on the iron-carbon equilibrium phase diagram.
Table 5.6

Net Reactions in DRI and Their Enthalpy Requirements, (cal/mole) *

Below the Iron-Carbon Eutectoid

\[
\text{FeO(s)} + \frac{1}{2 - X_{CO}} \text{C(gr)} = \text{Fe(a)} + \frac{X_{CO}}{2 - X_{CO}} \text{CO(g)} + \frac{1 - X_{CO}}{2 - X_{CO}} \text{CO}_2(g)
\]

\[
\Delta H_{Rxn} = \frac{X_{CO}}{2 - X_{CO}} (-26,770) + \frac{1 - X_{CO}}{2 - X_{CO}} (-94,320) - (-62,940)
\]

\[
\text{FeO(s)} + \frac{1}{2 - X_{CO}} \text{Fe}_3\text{C(s)} = 1 + \frac{3}{2 - X_{CO}} \text{Fe(a)} + \frac{X_{CO}}{2 - X_{CO}} \text{CO(g)} + \frac{1 - X_{CO}}{2 - X_{CO}} \text{CO}_2(g)
\]

\[
\Delta H_{Rxn} = \frac{X_{CO}}{2 - X_{CO}} (-26,770) + \frac{1 - X_{CO}}{2 - X_{CO}} (-94,320) - \frac{1}{2 - X_{CO}} (5,200) - (-62,940)
\]

Above the Iron-Carbon Eutectoid

\[
\text{FeO(s)} + \frac{1}{2 - X_{CO}} \text{C(gr)} = \text{Fe}_\gamma + \frac{X_{CO}}{2 - X_{CO}} \text{CO(g)} + \frac{1 - X_{CO}}{2 - X_{CO}} \text{CO}_2(g)
\]

\[
\Delta H_{Rxn} = \frac{X_{CO}}{2 - X_{CO}} (-26,770) + \frac{1 - X_{CO}}{2 - X_{CO}} (-94,320) + (979) - (-62,940)
\]

\[
\text{FeO(s)} + \frac{1}{2 - X_{CO}} \text{C(77\% in } \gamma \text{Fe}) = \text{Fe}_\gamma + \frac{X_{CO}}{2 - X_{CO}} \text{CO(g)} + \frac{1 - X_{CO}}{2 - X_{CO}} \text{CO}_2(g)
\]

\[
\Delta H_{Rxn} = \frac{X_{CO}}{2 - X_{CO}} (-26,770) + \frac{1 - X_{CO}}{2 - X_{CO}} (-94,320) + (979) - \frac{1}{2 - X_{CO}} (12,480) - (-62,940)
\]

* Using heats of formation at 1000K, according to reference (77).
5.4.2.6. **Heat of Fusion**

The heat of fusion of DRI is calculated using Kopp's rule. In most cases, the calculated heat of fusion does not differ significantly from the heat of fusion for pure iron, (60 cal/g Fe) since the only components remaining in the pellet at the onset of melting in most cases are iron and gangue.
CHAPTER 6

DISCUSSION

Information obtained from the comparison of the experimental results in Chapter 4 with predictions from the models developed in Chapter 5 is discussed in this chapter. The comparisons are utilized to gain information about the heating and melting process for DRI that is not directly obtainable by experimentation or modeling along.

In section 6.1, the kinetic models, that were developed in section 5.2, are evaluated by comparing predictions from the models with the results from the experiments described in section 3.3.

In section 6.2, predictions of the heating rate of a solid iron sphere in molten slag, based on the model described in section 5.1, are compared with experimental measurements described in section 3.2. Similar comparisons are also made in sections 6.3 and 6.4 for non-reactive DRI pellets and reactive DRI pellets, respectively.

6.1. Comparison of Kinetic Model Predictions with Experiment

The kinetic models that were developed in section 5.2 to predict the rate of reaction of FeO and carbon in DRI are evaluated in this section. The models are evaluated by comparing experimental rates of gas evolution, obtained from the uniform heating tests described in section 3.3, with predicted rates of gas evolution. Predictions for a given kinetic model were made by integrating the kinetic expression numerically using the initial composition of the DRI, and the time-temperature data from an experiment.
The terms in a given kinetic model that did not depend on temperature or composition were grouped together to form a single adjustable parameter. The value of this parameter was varied to determine whether the kinetic model was capable of predicting the position and the height of the peak of gas evolution on a plot of gas evolution rate vs. time. Only the high temperature peak was modeled by this procedure, since that peak was the only one that exhibited a substantial dependence on the composition of DRI (cf. section 4.3).

To facilitate the direct comparison of the high temperature experimental and computed rates of gas evolution, the amount of FeO consumed in an experiment by low temperature reactions was calculated from the volume of gas generated during this period. This FeO was subtracted from the initial amount of FeO in the sample, and the corrected FeO content was used in the kinetic model. By this procedure, the calculated peak in the rate of gas evolution could be compared directly to the high temperature experimental peak without having to model the low temperature reactions. The region encompassing the low temperature reactions that was used to evaluate the amount of FeO consumed is identified in the sections that follow by a shaded region in the plot of gas evolution rate vs. time.

6.1.1. Gaseous Pore Diffusion Control

The kinetic model based on gaseous equimolar counterdiffusion of CO and CO$_2$ through a porous iron product layer as the rate limiting step (cf. section 5.2.2) was evaluated using equations 5-23 and 5-24.

* Carbon gasification equilibrium was assumed, cf. equation 5-43.
Two mechanisms of diffusion were investigated: gaseous molecular diffusion, and Knudsen diffusion. Molecular diffusion through the porous region predominates for large pores and low temperatures. Knudsen diffusion through the porous region predominates for small pores and high temperatures.

The rate equation for molecular diffusion was expressed in the following form,

$$\frac{dX'_{FeO}}{dt} = -K' T^{-0.67} \left( X'_{CO}(T) - X_{CO}^T(T) \right) \frac{\left(zX'_{FeO}\right)^{1/3}}{1-\left(zX'_{FeO}\right)^{1/3}}$$ (6-1a)

where $$K' = 3.57 \times 10^{-5} \frac{e \text{m}}{R^{2/3} \rho_{FeO}^{2/3} \tau R'}$$ (6-1b)

The variable, $K'$, contains parameters from the model that do not vary with temperature or composition.

Similarly, the rate expression for Knudsen diffusion was expressed in the form,

$$\frac{dX'_{FeO}}{dt} = -K' T^{-0.5} \left( X'_{CO}(T) - X_{CO}^T(T) \right) \frac{\left(zX'_{FeO}\right)^{1/3}}{1-\left(zX'_{FeO}\right)^{1/3}}$$ (6-2a)

where $$K' = 3429 \frac{\text{e \text{m}}}{R^{2/3} \rho_{FeO}^{2/3} \tau R'}$$ (6-2b)

The rates of gas evolution that are predicted by the gaseous pore diffusion models are compared to an experimental rate profile for a type CD-7 sample of DRI in Figs. 6.1 and 6.2 assuming molecular diffusion and
Figure 6.1 - A comparison of experimental and predicted rates of gas evolution, assuming pore diffusion control by molecular diffusion. The dashed lines are the predictions. The shaded region shows the low temperature rate data that were used to evaluate the amount of FeO consumed by the low temperature reactions.

Figure 6.2 - A comparison of experimental and predicted rates of gas evolution assuming gaseous pore diffusion control by Knudsen diffusion. The dashed lines are the predictions.
Knudsen diffusion, respectively. In these figures, the value of $K'$ has been varied in an attempt to force the computed peak for the rate of gas evolution to agree with the experimental peak.

The results presented in Figs. 6.1 and 6.2 indicate that the models based on gaseous pore diffusion are incapable of predicting the position of the peak in the rate of gas evolution for the type CD-7 sample. In addition, the values of $K'$ that must be used to produce theoretical rates of gas evolution that are comparable to the experimental rates are much smaller than the values of $K'$ that are estimated by evaluating equations 6-1b and 6-2b. Such values for $K'$ could only be realized if the iron product layer had an extremely low porosity ($\varepsilon_m << 0.01$) or if the pores were extremely tortuous (i.e., large $\tau$). It, therefore, seems unlikely that the rate of reaction is controlled by a mechanism involving gaseous pore diffusion.

6.1.2. Solid State Diffusion of Oxygen

The kinetic model based on the diffusion of oxygen through a dense iron product layer as the rate limiting step (cf. section 5.2.3) was evaluated using equations 5-23 and 5-26. The rate equation was expressed in the following form,

$$\frac{dX'_{FeO}}{dt} = K_o \exp \left( -\frac{62,000 \text{[cal/mole]}}{R'T} \right)$$

(6-3a)

where

$$K_o = \frac{257.1}{R^{2/3} \rho_{FeO}^{2/3}}, \text{[s}^{-1}\text{].}$$

(6-3b)
The rate of gas evolution that is predicted by the solid state oxygen diffusion model is compared to an experimental rate profile for a type CD-7 sample of DRI in Fig. 6.3. In this figure, the value of \( K \) has been varied in an attempt to obtain an agreement between the experimental and predicted peaks.

The results presented in Fig. 6.3 indicate that the solid state oxygen diffusion model is capable of predicting the position of the gas evolution rate peak. However, the model predicts a rate of gas evolution that is much larger than the rate observed in the experiment with the type CD-7 sample. The value of \( K \) that was used to position the predicted peak so that it agreed with the experimental peak is about an order of magnitude smaller than the estimates of \( K \) that are calculated from equation 6-3b. Interestingly enough, the calculation suggests that the rates of reaction observed in the experiments are smaller than the rates of reaction that could be attained if the rate was controlled by the solid state diffusion of oxygen through the iron product layer. Because dense layers of iron were observed in the present study (cf. section 4.1.2), it is likely that the carbon and FeO in the samples of DRI employed in this study react by the solid state diffusion of oxygen through the iron product layer. However, the results from this analysis suggest that the solid state diffusion of oxygen is not the rate limiting step.

6.1.3. **Interfacial Reaction Control**

The kinetic model that was developed based on the assumption that a reaction at the Fe/FeO interface controls the overall rate of
Figure 6.3 - A comparison of experimental and predicted rates of gas evolution assuming control by the solid state diffusion of oxygen in metallic iron. The dashed lines are the predictions. Type CD-7 sample.

\[
\frac{dX}{dt} = K_0 \exp\left(-\frac{2}{RT}\right) \frac{(zX)^{1/3}}{1-(zX)^{1/3}}
\]

1. \( K_0 = 10^8 \text{ s}^{-1} \)
2. \( K_0 = 10^7 \text{ s}^{-1} \)

\( Q = 62 \text{ kcal/mole} \)
reaction was evaluated using equations 5-23 and 5-28. The kinetic expression was written in the form,

$$\frac{dX'}{dt} = -K_o \exp \left( -\frac{20,000 \text{[cal/mole]}}{RT} \right) \frac{X'}{FeO}^{2/3}$$  \hspace{1cm} (6-4a)

where

$$K_o = \frac{3k\tau}{R_o \rho_{FeO}} \text{, [s}^{-1}\text{]}$$  \hspace{1cm} (6-4b)

The value of the activation energy, 20 kcal/mole, are estimated from values reported in literature, (34,37,40,88) from experimental studies that were designed to investigate the kinetics of FeO reduction by C and CO in the absence of mass transfer or diffusional effects. The activation energies reported in these studies range from 13.4 kcal/mole to 27 kcal/mole.

The rate of gas evolution that is predicted by the interface reaction model is compared to an experimental rate profile for a type CD-7 sample of DRI in Fig. 6.4. Once again, the value of $K_o$ has been varied in an attempt to obtain an agreement between the experimental and predicted peaks in the rate of evolution of gases.

The results presented in Fig. 6.4 indicate that the kinetic model based on interface reaction control provides an excellent representation of the position of the gas evolution rate peak and the rate of gas evolution. Furthermore, Fig. 6.5 demonstrates that the model is capable of predicting the position and height of the peak at different heating rates, using the same value of $K_o$. The ability of the model to represent the rate of gas evolution from a type CD-9A sample and a type
Figure 6.4 - A comparison of experimental and predicted rates of gas evolution assuming interface reaction control. Type CD-7 sample. Heating rate was approx. 200 °C/min. The dashed lines are the predictions.

Figure 6.5 - A comparison of experimental and predicted rates of gas evolution assuming interface reaction control. Type CD-7 sample. Heating rate was approx. 130 °C/min. The dashed line is the prediction.
CD-8 sample of DRI is also demonstrated in Figs. 6.6 and 6.7, respectively.

The success in applying the interface reaction model to the experimental measurements, and the observations made in section 6.1.3 which indicate that the observed experimental reaction rates are lower than the rates predicted by solid state oxygen diffusion control, suggest that the reaction of carbon and oxygen in DRI is controlled by a slow reaction at the Fe/FeO interface. The simplifications involved in the development of the structural model for DRI (cf. section 5.2.1) must be kept in mind, however. Factors such as the distribution in the size and extent of reduction of individual grains of wustite in DRI have not been considered in the model.

Because of the success of the model in predicting the reactivity of different samples of DRI, the interface reaction model was used in the computer simulation of the heating and melting process for a DRI pellet. In this application, the kinetic expression was applied to the individual isothermal elements as described in Chapter 5. The application of the kinetic model to the computer simulation is discussed further in section 6.3.

6.2. Predictions for a Solid Iron Sphere Heated in Molten Slag

The heating rate of a solid iron sphere was predicted using the computer simulation described in Chapter 5. The relatively simple and well characterized system was used to evaluate the general performance of the computer simulation, and to investigate the accuracy of some of the estimations employed in the simulation. The temperature predictions
Figure 6.6 - A comparison of experimental and predicted rates of gas evolution based on interface reaction control. Type CD-9A sample. The dashed line is the prediction.

Figure 6.7 - A comparison of experimental and predicted rates of gas evolution based on interface reaction control. Type CD-8 sample. The dashed line is the prediction.
from the model were compared to temperature measurements made at the center of a solid iron sphere (pellet SP-4) that was heated in molten slag (cf. section 4.2.2.1).

Initial comparisons of experimental measurements with predictions from the model indicated that there was a lag in the response of the thermocouple at the center of the solid iron sphere. This lag resulted from incomplete thermal contact between the thermocouple bead and the solid iron pellet. The effect of varying the fraction of the interfacial area between the thermocouple bead and the pellet that is not in direct thermal contact, $\chi_{p,b}$, on the temperature profile predicted by the model is shown in Fig. 6.8. As shown in this figure, the assumption of partial contact between the bead and the pellet improves the agreement between experimental and theoretical temperature profiles at low temperatures.

Attempts to improve the high temperature agreement between the experimental and predicted temperature profiles in Fig. 6.8 led, ultimately, to a revision in the initial estimates of the heat of fusion of the slag. The heat of fusion of the slag was estimated initially to be the same as the heat of fusion of calcium silicate $^{(68)}$ ($L_s = -130$ cal/g). The final procedure that was used to estimate the heat of fusion of the slag is summarized in section 5.3.1. The estimate employed Kopp's law, to give a higher value for the latent heat of fusion of the slag ($L_s = -220$ cal/g). The prediction that employed the Kopp's law value of the heat of fusion, and the heat transfer coefficient for natural convection calculated from equation 5-29 ($h = 0.005$ cal/cm² s °C) is shown in Fig. 6.9. The values of other variables
Figure 6.8 - A comparison of experimental and predicted temperature profiles for a solid iron sphere heated in Slag B. The effect of varying the fraction of the surface area of the thermocouple bead that does not contact the pellet, $\chi_{b}$, on the model predictions is shown. (1) indicates complete contact, and (2) indicates 0.37 percent contact.
Figure 6.9 - (a) A comparison of experimental and predicted temperature profiles for a solid iron sphere heated in Slag B, based on the properties for the slag reported in Table 5.1. The predicted slag shell thickness is also shown in (b).
that were employed in this prediction are summarized in Table 5.1. These values produced a predicted temperature profile that was in good agreement with the experimental temperature measurement. Some of the initial investigations of the effects of changing the values of $L_s$ and $h$ on the temperature profile, that lead to the prediction shown in Fig. 6.9, are shown in Figs. 6.10 and 6.11. These figures illustrate the sensitivity of the model predictions to changes in $L_s$ and $h$.

6.3. Predictions for Non-Reactive DRI Pellets

The experimental conditions for two porous, non-reactive, DRI pellets (LR-1B-1 and LR-2J-1) were reproduced using the computer simulation to allow a comparison of the experimental and predicted temperature profiles at the center of the pellets. Because the pellets were non-reactive, the heat transfer in the slag was assumed to occur by natural convection ($h = 0.005 \, \text{cal/cm}^2 \, \text{s} \, ^\circ \text{C}$).

The thermal conductivity of the pellets was evaluated by performing calculations with the model using the thermal conductivity as an adjustable parameter to fit the early portion of the experimental temperature profiles (cf. section 5.3.2.2). The thermal conductivities determined by this procedure are reported in Table 5.3, and plotted in Fig. 5.14 along with thermal conductivity data for DRI reported by other investigators. As shown in Fig. 5.14, the thermal conductivities obtained by fitting the early portion of the experimental temperature profile are in good agreement with the results of other investigators. The agreement was achieved assuming complete contact between the thermocouple bead and the pellet, which is reasonable for a porous
Figure 6.10 - A comparison of experimental and predicted temperature profiles for a solid iron sphere heated in Slag B, showing the effect of varying the heat of fusion of the slag, $L_s$, on the model prediction.
Figure 6.11 - A comparison of experimental and predicted temperature profiles for a solid iron sphere heated in Slag B, showing the effect of varying the heat transfer coefficient, $h$, on the model prediction.

TYPE SP-4

- $L_s = -130$ cal/g
- $X_{p,b} = 0.997$
- (1) $h = 0.05$ cal/cm$^2$ s C
- (2) $h = 0.02$ cal/cm$^2$ s C
- (3) $h = 0.01$ cal/cm$^2$ s C
pellet. The porous pellets have a structure that is compressed around the thermocouple bead easily using the peening procedure described in section 3.2.1.5. In contrast, it was difficult to attach a thermocouple to the solid iron sphere discussed in the previous section because the solid iron could not be compacted around the thermocouple bead.

A comparison of the experimental and the predicted temperature profiles for pellet LR-1B-1 and pellet LR-2J-1 are presented in Figs. 6.12 and 6.13, respectively. The thickness of the slag shell predicted by the model is also shown in these figures. The properties of the slag that were used in the calculations are summarized in Table 5.1 (Slag B). The physical characteristics of the pellets are reported in Table 3.2. The figures show that the model predicts the heating rate of porous non-reactive pellets quite accurately up to the solidus temperature of the slag. The agreement in Figs. 6.12 and 6.13 was achieved with only one adjustable parameter: the effective thermal conductivity of the pellet. Although the thermal conductivities were chosen to fit the experimental heating curves, the results in Fig. 5.14 indicate that the values of thermal conductivity that were chosen agree quite well with the effective thermal conductivity vs. porosity relationship of Koh and Fortini, \(^{(80)}\) and the experimental measurements of Beer. \(^{(79)}\)

In the vicinity of the solidus temperature of the slag, the experimental temperature profile in Figs. 6.12 and 6.13 rises above the solidus temperature before the model predicts that the slag shell has melted away. The slow melting rate of the slag shell that is predicted by the model is a direct consequence of the low rate of heat transfer from the slag bath under conditions of natural convection. The melting
Figure 6.12 - (a) A comparison of the experimental temperature profile with the predicted temperature profile for a porous, non-reactive DRI pellet. The predicted thickness of the slag shell is also shown in (b).
Figure 6.13 - (a) A comparison of the experimental temperature profile with the predicted temperature profile for a porous, non-reactive DRI pellet. The predicted thickness of the slag shell is also shown in (b).
rates of the shells shown in the figures agree well with the maximum allowable melting rates calculated from equation 5-34b, thereby confirming the prediction of a slow melting rate by the model.

A possible explanation for the discrepancy is that local melting of the slag shell may have occurred. Localized melting through the moderately thick shells predicted by the model could occur when the temperature gradient in the shell becomes small. Under these conditions, a local perturbation in the thickness of the shell would no longer be prevented from growing by lower temperatures in the slag shell ahead of the perturbation. Once the perturbation passed through the shell, the molten slag would be drawn into the pellet and temperature of the pellet would increase.

An observation that favors this mechanism is that the point in time, at which the experimental temperature profile deviates from the predicted profile, corresponds almost exactly to the time at which the temperature gradients in the pellet and the slag shell are predicted to become very small. At this point, the pellet and the slag shell are predicted to be at the same uniform temperature in Figs. 6.12 and 6.13.

6.4. Predictions for Reactive DRI Pellets

The experimental conditions for a number of reactive DRI pellets were reproduced using the computer simulation to aid in the interpretation of the experimental results in section 4.2.2, and to evaluate the performance of the model. In the first part of this section, different assumptions regarding the reactions in DRI are explored using the model. In the second part, predictions made from the model are compared to
independent measurements of the temperature at the surface and the center of a reactive pellet, the thickness of the slag shell on the pellet, and the volume and rate of gas evolution from the pellet. In the remaining parts of this section, the effects of pellet size, pellet preheat, slag type, and reactivity are explored using the model.

6.4.1. Mechanism of Reaction in DRI

The kinetics that are assumed to govern the reactions in DRI represent an important aspect of the heat transfer model. The time dependence of the rate of reaction controls, ultimately, how heat is consumed within the pellet. Similarly, changes in the state of components in the pellet also influence the details of the enthalpy demands in the pellet. Both points are considered in this section.

6.4.1.1. Reaction Kinetics

In section 6.1., it was demonstrated that an interface reaction model (cf. equation 6-4) adequately represented the primary high temperature reaction peak in experiments with uniformly heated samples of DRI. In this modeling process, however, the low temperature reactions were neglected. In the present treatment of the reaction kinetics, the same high temperature reaction model is used in the computer simulation. The effects of low temperature reactivity are also investigated by assuming that these reactions occur at a constant rate which is independent of the temperature and composition.* The equilibrium for

* The insensitivity of the low temperature reaction peaks to variations in the composition of DRI was demonstrated in section 4.3.
the carbon gasification reaction (cf. equation 5-43) is assumed to control the composition of the gases evolved by the high temperature and the low temperature reactions.

The predictions from the computer model for a 32g type CD-7 pellet considering (1) the high and low temperature reactions, (2) the high temperature reaction alone, and (3) no reactions in the pellet are shown in Figs. 6.14 and 6.14b. These figures show that the best agreement between the experimental and predicted temperature profiles and gas evolution rate profiles is obtained by including the low temperature reactivity. In the treatment of the low temperature reaction, the following form for the kinetic expression was used,

\[
\frac{dX_{FeO}}{dt} = K_0
\]  

(6-5)

This form imposes a constant reaction rate per unit mass of DRI at each element in the model. The values of \( K_0 \) that were used for the low temperature reaction rate ranged from 0.0012 to 0.0016 s\(^{-1}\) which, when substituted into equation 5-23, gives normalized rates of gas evolution of 11 to 15 cm\(^2\)/g min STP. In condition (1) of Fig. 6.14, both equations 6-5 and 6-4 were used to calculate the rate of reaction within an individual element in the model. In condition (2), only equation 6-4 was used. In condition (3), no reactions were assumed to occur.

The results of Fig. 6.14 demonstrate the importance of including the enthalpy requirements for the reactions in the model of the heating process for a DRI pellet. Furthermore, the calculations demonstrate
Figure 6.14a - A comparison of experimental and predicted heating rates for a type CD-7 pellet in Slag B, employing various assumptions in the reaction model.
Figure 6.14b (cont.) - A comparison of experimental and predicted gas evolution rates for a type CD-7 pellet in Slag B, employing various assumptions in the reaction model.
that the effect of the gas evolution on the heat transfer from the slag is small in comparison to the heat requirements for the reactions in isolated pellets. Therefore, the reactive pellets heat more slowly than non-reactive pellets of comparable mass, as observed in section 4.2.2.8.

6.4.1.2. Carbon Dissolution

Above the eutectoid temperature of the iron carbon system (727 °C), up to 2.1 percent carbon can dissolve in γFe. In a reacting DRI pellet, the dissolution of carbon (as C_{gr} or Fe_3C) may or may not have time to occur. If the dissolution process is sufficiently rapid, the overall reaction of carbon and FeO proceeds in two stages,

\[
C_{(gr)} \rightarrow C_{(in \gamma Fe)} \tag{6-6a}
\]

\[
C_{(in \gamma Fe)} + FeO \rightarrow Fe + CO + CO_2 \tag{6-6b}
\]

Alternatively, if carbon dissolution does not occur, the reaction proceeds as follows,

\[
C_{(gr)} + FeO \rightarrow Fe + CO + CO_2 \tag{6-7}
\]

The overall enthalpy requirement for each reaction path is the same. However, the time dependence of the heat requirements for the two reaction paths is quite different. The sequence of reactions in equation 6-6 results in a large enthalpy demand early in the heating process, when dissolution occurs, and a smaller enthalpy requirement later in the heating process as the reaction proceeds. On the other hand, the enthalpy demand for reaction 6-7 is larger, later in the heating process.
To investigate the effects of carbon dissolution on the heating rate of a DRI pellet, the conditions of an experiment with a 32g type CD-8 pellet were reproduced using the computer simulation. Two conditions were simulated. In the first condition, no carbon dissolution was assumed to occur. In the second condition, the carbon in the pellet was assumed to dissolve within a 100 °C temperature range above the eutectoid temperature. The procedure that was used to model the enthalpy requirement of the dissolution reaction is described in section 5.4.2.3. The results of the calculations are compared to the experimental measurements in Fig. 6.15.

The agreement of the experimental temperature profile with the predicted temperature profile that included carbon dissolution suggests that carbon dissolution does occur in DRI, and that the reactions in DRI proceed by the two-step sequence described by reaction 6-6. A comparison of the two predicted temperature profiles also indicates that the effect of carbon dissolution on the heating rate is only important in the range of temperatures in which the dissolution process occurs. Only a slightly higher heating rate is predicted for the case in which carbon is assumed not to dissolve.

6.4.2. Comparison of Experimental and Predicted Results

The experimental conditions for two reactive DRI pellets were reproduced using the computer simulation to predict various aspects of the heating behavior of the pellets. The results from the simulations were compared to experimental measurements of: (1) the temperature at the center of the pellet, (2) the temperature at the surface of the
Figure 6.15 - A comparison of experimental and predicted heating rates for a type CD-8 pellet in Slag B, showing the effect of carbon dissolution on the temperature profile.
pellet, (3) the thickness of the solid shell of slag on the pellet at various times after immersion, (4) the volume of gas evolved from the pellet, and (5) the rate of gas evolution from the pellet. The comparisons for a 32g type CD-7 pellet are summarized in Figs. 6.16a and 6.16b. The comparisons for a 32g type CD-8 pellet are summarized in Figs. 6.17a and 6.17b.

The calculations for the two pellets were performed by using the properties of the slag reported in Table 5.1, and the thermal conductivities reported for the pellets in Table 5.3. The composition of the pellets was taken directly from Table 4.1. The composition was used to predict the reactivity of the pellet using equations 6-4 and 6-5. Other properties of the systems were calculated as described in Chapter 5.

The predictions made using the computer simulation are in remarkably good agreement with all phases of the experimental measurements for both pellets. The agreement of the predicted temperatures at the center and the surface of the pellet with the measured temperatures at early times (when effects of thermal diffusion are most important) indicates that the thermal properties of the pellet and the solid slag shell have been estimated with sufficient precision. The predicted thickness of the slag shell is in agreement with the measured thickness of the slag shell. The predictions from the model indicate that the line of bubbles observed within the shell marks the original surface of the shell that existed before the pellet was withdrawn from the slag bath (cf. section 4.2.1.1). The rate and total volume of gas evolved from each pellet is also represented by the model with reasonable precision.
Figure 6.16a - An overall comparison of experimental measurements with model predictions for a 32g type CD-7 pellet in Slag B. (a) Temperature, (b) slag shell thickness.
Figure 6.16b (cont.) - An overall comparison of experimental measurements with model predictions for a 32g type CD-7 pellet in Slag B. Gas evolution rate and gas volume.
Figure 6.17a - An overall comparison of experimental measurements with model predictions for a 32g type CD-8 pellet in Slag B. (a) Temperature, (b) slag shell thickness.
Figure 6.17b (cont.) - An overall comparison of experimental measurements with model predictions for a 32g type CD-8 pellet in Slag B. Gas evolution rate and gas volume.
6.4.3. **Effect of the Size of the Pellet on the Predicted Results**

The computer simulation was employed to reproduce the experimental conditions for a 14.8 g type CD-8 pellet that was heated in Slag B. The calculation was performed to determine if the model was capable of predicting the heating rate and reactivity of a smaller pellet that was otherwise identical to the pellet described in Fig. 6.17. The results from the simulation are presented, along with results from the experiment, in Figs. 6.18a and 6.18b.

The experimental and predicted results for the small type CD-8 pellet are, again, in excellent agreement. The ability of the model to predict, accurately, the heating rates and reactivities of pellets of different size supports, further, the precision of the estimates employed in section 5.4 to estimate the properties of the pellet and the slag.

6.4.4. **Predicted Effects of Preheating**

The effect of the initial temperature of a pellet on the heating rate and reactivity of the pellet was investigated using the computer simulation. The conditions of an experiment with a type CD-8 pellet in Slag B were reproduced. The conditions of the experiment were such that the pellet was not preheated uniformly (cf. section 4.2.2.6). A direct comparison between the experimental and predicted results is, therefore, not possible.

The results of the model predictions for different levels of uniform preheat, and the experimental results for the non-uniformity preheated pellet are summarized in Figs. 6.19a and 6.19b. The predicted
Figure 6.18a - (a) A comparison of the experimental and predicted temperature profiles for a 14.8g type CD-8 pellet in Slag B, and (b) the thickness of the slag shell predicted by the model.
Figure 6.18b (cont.) - A comparison of the experimental and predicted gas evolution profiles for a 14.8g type CD-8 pellet in Slag B.
Figure 6.19a - Experimental results for a non-uniformly preheated pellet, and predictions of the effects of various levels of uniform preheat on the temperature profile and the thickness of the slag shell on a 32g type CD-8 pellet in Slag B.
Figure 6.19b (cont.) - Predictions of the effect of various levels of uniform preheat on the rate of gas evolution from a 32g type CD-8 pellet in Slag B.
results are in qualitative agreement with the effects of preheat indicated by the experiment. The predictions support the observations made in section 4.2.2.6 that indicate that preheating results in the formation of a thinner slag shell and a more rapid heating rate. However, the results reported in Figs. 4.65 to 4.67 indicate that a non-uniform preheat, in which the temperature at the surface of the pellet is substantially greater than the temperature at the center, causes a thinner slag shell to form than the corresponding isothermal case. This observation has practical applications in that it suggests that a pellet does not have to be preheated uniformly to a high temperature to produce a substantial improvement in the heating rate of the pellet.

6.4.5. Predicted Effects of Slag Type

The experimental conditions for a type CD-7 pellet, that was heated in Slag A, were reproduced using the computer simulation. The calculations were performed to investigate the ability of the model to predict the heating rate of a pellet in a slag which had a lower solidus temperature and which was subject to foam formation (cf. section 4.2.2.5).

The results from the experiment are compared to the predictions from the model in Figs. 6.20a. The agreement is not very good, using the solidus temperature of 1230 °C for Slag A that was estimated from data for a similar slag reported by Nauman. Better agreement is obtained if a lower solidus temperature for the slag is used. The predicted temperature profile using a solidus temperature for the slag
Figure 6.20a - (a) A comparison of experimental and predicted heating rates for a 32g type CD-7 pellet in Slag A. The thickness of the slag shell predicted by the model is also shown in (b). Slag foaming occurred during the experiment.
Figure 6.20b (cont.) - Rates of gas evolution predicted by the model for a 32g type CD-7 pellet in Slag A. Note the predicted rise in the rate of gas evolution in (1) due to slag penetration.
that is 100 °C lower than the value reported by Nauman is also shown in Fig. 6.20. The lower solidus temperature improves the agreement between the predicted and experimental temperature profiles. The use of a lower solidus temperature may be justified, because Slag A contained approximately 5 percent more FeO than the slag used in Nauman's study.

The thickness of the slag shell that forms on a pellet has been shown to have a strong dependence on the level of superheat in the slag bath. The same result is also observed in Fig. 6.20a. The predictions also show that slag penetration can have a strong influence on the heating rate of a pellet when the slag shell is melted away quickly. The rapid melting of the slag shell can also lead to the generation of a foamy slag. The prediction that employed the lower solidus temperature resulted in the melting of the slag shell and the penetration of liquid slag into the pellet before gas evolution was complete. As shown in Fig. 6.20b, the slag penetration caused an increase in the rate of gas evolution, due to the rapid rise in the temperature of the pellet that accompanies slag penetration. As discussed in section 4.2.2.5, the combination of slag penetration into the pellet, and gas evolution from the pellet can lead to foaming of the slag. The calculation based on the lower solidus temperature for the slag, therefore, predicts conditions that are favorable for the formation of a foamy slag, which is in agreement with experimental observations.

6.4.6. Predicted Effects of Reactivity

The experimental conditions for a type HR1-8 pellet in Slag B were reproduced using the computer model to aid in the interpretation of
the results presented in Figs. 4.75 and 4.76. The pellet was prepared from type CD-8 powder that was treated to remove most of the reactive carbon and oxygen from the powder (cf. section 4.2.2.8). Because the type HR1-8 powder was heat treated, the thermal conductivity of the pellet prepared from this powder was determined by fitting the low temperature portion of the experimental data, using thermal conductivity as an adjustable parameter. The value of the thermal conductivity obtained by this method is reported in Table 5.3, and compared to the thermal conductivity of other pellets in Fig. 5.14.

The results of the computer simulation for the type HR1-8 pellet are presented in Figs. 6.21a and 6.21b. The computed results are in excellent agreement with the experimental temperature profile and gas evolution rate profile. The results from this analysis, and the analysis presented in Figs. 6.17a and 6.17b for an untreated CD-8 pellet, indicate that the heat treatment of the CD-8 powder in H₂ resulted in two differences between the CD-8 pellet and the HR1-8 pellet. First, the heat treatment resulted in an increased thermal conductivity for the HR1-8 pellet, as demonstrated in Table 5.3. Such an increase is expected, because of the sintering that accompanies the prolonged high temperature exposure during heat treatment. Second, the heat demands from reactions have been reduced due to the removal of most of the reactive carbon and oxygen from the HR1-8 sample. The removal of reactive carbon and oxygen is indicated in Table 4.1, and is reflected in the reactivities reported in Fig. 6.21b.
Figure 6.21a - (a) A comparison of experimental and predicted heating rates for a 32g type HR1-8 pellet in Slag B. The predicted thickness of the slag shell is also shown in (b).
Figure 6.21b (cont.) - A comparison of experimental and predicted rates of gas evolution from a 32g type HR1-8 pellet in Slag B.
The combined effects of an increase in thermal conductivity and a decrease in reactivity resulted in a faster rate of heating for the HR1-8 pellet than for the CD-8 pellet (cf. Fig. 6.17a). The computations, therefore, support the experimental observations made in section 4.2.2.8.
PREDICTIONS FOR MELTING DRI PELLETS

In this chapter, the computer simulation is used to predict the melting rates of single DRI pellets in electric furnace slags. The calculations in this section are based on the assumption that melting occurs to completion within the slag layer. The conditions for which this assumption may not be true are discussed in section 5.1 and are identified in the sections that follow.

Calculations of the melting behavior of single, isolated, DRI pellets were performed to evaluate the effects of changes in the properties of the pellet and changes in the condition of the melting environment on the total melting time for a pellet. The following variables were investigated:

1) the steady state heat transfer coefficient,
2) the apparent density of the pellet,
3) the thermal conductivity of the pellet,
4) the reactivity of the pellet,
5) the initial temperature of the pellet, and
6) the solidus temperature of the slag.

7.1. General Features of the Model Predictions

In this section, some of the important features of the predicted melting profiles and predicted temperature profiles will be discussed. The predicted results are in agreement with the qualitative description of the stages of the melting process described in Fig. 5.1. The pellets
exhibit an initial stage of heating that is characterized by the presence of a solid shell of slag, and the evolution of gas. Upon complete remelting of the slag shell, molten slag penetrates the pores of the pellet. Finally, after a short additional period of heating, the pellet begins to melt.

The conditions that are employed in the model as a base for subsequent calculations are presented in Table 7.1. They have been chosen to be typical of the electric furnace environment. The value of the steady state heat transfer coefficient that is used for the base calculations was chosen to represent a relatively mild state of agitation in the furnace. This condition was chosen so that the effects of transient forced convection, that results from local gas evolution from the pellet, could be investigated. At higher levels of steady state agitation, the effects of local gas evolution are less pronounced.

The predictions for a 10g pellet, based on the conditions presented in Table 7.1, are summarized in Figs. 7.1 to 7.3. For these conditions, the total melting time for the pellet is 220 seconds, and the lifetime of the solid slag shell is almost 50 seconds, as shown in Fig. 7.1. The gas evolution rate profile, shown in Fig. 7.3, indicates that gas evolution from the pellet is nearly complete when the slag shell melts. Thus, a foamy slag will not be generated under the conditions outlined in Table 7.1 (cf. section 4.2.2.5).

The temperature profiles (cf. Fig. 7.2) indicate that a substantial gradient in temperature exists in the pellet and the slag shell (while it is present), until the pellet begins to melt. Shortly after melting begins, the temperature gradient in the pellet diminishes, and the
Table 7.1

Base Conditions for Calculations

**Properties of Slag:**

Same as properties for Slag B in Table 5.1

**Properties of Pellet**

(a) **Composition:** Same as composition of type CD-7 DRI in Table 4.1

(b) **Mass:** \( W_p = 10g \)

(c) **Density:** \( \rho_p = 3.0 \text{ g/cm}^3 \)

(d) **Diameter:** \( d_p = 1.854 \text{ cm} \)

(e) **Thermal Conductivity:** \( k_p = 0.010 \text{ cal/cm s °C} \)

(f) **Initial Temperature:** \( T_i = 25°C \)

**Conditions in Slag Bath**

(a) **Bath Temperature:** \( T_\infty = 1600 °C \)

(b) **Steady State Heat Transfer Coefficient:** \( h_{ss} = 0.010 \text{ cal/cm}^2 \text{ s °C} \)
Figure 7.1 - The predicted time dependent radius of a 10g pellet during heating and melting, based on the conditions reported in Table 7.1.
Figure 7.2 - The predicted time dependent temperatures at the center and the surface of a 10g pellet during heating and melting, based on the conditions reported in Table 7.1.
Figure 7.3 - The predicted rate of gas evolution from a 10g pellet during heating and melting, based on the conditions reported in Table 7.1.
melting proceeds isothermally. The isothermal melting condition is reflected in the nearly linear decrease in the radius of the pellet with time during melting. In this case, the condition given by equation 5-34 holds for the melting pellet, so that the slope of the line gives an indication of the heat transfer coefficient of the system. The slight upward concavity in the melting profile is a result of the effects of the slowly dampening forced convection that arises from the local gas evolution from the pellet (cf. 5.3.3).

The penetration of slag into the pellet is calculated to occur very rapidly once the slag shell melts away, as shown in Fig. 7.1. The slag penetration produces an increase in the heating rate in the vicinity of the solidus temperature of the slag. The jump in the temperature of the pellet is similar to the observations made in the pellet heating experiments (cf. section 6.4.5) and reflects the transport of heat into the pellet by the penetrating slag.

The general shape of the melting profile shown in Fig. 7.1 can be altered significantly by changes in the properties of the pellet and changes in the condition of the melting environment. Two examples of the kinds of changes that can occur in the melting profile are given in Figs. 7.4 and 7.5. In Fig. 7.4, the conditions for a low density pellet are modeled. In Fig. 7.5, the conditions for a pellet in a well agitated slag bath are modeled. In both cases, a downward concavity in the radius vs. time curves is apparent during melting. This indicates that thermal transport within the pellet has become important during the melting process, and that melting no longer occurs isothermally. A
Figure 7.4 - The predicted melting rate of a low density pellet $(\rho = 1.0 \text{ g/cm}^3, k = 0.0016 \text{ cal/cm s °C})$. Other properties are as reported in Table 7.1.
Figure 7.5 - The predicted melting rate of a 10g pellet in a well agitated bath ($h_s = 0.05 \text{ cal/cm}^2 \text{ s} \degree \text{C}$). Other properties are as reported in Table 7.1.
large difference in the total melting time for the pellets is also apparent.

The effects of changes in the properties of the pellet and the conditions of the melting environment on the total melting time for the pellet are discussed in the following sections. In these sections, the conditions reported in Table 7.1 are used except where noted otherwise.

7.2. Effects of Steady State Convection

The effect of steady state convective heat transfer in the slag on the total melting time of a 10g pellet is presented in Fig. 7.6. Included also is the time required to melt the solid slag shell, and the time at which the pellet begins to melt. The steady state rate of convective heat transfer to the pellet is characterized by a heat transfer coefficient, \( h_{ss} \). The value of this steady state convective heat transfer coefficient depends on the properties of the slag and the level of agitation in the slag bath. The agitation in the slag may arise from a steady carbon boil in the furnace, or from the cumulative effects of gas evolution from other pellets in the system that are being fed into the furnace at a constant rate, as discussed previously in section 5.3.2.

The melting time of the pellet and the slag shell is a strong function of \( h_{ss} \) at low levels of agitation. The dependence becomes less pronounced at high levels of agitation. The calculated results in Fig. 7.6 indicate that modest levels of bath agitation can result in a dramatic reduction in the total melting time for an individual pellet. The small improvements in the melting rate at high levels of bath
Figure 7.6 - The predicted effect of the amount of steady state agitation in the slag on the melting time of a 10g pellet. Other properties are as reported in Table 7.1.
agitation do not justify operating a furnace at extreme levels of agitation, however.

7.3. Effects of Apparent Density of the Pellet

The calculated effects of the apparent density of a 10g pellet on the total melting time for the pellet, and the melting time for the slag shell, are shown in Fig. 7.7. In this calculation, the thermal conductivity of the pellet is varied with the apparent density of the pellet, in accordance with equation 5-39.

The minimum in the total melting time results from two limiting conditions in the heat transfer process. At low apparent densities, when the thermal conductivity of the pellet is low, the resistance to heat flow within the pellet is large compared to the resistance to heat flow by convective transport at the surface of the pellet. As the apparent density of the pellet is decreased, the flow of heat within the pellet begins to dominate the heating process, resulting in a thinner slag shell on the pellet, and an increased melting time for the pellet. At high apparent densities, when the thermal conductivity of the pellet is high, the resistance to heat flow by convection at the surface of the pellet is large compared to the resistance to heat flow within the pellet. The pellet, therefore, approaches the conditions for Newtonian heating. Under these conditions, a larger surface area for a given pellet mass results in a faster heating rate. The result is an increase in melting time with increasing apparent density.

Because the minimum in the melting time of a pellet with apparent density results from a transition from limitations by the conduction of
Figure 7.7 - The predicted effect of the density of a 10g pellet on the melting time. The change in thermal conductivity of the pellet with porosity is included in the calculation. The dashed lines indicate conditions for which the present calculations may not apply due to the probable passage of the pellet to the slag-metal interface. Other properties are as reported in Table 7.1.
heat inside the pellet to limitations by convective heat transport at the surface of the pellet, the minimum in the melting time will depend on the magnitude of convective heat transfer in the system. Thus, if \( h \) is increased, the minimum in the melting time with apparent density shown in Fig. 7.7 would be shifted to shorter melting times and to higher apparent densities.

7.4. Effects of the Thermal Conductivity of the Pellet

The predicted effects of the thermal conductivity of a 10g pellet on the total melting time for the pellet, the time for the onset of melting, and the melting time for the slag shell are shown in Fig. 7.8. The figure demonstrates that the thermal conductivity of the pellet has a relatively minor effect on the total melting time of the pellet, except at very low values of thermal conductivity. The relatively minor dependence of the melting time on the apparent density of the pellet is in agreement with observations made in section 7.1 that indicate the melting process for the pellet proceeds isothermally under the conditions given in Table 7.1. Under isothermal conditions, the melting rate of the pellet is independent of the thermal conductivity of the pellet. The slight dependence of the total melting time of the pellet on thermal conductivity arises from the dependence of the initial stages of heating of the pellet on the thermal conductivity. During this stage of the process a slag shell is present on the pellet and thermal gradients in the pellet and the slag shell are large (cf. Fig. 7.2).

At low levels of thermal conductivity the influence of the thermal conductivity of the pellet on the total melting time for the pellet
Figure 7.8 - The predicted effect of the thermal conductivity of a 10g, 3.0 g/cm³ pellet on the melting time of the pellet. Other properties are as reported in Table 7.1.
becomes more pronounced, leading to a large increase in melting time at low thermal conductivities. The melting time for the slag shell is also reduced, because of a reduction in the thickness of the slag shell that forms on the pellet, as the thermal conductivity of the pellet is reduced. In the present calculations, the effects of thermal conductivity are realized only at low values of thermal conductivity. However, as convective transport to the pellet is increased (i.e., increase $h_{ss}$) the effect of the thermal conductivity on the total melting time for the pellet will become increasingly important. In Fig. 7.8, an increase in $h_{ss}$ will result in a shift of the total melting curve to shorter times and to the right to higher values of thermal conductivity.

7.5. Effects of the Solidus Temperature of the Slag

The predicted effects of the solidus temperature of the slag on the total melting time of the pellet, the time for the onset of melting, and the melting time for the slag shell are shown in Fig. 7.9. The effects are relatively minor, except as the solidus temperature approaches the temperature of the slag bath. As the value of $(T_{\infty} - T_{MS})$ becomes small, the melting time of the pellet increases and the melting time for the slag shell increases.

As the solidus temperature of the pellet is increased, Fig. 7.9 also demonstrates that the time for the onset of melting of the pellet and the time for complete melting of the slag shell approach a common value. The curves would intersect when the solidus temperature of the slag equals the melting temperature of the pellet. If the solidus temperature of the slag is increased beyond the melting point of the pellet, the pellet would begin to melt before the slag shell had melted.
Figure 7.9 - The predicted effect of the solidus temperature of the slag on the melting time for a 10g pellet. Other properties are as reported in Table 7.1.
completely. Such conditions could only occur if a slag with an extremely high solidus temperature was used, or if the pellet contained a large amount of excess carbon. Such conditions have been excluded from the present analysis.

7.6. Effects of the Reactivity of the Pellet

The predicted effects of the reactivity of a DRI pellet on the total melting time of the pellet were investigated by increasing the amount of reactive FeO in the pellet while maintaining a balanced level of carbon in the pellet. The results are presented in Fig. 7.10. At the present level of steady state bath agitation employed in these calculations ($h_{ss} = 0.01 \text{ cal/cm}^2 \text{ s } ^\circ\text{C}$) the increase in reactivity produces a moderate decrease in the melting time of the pellet. This decrease in the melting time is brought about from the slowly decaying transient convection that is produced by local gas evolution from the pellet. The results presented here are somewhat speculative because of the estimates employed in equation 5-33. The decrease in the melting time results primarily from the decay of the transient forced convection from gas evolution from the pellet. Therefore, the value of the decay constant, $\tau_o$, has a strong influence on the predicted results.

As discussed previously in section 1.3, a tradeoff exists between the beneficial effects of gas evolution from the pellet, and the enthalpy demands for the reactions in the pellet. The effects on the total melting time for the slag shell are apparent in Fig. 7.10. As

---

*Because gas evolution occurs during the time that the slag shell is present on the pellet, equation 5-32 dominates during the formation and remelting of the slag shell, and the effects of $\tau_o$ in equation 5-33 are relatively unimportant during this period.*
seen in the figure, there is a slight minimum in the melting time of the slag shell. The minimum reflects the beneficial effects of gas evolution due to enhanced convection. As the reactivity of the pellet increases, however, the enthalpy demands begin to outweigh the effects of the forced convection due to gas evolution, and the heat demands result, ultimately, in the formation of a thicker slag shell.

At higher levels of steady state agitation in the bath, the results presented in Fig. 7.10 will be altered, because the steady state convection will dominate the convective heat transfer to the pellet. In this case, the effects of local gas evolution from the pellet on the convective heat transfer process will be relatively minor. Because local gas evolution from the pellet no longer produces a beneficial effect on heat transfer at high levels of steady state agitation in the bath, the effects of FeO content on the melting time will be opposite the effects shown in Fig. 7.10. In this case, the melting time for the pellet will increase with increasing FeO content, because of the increased thermal requirement for the reactions.

The effects of transient gas evolution from a single pellet, and the effects steady state agitation the slag bath have been treated separately up to this point. The local evolution of gas from a number of pellets that are fed continuously into the furnace may control, ultimately, the level steady state agitation in the system. Interestingly enough, it is the total volume of gas that is evolved from a single DRI pellet, and the feed rate of the pellets into the furnace
Figure 7.10 - The predicted effect of increasing the FeO content of the pellet, with a corresponding increase in carbon content, on the melting time of a 10g pellet. Other properties are as reported in Table 7.1.
that controls the level of steady state agitation in the system, and that controls, ultimately, the relative importance of local gas evolution from a single pellet on its melting rate.

7.7. **Effects of Preheating the Pellet**

The predicted effects of preheating the pellet on the total melting time of the pellet, the time for the onset of melting, and the time required to melt the slag shell are presented in Fig. 7.11. The predictions indicate that preheating has a relatively minor effect on the total melting time for the pellet. A small reduction in the melting time with increasing pellet temperature is observed. A corresponding reduction in the melting time of the slag shell is also observed.

The relatively small effect of preheat on the total melting time for the pellet reflects the fact that the melting step accounts for the largest portion of the total time requirement for the heating and melting of a pellet. In contrast, the pellet heating experiments in section 6.4.4 indicated that pellet preheat had a strong influence on the heating rate of a pellet in the absence of melting.

7.8. **Summary for Melting Predictions**

The results that are presented in this chapter indicate that the level of steady state convection in the furnace is the most influential of the variables investigated on the melting time for a single DRI pellet in an electric furnace slag. In contrast, local gas evolution from a single pellet has only a minor influence on the melting time. It is the cumulative effects of the gas evolution from a large number of pellets in the slag that contributes to substantial changes in the level
Figure 7.11 - The predicted effect of preheating the pellet on the melting time of a 10g pellet. Other properties are as reported in Table 7.1.
of steady state agitation in the furnace, and this effect is controlled
primarily by the total volume of gas that is evolved from a pellet and
the feed rate of the pellets into the furnace.

The apparent density of the pellet has also been shown to have a
strong influence on the total melting time of a pellet. The minimum
melting time, however, depends on the magnitude of convective heat
transfer in the system. This minimum moves to higher values of apparent
density as the convection in the system is increased. At high densi-
ties, the pellet may fall to the slag metal-interface, where melting may
proceed very rapidly.

The thermal conductivity of the pellet has been shown to have only
a minor effect on the total melting time. However, this variable also
becomes more important when convection in the slag bath is increased.

The preheat temperature of the pellet, has only a modest effect on
the total melting time. It is necessary to preheat to high temperatures
to reduce the total melting time substantially.

The solidus temperature of the slag only becomes important when the
solidus temperature approaches the temperature of the bath. Its effect
on melting time is otherwise very small.
CHAPTER 8

SUMMARY AND CONCLUSIONS

Experiments were conducted to study the heating rate of spherical DRI pellets in electric furnace steelmaking slags. Pellets were produced from commercial DRI, DRI produced in the laboratory, and solid iron to investigate the effects of the structure and composition of the pellet on the heating rate. The tests were performed with single pellets by plunging the pellet into a bath of molten slag and measuring the temperature inside the pellet and the volume of gas that evolved from the pellet continuously as the pellet was held in the slag. Additional tests were performed by plunging a pellet into the slag and then removing it after a specified time of immersion. This procedure was used to investigate the structure of the solid slag shell that formed on the pellet, and to investigate the structural changes that occurred within the pellet as it was heated in the slag.

Several important observations were made in the pellet heating experiments. Measurements of the volume of gas that evolved from a pellet being heated in the slag indicated that the reaction of carbon and FeO in DRI proceeds to completion. Microstructural examinations of pellets heated in the slag indicated that molten slag permeates the pore structure of the pellet after solid shell of slag melts away. The effects of slag penetration were also observed in the temperature measurements. A sharp rise in the heating rate was observed in conjunction with the penetration of slag.
Additional experiments were also performed to determine the composition of DRI powders employed in the heating experiments. The reactivity of some of these powders was also investigated by heating a sample of powder in a sealed container, in the absence of slag, and measuring the volume of gas that evolved from the sample as it was heated uniformly.

The kinetics of the reaction of carbon and FeO in DRI were described by a simple structural model for the distribution of these two constituents in DRI. Several rate limiting steps for the reaction were evaluated and compared with experimental measurements of the reactivity of DRI. A model based on kinetic control at the Fe/FeO interface gave the best overall agreement with the experiments.

A computer model was developed to describe the heating and melting process for a DRI pellet in molten slag. The governing equations of heat and mass transfer were represented in finite difference form and an explicit numerical scheme was employed to perform the appropriate calculations. The effects of temperature dependent thermophysical properties, heats of transformation, and heats of reaction were included in the model. The heat of reaction of carbon and FeO in the pellet was evaluated by using the reaction kinetics that were developed previously. In accordance with experimental observations, the effects of slag penetration into the pellet were also included in the model.

The computer model was used to simulate the pellet heating experiments in molten slags. The model is capable of predicting the internal temperature and the surface temperature of the pellet, the thickness of the slag shell on the pellet, the volume of gas evolved from the pellet,
and the rate of gas evolution from the pellet. The predictions from the model were compared to experimental measurements of the same variables. Excellent agreement was obtained in most cases.

The melting behavior of individual DRI pellets in molten slag at steelmaking temperatures was predicted for different conditions in the pellet and the melting environment using the computer model. The level of steady state agitation in the slag had the strongest effect on the total melting time for a pellet. The total melting time was also influenced strongly by the density of the pellet. The importance of other variable depended on the specific conditions in the melting environment.
APPENDIX A

Procedure for Calculating the Composition of DRI

The composition of a sample of DRI powder was determined from the oxidation-reduction procedure described in section 3.1 using the following calculations,

\[
\text{wt. % carbon, } \%C = 100 \frac{12}{44} \frac{\Delta W_{\text{CO}_2} - B_{\text{CO}_2}}{W_i'}
\]  

\[
\text{wt. % total iron, } \%\text{total iron} = \frac{(2)(55.85)}{(3)(16)} \frac{W_\text{m} - W_f}{W_i'}
\]  

\[
\text{wt. % oxygen, } \%O = 100 \frac{W_i' - W_f}{W_i'} - \%C
\]  

\[
\text{wt. % FeO, } \%\text{FeO} = \frac{71.85}{16} \%O
\]  

\[
\text{wt. % Fe as FeO, } \%\text{Fe}_0 = \frac{55.85}{16} \%O
\]  

\[
\% \text{metallization, } \%\text{Met} = 100 \frac{\%\text{Fe}_T - \%\text{Fe}_0}{\%\text{Fe}_T}
\]  

\[
\% \text{gangue, } \%G = 100 - \%\text{Fe}_T - \%O - \%C
\]  

where \( W_i' = W_i - (\Delta W_{\text{H}_2\text{O}} - B_{\text{H}_2\text{O}}) \)  

is the dry sample weight. The raw data for a typical run (run CD-7) is presented in Table A.1, along with a definition of terms. It is to be noted that the only blanks that were employed in the calculations (A-1) through (A-8) were for the \text{H}_2\text{O} collection bulb and the \text{CO}_2 collection bulb.
**Table A.1.**

Typical Raw Data for the analysis of DRI - Run CD-7

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Sample Wt., $W_i$</td>
<td>4.5456g</td>
</tr>
<tr>
<td>Oxidized Sample Wt., $W_m$</td>
<td>6.0140g</td>
</tr>
<tr>
<td>Reduced Sample Wt., $W_f$</td>
<td>4.2973g</td>
</tr>
<tr>
<td>Wt. gain of CO$<em>2$ collection bulb during oxidation, $\Delta W</em>{CO_2}$</td>
<td>0.3980g</td>
</tr>
<tr>
<td>Wt. gain of H$<em>2$O collection bulb during oxidation, $\Delta W</em>{H_2O}$</td>
<td>+0.0451g</td>
</tr>
<tr>
<td>Wt. gain of Blank collection bulb during oxidation, $\Delta W_b$</td>
<td>-0.0003g</td>
</tr>
<tr>
<td>Wt. change of silica boat in blank oxidation run, $B_{1,2}$</td>
<td>0.00000g</td>
</tr>
<tr>
<td>Wt. change of silica boat in blank reduction run, $B_{2,3}$</td>
<td>-0.0002g</td>
</tr>
<tr>
<td>Wt. gain of CO$<em>2$ collection bulb in blank oxidation run, $B</em>{CO_2}$</td>
<td>+0.0024g</td>
</tr>
<tr>
<td>Wt. gain of H$<em>2$O collection bulb in blank oxidation run, $B</em>{H_2O}$</td>
<td>+0.0303g</td>
</tr>
<tr>
<td>Wt. gain of blank collection bulb in blank oxidation run, $B_b$</td>
<td>-0.0011g</td>
</tr>
</tbody>
</table>
APPENDIX B
Purity of Materials

The purity of the materials used in the preparation of synthetic electric furnace slags, as reported by the manufacturers are,

Silica, SiO₂ City Chemical Corp.
acid washed

Hematite, Fe₂O₃ Baker Chemical Co.
reagent grade, 98% min.

Calcium Oxide, CaO Baker Chemical Co.
purified, 5% max. loss on ignition

Aluminum Oxide, Al₂O₃ Norton Co.
Alundum 38, fused, 99.3% Al₂O₃ typ.
0.05% SiO₂, 0.15% Fe₂O₃, 0.02% TiO₂,
0.50% Na₂O typ.

Magnesium Oxide, MgO Norton Co.
Magnorite, fused, 98.2% MgO typ.
0.90% CaO, 0.45% SiO₂, 0.20% Fe₂O₃,
0.25% Al₂O₃ typ.

electrolytic, 99.0% min.

The purity of the iron used in the preparation of the spherical pellet (cf. section 4.2.2.1.) is reported as,

Ferrovac E, Fe Crucible Steel Corp.
0.005% C, 0.001% Mn, 0.003% P, 0.005 S,
0.006% Si, 0.007% Ni, 0.007% Cr, 0.004% V,
0.01% W, 0.005% Mo, 0.002% Cu, 0.002% Co,
0.001% Al, 0.004% Sn, 0.0078% O
APPENDIX C

Procedure for Calculating STP Gas Volumes and Gas Evolution Rates from Raw Gas Volume Data

The raw gas volume data from an experiment (cf. section 3.2) is recorded, discretely, at time intervals of 1 second, and for a total time of 300 seconds. The volume drift for an experiment, \( \dot{V}_{\text{drift}} \), is obtained from a least squares analysis\(^{69} \) of the last 100 seconds of the raw gas volume data, \( V_{T,j} \),

\[
\dot{V}_{\text{drift}} = \frac{100 \sum_{n=100}^{n} V_{T,j} t_j - \sum_{n=100}^{n} V_{T,j} \sum_{n=100}^{n} t_j}{100 \sum_{n=100}^{n} t_j^2 - \left( \sum_{n=100}^{n} t_j \right)^2} \tag{C-1}
\]

The corrected, STP gas volume, \( V_{\text{STP},j} \), is then calculated for each data point,

\[
V_{\text{STP},j} = \frac{273}{273 + T_s} \left( V_{T,s,j} - \dot{V}_{\text{drift},j} \right) \tag{C-2}
\]

The rate of gas evolution is calculated from the corrected STP gas volume data by performing a least squares analysis on a small group of data points about data point \( j \),

\[
\left( \frac{dV_{\text{STP}}}{dt} \right)_j = \frac{(2R+1) \sum_{j-R}^{j+R} V_{\text{STP},j} t_j - \sum_{j-R}^{j+R} V_{\text{STP},j} \sum_{j-R}^{j+R} t_j}{(2R+1) \sum_{j-R}^{j+R} t_j^2 - \left( \sum_{j-R}^{j+R} t_j \right)^2} \tag{C-3}
\]
Using this procedure, the slope at point \( j \) was determined from a straight line fitted through \( 2R+1 \) data points. For the calculated gas evolution rates that are presented in this study, a value of \( R=3 \) was used. Thus, the slope at each point, \( j \), was determined from the data points within a 7 second interval about point \( j \).
APPENDIX D

Estimate of the Thickness of the Retained Slag Layer

The thickness of the retained layer of slag on a pellet, as it is withdrawn from the slag bath, is estimated from a simplified calculation of the thickness of the layer of fluid that is retained on a flat plate as it is withdrawn from a liquid. Assuming laminar flow conditions, the thickness of the retained fluid layer is given by,

\[ s = \left( \frac{u_L U_0}{\rho_L g} \right)^{\frac{1}{2}} \]  

where \( s \) is the thickness of the retained fluid layer, \( u_L \) is the viscosity of the fluid, \( \rho_L \) is the density of the fluid, \( g \) is the gravitational constant, and \( U_0 \) is the withdrawal velocity.

Using the properties of slag B from Table 5.1, and estimating the withdrawal velocity to be approximately 10 cm/s, the retained thickness calculated using equation D-1 is about 1.3 mm, which is in qualitative agreement with the experimental observations in section 4.2.1.
APPENDIX E

Estimation of the Wetability of Iron by Molten Slag

The ability of a liquid slag to wet solid iron may be determined by evaluating the spreading coefficient, $S$, defined as,

\[ S = \gamma_{Fe/g} - \gamma_{S/g} - \gamma_{S/Fe} \]  

(E-1)

where $\gamma_{Fe/g}$ is the surface energy of solid Fe

$\gamma_{S/g}$ is the surface energy of liquid slag

$\gamma_{S/Fe}$ is the slag/iron interfacial energy.

If the value of $S$ in equation E-1 is $> 0$, then the slag wets the iron surface. If $S < 0$, then the slag does not wet the iron surface. In the present analysis, the surface energy of solid iron and the interfacial energy for solid iron and liquid slag will be approximated by the values reported for molten iron, (84,85)

$\gamma_{S/g} \approx 400 \text{ dyne/cm}$

$\gamma_{Fe/g} \approx 1788 \text{ dyne/cm}$

$\gamma_{S/Fe} \approx 1300 \text{ dyne/cm}$

These values, when substituted into equation E-1, give $S > 0$. The calculation therefore suggests that the slag wets solid iron.
APPENDIX F

Computer Program for the Simulation of the Heating and Melting of a Spherical DRI Pellet in Molten Slag

The computer program that was used to predict the heating and melting behavior of a DRI pellet in molten slag is documented and listed in this section. The program was written in Fortran 77. The program is composed of 25 subroutines which are linked to a main program that organizes the calling order for the subroutines. The program structure was adapted from a computer program developed by S. Olsen. The structure of the program used in this study is shown in Fig. F.1. A brief description of the function of each subroutine follows:

BOUND - A subroutine that calculates the movement of the solid/liquid interface during solidification or melting, using equation 5-17.

COM - A subprogram that defines the COMMON variables in the FORTRAN program, which is included in each subroutine and the main program.

COMP - A subroutine that calculates the time dependent composition of each spatial element.

COMPUT - A subroutine that performs the following functions:
(1) Organizes the calling of subroutines for each spatial domain;
(2) Scans each spatial element in increments of Δr;
(3) Controls the calling of PRINT;
(4) Performs the slag penetration calculations as discussed in section 5.1.6.

ELEM - A subroutine that calculates the radius, area, volume, and thickness of each spatial element.

EVL - A subroutine that performs the following functions:
(1) Sums the gas volume and gas evolution rate contributed by each spatial element in the pellet;
(2) Calculates the heat transfer coefficient for the pellet as discussed in section 5.3.
Figure F.1 - Subroutine calling structure for the computer program.
FDCALC - A subroutine that calculates the temperature of an element at time $t + \Delta t$, using equation 5.1.

GRID - A subroutine that adjusts the thickness of spatial elements to account for shrinkage of the pellet (not used in this study).

INIT - A subroutine that initializes the variables at the start of a calculation.

MAIN - The main program that organizes the calling order of the subroutines and scans the time domain in increments of $\Delta t$.

OUTS - A subroutine that assigns a temperature to the elements that are outside of the spatial domains of the pellet and the solid slag shell.

PBODY - A subroutine that calculates the temperature of spatial elements within the body of the pellet, using FDCALC.

PIH - A subroutine that calculates the temperature of the surface element of the pellet when no solid slag shell is present and the pellet has not yet begun to melt. Boundary condition 5-14 is employed.

PIM - A subroutine that calculates the melting rate at the surface of the pellet, using BOUND.

PPROP - A subroutine that organizes the calculation of the properties of a spatial element in the pellet.

PRINT - A subroutine that formats the calculated output data.

PSPHT - A subroutine that calculates the effective specific heat of a spatial element in the pellet from the procedures discussed in section 5.3.2.3.

PSURF - A subroutine that calculates the temperature of the surface element of the pellet when a solid shell of slag exists on the pellet. Boundary conditions 5-3 and 5-4 are employed.

PTCOND - A subroutine that calculates the thermal conductivity of a spatial element in the pellet.

READ - A subroutine that reads the input data.

RXN - A subroutine that calculates the rate of reaction of FeO and carbon in a spatial element of the pellet. The volumetric heat requirement for the reaction in an element is also calculated.
SBODY - A subroutine that calculates the temperature of a spatial element in the solid slag shell, using FDCALC.

SHIFT - A subroutine that shifts data from the newly calculated data array, $t + \Delta t$, to the present time data array, $t$, for calculations in the next time step.

SLIN - A subroutine that calculates the temperature of the spatial element in the solid slag shell that is adjacent to the surface of the pellet. Boundary conditions 5-3 and 5-4 are employed.

SPROP - A subroutine that calculates the properties of the solid slag shell and calls STCOND.

SSE - A subroutine that calculates the solidification rate or melting rate at the surface of the solid slag shell, using BOUND.

STCOND - A subroutine that calculates the thermal conductivity of an element in the solid slag shell.

The finite difference techniques that have been employed in the model are discussed in detail in 5.1. Because an explicit finite difference technique was employed, the calculations are not stable for any arbitrary choice of $\Delta t$ and $\Delta r$. The stability of the numerical solution is governed by the value of the following dimensionless modulus, $(69,70)$

$$\phi = \frac{\alpha \Delta t}{\Delta r^2} \quad (F-1)$$

where $\alpha$ is the thermal diffusivity of solid (pellet or slag shell). For an explicit formulation that uses forward differences, a value of $\phi < 0.5$ is required for stability, $(69,70)$ and a value of $\phi < 0.25$ is recommended $(70)$ for a convergent solution. An additional restriction, that is a consequence of the moving boundary, is that, $(13,14)$

$$| R_i^* - R_i | < \Delta R_i \quad (F-2)$$
This restriction simply states that the change in the overall radius of the pellet during a single time step, $\Delta t$, may not exceed the width of a spatial element, $\Delta r$.

For the calculations performed in this study, the maximum value of $\Phi$ for the slag was,

$$\Phi_s = \frac{(0.003)(0.01)}{(0.02)^2} = 0.075,$$

and the maximum value of $\Phi$ for the pellet was,

$$\Phi_p = \frac{(0.06)(0.01)}{(0.06)^2} = 0.167.$$

In all cases, condition F-2 was also satisfied.

A listing of the computer program and a listing of each variable in the program, along with a brief description of the variable, is presented in the following section.
PROGRAM FOR A DRI PELLET
## Definition of Variables

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<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td>- Variable defined in SSE</td>
</tr>
<tr>
<td>AA1</td>
<td>- Mass * Specific heat of new slag entering an element</td>
</tr>
<tr>
<td>AA2</td>
<td>- Mass * Specific heat of the pellet solids and the slag already in the element</td>
</tr>
<tr>
<td>AERH</td>
<td>- Activation energy for the high temp rxn, cal/mole</td>
</tr>
<tr>
<td>AERL</td>
<td>- Activation energy for the low temp rxn, cal/mole</td>
</tr>
<tr>
<td>ALP</td>
<td>- Variable defined in Pbody</td>
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<tr>
<td>AREAi</td>
<td>- Inner surface area of a spatial element, cm²</td>
</tr>
<tr>
<td>AREAO</td>
<td>- Outer surface area of a spatial element, cm²</td>
</tr>
<tr>
<td>ATKH</td>
<td>- Thermal conductivity of pellet above C4TF, cal/cm² s K</td>
</tr>
<tr>
<td>ATKL</td>
<td>- Thermal conductivity of pellet below C4TS, cal/cm² s K</td>
</tr>
<tr>
<td>BB</td>
<td>- Variable defined in SSE</td>
</tr>
<tr>
<td>BDT</td>
<td>- Temp drop across the pellet/thermocouple interface</td>
</tr>
<tr>
<td>BD1</td>
<td>- Temp range for Fe3C dissolution</td>
</tr>
<tr>
<td>BD2</td>
<td>- Temp range for A-G trans in Fe</td>
</tr>
<tr>
<td>BD3</td>
<td>- Temp range for G-D trans in Fe</td>
</tr>
<tr>
<td>BDTB</td>
<td>- Fraction of BDT due to thermocouple, see Pbody</td>
</tr>
<tr>
<td>BDTp</td>
<td>- Fraction of BDT due to pellet</td>
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<td>- Mid temp of Fe3C dissolution, K</td>
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<tr>
<td>BT2</td>
<td>- Mid temp of A-G trans in Fe, K</td>
</tr>
<tr>
<td>BT3</td>
<td>- Mid temp of G-D trans in Fe, K</td>
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<td>- Temperature of slag bath, K</td>
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<td>- Completion temp for shift to high temp thermal conductivity of pellet, K</td>
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<tr>
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<td>- Starting temp for shift from low temp thermal conductivity of pellet, K</td>
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<td>- Specific heat of thermocouple bead, cal/g K</td>
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<td>- Spec heat of carbon soot, cal/g K</td>
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<tr>
<td>CFE</td>
<td>- Specific heat of Fe, cal/g K</td>
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<td>- Spec heat of gamma Fe, cal/g K</td>
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<td>SPECIFIC HEAT OF GANQUE, CAL/G K</td>
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<td>SPECIFIC HEAT OF PELLET W/O SLAG PENETRATION, CAL/G K</td>
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<td>CRG</td>
<td>COEF FOR CONST RXN RATE DUE TO INTERNAL CIRCULATION OF RED GAS, 1/SEC</td>
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<td>PRE EXP COEF FOR HIGH T RXN, 1/SEC</td>
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<td>PRE EXP COEF FOR LOW T RXN, 1/SEC</td>
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<td>EFF SPEC HEAT OF CARBIDE DISSOLUTION, CAL/G K</td>
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<td>EFF SPEC HEAT OF A-G TRANS FOR FE, CAL/G K</td>
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<td>CRXN3</td>
<td>EFF SPEC HEAT OF G-D TRANS FOR FE, CAL/G K</td>
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<td>SPECIFIC HEAT OF SLAG SHELL, CAL/G K</td>
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<tr>
<td>CSL</td>
<td>SPECIFIC HEAT OF SLAG, CAL/G K</td>
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<td>THERMOCOUPLE BEAD DIA, CM</td>
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<td>DC</td>
<td>SPECIFIC HEAT (DUMMY VAR), CAL/G K</td>
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<td>DENSITY OF CARBON SOOT, G/CM³</td>
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<td>DENSITY (DUMMY VAR), G/CM³</td>
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<td>WIDTH OF MOVING BOUNDARY ELEMENT IN ELEMENT M1 AT PRESENT TIME STEP, CM</td>
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<td>DENSITY OF FE3C, G/CM³</td>
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<td>DENSITY OF GANQUE, G/CM³</td>
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<td>DISTANCE FROM PELLET CENTER TO THE CENTER OF AN ELEMENT, CM</td>
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<td>INIT DENS OF PELLET, G/CM³</td>
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<td>DIAMETER OF PORES IN PELLET, CM</td>
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<td>DIAMETER OF PORES IN SLAG SHELL, CM</td>
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<td>DISTANCE BETWEEN NODE I AND I-1, CM</td>
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<td>DRO</td>
<td>DISTANCE BETWEEN NODE I AND I+1, CM</td>
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<td>DT1</td>
<td>TIME STEP SIZE FOR FIRST SEC OF CALCULATION</td>
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<tr>
<td>DT2</td>
<td>TIME STEP FOR 1 TO 30 SEC</td>
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<td>DT3</td>
<td>TIME STEP FOR &gt; 30 SEC</td>
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<td>DTK</td>
<td>THERMAL CONDUCTIVITY AT NODE I (DUMMY VAR), CAL/CM S K</td>
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<td>THERMAL CONDUCTIVITY BETW NODE I AND I-1 (DUMMY VAR), CAL/CM S K</td>
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<td>DTKO</td>
<td>THERMAL CONDUCTIVITY BETW NODE I AND I+1 (DUMMY VAR), CAL/CM S K</td>
</tr>
<tr>
<td>DW</td>
<td>SPACIAL STEP SIZE, CM</td>
</tr>
</tbody>
</table>
DWA - VARIABLE DEFINED IN PIM
DWP - SPATIAL STEP SIZE IN PELLET, CM
DWS - SPATIAL STEP SIZE IN SLAG, CM
EMTY - VARIABLE DEFINED IN COMPUT
ENTH - ENTHALPY OF HIGH TEMP RXN - DISSOLVED C + FEO, CAL/MOLE
ENTHL - ENTHALPY OF LOW TEMP RXN - F3C + FEO, CAL/MOLE
EQCG - CARBON GASIFICATION EQUILIBRIUM CONST
FRC - FRACT CARBON AS CARBIDE, DEFINED IN RXN
FRCARB - FRACTION OF CARBON IN PELLET AS CARBIDE
GRATE - RATE OF GAS EVOLUTION FROM PELLET, CM³/MIN STP
GRMAX - MAX RATE OF GAS EVOLUTION FROM PELLET, CM³/MIN STP
GVOL - VOLUME OF GAS EVOLVED FROM PELLET, CM³ STP
HCONV - CONVECTIVE HEAT TRANSFER COEFFICIENT DUE TO LOCAL GAS EVOLUTION, CAL/CM² S K
HDAMP - HEAT TRANSFER COEF DETERMINED BY THE GRADUAL DECAY OF HMAX AFTER GAS EVOLUTION, CAL/CM² S K
HMAX - MAXIMUM OBSERVED VALUE OF HCONV
HMIN - MINIMUM HEAT TRANSFER COEFFICIENT FOR THE SYSTEM, CAL/CM² S K
HTRANS - HEAT TRANSFER COEFFICIENT, CAL/CM² S K
I - SPATIAL ELEMENT COUNTER (INTEGER)
IFLAG - TEST VARIABLE TO CHECK FOR INSTABILITIES OR REDUNDANT SUBROUTINE EXECUTIONS (INTEGER)
II - SPATIAL ELEMENT COUNTER IN COMP (INTEGER)
III - SPATIAL ELEMENT COUNTER IN ELEM (INTEGER)
IPS - ELEMENT IN THE PELLET TO WHICH SLAG HAS PENETRATED (INTEGER)
IREM - VARIABLE IN PBODY (INTEGER)
K - NUMBER OF ELEMENTS IN PELLET (INTEGER)
KL - NUMBER OF TIME STEPS TAKEN (INTEGER)
KLMAX - MAX NUMBER OF ALLOWABLE TIME STEPS (INTEGER)
L1 - COUNTER IN GRID (INTEGER)
L2 - COUNTER IN SHIFT (INTEGER)
L4 - COUNTER IN INIT (INTEGER)
L5 - COUNTER IN INIT (INTEGER)
L6 - COUNTER IN INIT (INTEGER)
M - MAX NUMBER OF SPATIAL ELEMENTS (INTEGER)
MELT - COUNTER IN COMPUT (INTEGER)
M1 - NUMBER OF ELEMENT CONTAINING MOVING BOUNDARY (INTEGER)
M11 - VALUE OF M1 AT START OF TIME INCREMENT (INTEGER)
NN1 - PARAMETER DEFINED IN COM (INTEGER)
NN2 - PARAMETER DEFINED IN COM (INTEGER)
NN3 - PARAMETER DEFINED IN COM (INTEGER)
NN4 - PARAMETER DEFINED IN COM (INTEGER)
PFUS - HEAT OF FUSION OF PELLET, CAL/G
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
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<tbody>
<tr>
<td>PHI</td>
<td>VARIABLE DEFINED IN COMP</td>
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<td>PHI1</td>
<td>VARIABLE DEFINED IN RXN</td>
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<td>PHI2</td>
<td>VARIABLE DEFINED IN RXN</td>
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<td>PMELT</td>
<td>MELTING TEMP OF PELLET, K</td>
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<td>PORINI</td>
<td>INITIAL POROSITY OF PELLET</td>
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<tr>
<td>PPOR(I,1)</td>
<td>POROSITY OF PELLET, PRESENT TIME STEP</td>
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<tr>
<td>PPOR(I,2)</td>
<td>POROSITY OF PELLET, NEXT TIME STEP</td>
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<td>QD</td>
<td>VOLUMETRIC HEAT GEN COEF DEFINED IN PBODY AND PSURF,K</td>
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<td>QRXN</td>
<td>VOLUMETRIC RATE OF HEAT GENERATION IN THE PELLET, CAL/CM^3 S</td>
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<td>RAD(I,1)</td>
<td>RADIUS TO INNER WALL OF ELEMENT I AT PRESENT TIME STEP, CM</td>
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<tr>
<td>RAD(I,2)</td>
<td>RADIUS TO OUTER WALL OF ELEMENT I AT NEXT TIME STEP, CM</td>
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<td>RADIUS TO INNER WALL OF ELEMENT I, CM</td>
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<td>RADIUS TO OUTER WALL OF ELEMENT I, CM</td>
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<td>RI</td>
<td>VARIABLE DEFINED IN PBODY AND PSURF, CM</td>
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<td>VARIABLE DEFINED IN SSE, CM</td>
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<td>VARIABLE DEFINED IN SSE, CM</td>
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<td>RM3</td>
<td>VARIABLE DEFINED IN SSE, CM</td>
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<td>VARIABLE DEFINED IN PBODY AND PSURF, CM</td>
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<tr>
<td>RRX1</td>
<td>RATE OF REACTION FROM LOW TEMP RXNS, 1/SEC</td>
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<tr>
<td>RRX2</td>
<td>RATE OF REACTION FROM HIGH TEMP RXNS, 1/SEC</td>
</tr>
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<td>RRX3</td>
<td>RATE OF REACTION FROM GAS CIRCULATION, 1/SEC</td>
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<td>RADIAL DISTANCE TO THE MOVING BOUNDARY, CM</td>
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<tr>
<td>RTPI</td>
<td>(3.1416)^1/2</td>
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<tr>
<td>SFUS</td>
<td>HEAT OF FUSION OF SLAG, CAL/G</td>
</tr>
<tr>
<td>SIG</td>
<td>STEPHAN-BOLTZMAN CONST, 1.36E-12 CAL/CM^3 S K^4</td>
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<tr>
<td>SMELT</td>
<td>MELTING TEMP OF SLAG SHELL, K</td>
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<td>SPCOND</td>
<td>THERMAL CONDUCTIVITY OF PORES IN SLAG SHELL, CAL/CM S K</td>
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<td>SPOR</td>
<td>POROSITY OF SLAG SHELL</td>
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<tr>
<td>TBPC</td>
<td>VARIABLE DEFINED IN PRINT, C</td>
</tr>
<tr>
<td>TEM</td>
<td>VARIABLE DEFINED IN PRINT, C</td>
</tr>
<tr>
<td>TEMIPS</td>
<td>TEMPERATURE OF ELEMENT IPS IF SLAG PENETRATES, K</td>
</tr>
<tr>
<td>TEMP(I,1)</td>
<td>TEMPERATURE OF ELEMENT I AT PRESENT TIME STEP, K</td>
</tr>
<tr>
<td>TEMP(I,2)</td>
<td>TEMPERATURE OF ELEMENT I AT NEXT TIME STEP, K</td>
</tr>
<tr>
<td>TGRMAX</td>
<td>TIME AT WHICH MAX RATE OF GAS EVOLUTION OCCURRED, SEC</td>
</tr>
<tr>
<td>THICK</td>
<td>THICKNESS OF SLAG SHELL, MM</td>
</tr>
<tr>
<td>TIC</td>
<td>VARIABLE DEFINED IN PRINT, C</td>
</tr>
<tr>
<td>TIME</td>
<td>ELAPSED TIME AFTER IMMERSSION, SEC</td>
</tr>
<tr>
<td>TINIT</td>
<td>INITIAL PELLET TEMP, K</td>
</tr>
<tr>
<td>TINT</td>
<td>TEMP AT THE SLAG SHELL/PELLET INTERFACE, K</td>
</tr>
<tr>
<td>TKBEAD</td>
<td>THERMAL CONDUCTIVITY OF THE THERMOCOUPLE BEAD, CAL/CM S K</td>
</tr>
<tr>
<td>TKCAR</td>
<td>THERMAL CONDUCTIVITY OF CARBON SOOT, CAL/CM S K</td>
</tr>
<tr>
<td>TKFE</td>
<td>THERMAL CONDUCTIVITY OF FE, CAL/CM S K</td>
</tr>
</tbody>
</table>
TKFE0 - THERMAL CONDUCTIVITY OF FEO, CAL/CM S K
TKFE3C - THERMAL CONDUCTIVITY OF FE3C, CAL/CM S K
TKGANG - THERMAL CONDUCTIVITY OF GANGUE, CAL/CM S K
TKGAS - THERMAL CONDUCTIVITY OF CO GAS, CAL/CM S K
TKPEL - THERMAL CONDUCTIVITY OF PELLET, CAL/CM S K
TKPOR - THERMAL CONDUCTIVITY OF THE PORES IN THE PELLET, CAL/CM S K
TKSH - THERMAL CONDUCTIVITY OF THE SLAG SHELL, CAL/CM S K
TKSL - THERMAL CONDUCTIVITY OF SLAG, CAL/CM S K
TKSOL - THERMAL CONDUCTIVITY OF SOLIDS IN THE PELLET, CAL/CM S K
TM - VARIABLE DEFINED IN SSE
TMAX - MAXIMUM TIME THAT SIMULATION IS TO BE RUN, S
TM1 - VARIABLE DEFINED IN SSE
TM2 - VARIABLE DEFINED IN SSE
TM3 - VARIABLE DEFINED IN SSE
TN2 - TEMP(I, 2)
T01 - TEMP(I-1, 1)
T02 - TEMP(I, 1)
T03 - TEMP(I+1, 1)
TPBINT - TEMP AT THE PELLET/ THERMOCOUPLE INT, K
TPLUS - VARIABLE DEFINED IN PRINT, C
TT - VARIABLE DEFINED IN PIH AND PIM, K
U - UNUSED COMMON BLOCK VARIABLE
UU - TEMPERATURE VALUE PASSED TO PTCND
VCOTOT - TOTAL VOL OF CO EVOLVED FROM PELLET UP TO PRESENT TIME, CM^3 STP
VGAS(I, 1) - VOL OF GAS EVOLVED FROM ELEMENT I UP TO PRESENT TIME, CM^3 STP
VGAS(I, 2) - VOL OF GAS EVOLVED FROM ELEMENT I UP TO NEXT TIME STEP, CM^3 STP
VOL - VOLUME OF ELEMENT I, CM^3
VOLCO - VOL OF CO EVOLVED FROM ELEM I TO PRESENT TIME, CM^3 STP
VOLIPS - VOLUME OF ELEMENT BEING FILLED WITH SLAG, CM^3
VOLREM - VARIABLE IN PIM, CM^3
VRATE(I, 1) - RATE OF GAS EVOLUTION AT PRESENT TIME STEP DUE TO LOW TEMP RXN + GAS CIRCULATION, CM^3/S STP
VRATE(I, 2) - RATE OF GAS EVOLUTION AT PRESENT TIME STEP DUE TO HIGH TEMP RXN + GAS CIRCULATION, CM^3/S STP
WBEAD - MASS OF THERMOCOUPLE BEAD, G
WCAR - WEIGHT OF CARBON IN ELEMENT I, G
WCARR(I) - WT OF CARBON IN ELEMENT I BEFORE FE3C DECOMP, G
WFPE - WT OF FE IN ELEMENT I, G
WFEO(I) - WT OF FEO IN ELEMENT I, G
WFER(I) - WT OF FE IN ELEMENT I BEFORE FE3C DECOMP, G
WFES3C - WT OF FE3C IN ELEMENT I, G
WFES3CR(I) - WT OF FE3C IN ELEM I BEFORE FE3C DECOMP, G
WGANG(I) - WT OF GANGUE IN ELEM I, G
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPELI</td>
<td>Initial WT of Pellet, G</td>
</tr>
<tr>
<td>WTOT(I)</td>
<td>Total WT of Elem I, G</td>
</tr>
<tr>
<td>WTOTI(I)</td>
<td>Initial Total WT of Elem I, G</td>
</tr>
<tr>
<td>XAG</td>
<td>WT Fraction of Fe as Gamma Fe</td>
</tr>
<tr>
<td>XCAR</td>
<td>WT Fraction Carbon in Element I (Fe3C excluded)</td>
</tr>
<tr>
<td>XCARI</td>
<td>Initial WT Fraction Carbon in Element I</td>
</tr>
<tr>
<td>XFE3C</td>
<td>WT Fraction of C as Fe3C in Element I</td>
</tr>
<tr>
<td>XCFE3I</td>
<td>Initial WT Fraction Fe3C in Element I</td>
</tr>
<tr>
<td>XCOAVG</td>
<td>Avg Vol Fraction of CO in Evolved Gas at Present Time</td>
</tr>
<tr>
<td>XCOSUM</td>
<td>Variable Defined in Evol, cm^3/s</td>
</tr>
<tr>
<td>XCO(I)</td>
<td>Vol Fraction of CO Evolved from Elem I</td>
</tr>
<tr>
<td>XFE</td>
<td>WT Fraction Fe in Element I</td>
</tr>
<tr>
<td>XFEI</td>
<td>Initial WT Fraction Fe in Element I</td>
</tr>
<tr>
<td>XFE0I</td>
<td>Initial WT Fraction FeO in Element I</td>
</tr>
<tr>
<td>XFE3CI</td>
<td>Initial WT Fraction Fe3C in Element I</td>
</tr>
<tr>
<td>XFE3CR</td>
<td>WT Fraction Fe3C in Element I Before Fe3C Dissolution</td>
</tr>
<tr>
<td>XGANG</td>
<td>WT Fraction Gangue in Element I</td>
</tr>
<tr>
<td>XGANGI</td>
<td>Initial WT Fraction Gangue in Element I</td>
</tr>
<tr>
<td>XGD</td>
<td>WT Fraction Fe as Delta Fe</td>
</tr>
<tr>
<td>XM</td>
<td>Forward Difference Modulus Defined in FDCalc, K</td>
</tr>
<tr>
<td>XP</td>
<td>Forward Difference Modulus Defined in FDCalc, K</td>
</tr>
<tr>
<td>XRAD</td>
<td>Fraction of Pellet/Slag Shell Interacial Area That is Not in Direct Thermal Contact</td>
</tr>
<tr>
<td>XRBead</td>
<td>Fraction of Pellet/Thermocouple Interacial Area That is Not in Direct Thermal Contact</td>
</tr>
<tr>
<td>XXM</td>
<td>Variable Defined in SLIN, K</td>
</tr>
<tr>
<td>XXP</td>
<td>Variable Defined in SLIN, K</td>
</tr>
<tr>
<td>Y</td>
<td>Time Element Counter for Printout Control in Comput</td>
</tr>
<tr>
<td>YCAR</td>
<td>Vol Fraction Carbon in Element I</td>
</tr>
<tr>
<td>YFE</td>
<td>Vol Fraction Fe in Element I</td>
</tr>
<tr>
<td>YFEO</td>
<td>Vol Fraction FeO in Element I</td>
</tr>
<tr>
<td>YFE3C</td>
<td>Vol Fraction Fe3C in Element I</td>
</tr>
<tr>
<td>YGANG</td>
<td>Vol Fraction Gangue in Element I</td>
</tr>
<tr>
<td>YM</td>
<td>Forward Difference Modulus Defined in Bound</td>
</tr>
<tr>
<td>YP</td>
<td>Forward Difference Modulus Defined in Bound</td>
</tr>
<tr>
<td>ZK</td>
<td>Real Equivalent of K in Init</td>
</tr>
<tr>
<td>ZTD</td>
<td>Temp Drop Across Pellet/Slag Shell Interface Due to Incomplete Thermal Contact See PSurf, K</td>
</tr>
<tr>
<td>ZTDp</td>
<td>Fract of ZDT Due to Pellet-See PSurf, K</td>
</tr>
<tr>
<td>ZDTS</td>
<td>Fract of ZDT Due to Shell-See PSurf, K</td>
</tr>
</tbody>
</table>
SUBROUTINE BOUND

INCLUDE 'COM.FOR'

********FINITE DIFF BOUNDARY MOTION DESC

YP = (DT*HTRANS)/(DD*DLF)
YM = (DT*DKI)/(DD*DLF*DRI)
DEL(2) = DEL(1) + YP*(BTEMP-DMELT) - YM*(DMELT-TO1)

RETURN
END
323

*******************************************

*

COMMON BLOCK DEFINITION FILE

*

*******************************************

********PROGRAM

COM.FOR

PARAMETER (NN1=50, NN2=2, NN3=20, NN4=3)

1
1
1
1

COMMON/ARRAYS/RAD(NN1,NN2),TEMP(NN1,NN2),
VGAS(NN3,NN2),PPOR(NN1,NN2),VRATE(NN3,NN4),
DEL(NN2),WFEO(NN3),WCARR(NN3),WFE3CR(NN3),
WFER(NN3),WGANG(NN3),WTOT(NN3),WTOTI(NN3),
XCO(NN3)

1
1
1
1
1
1
1

COMMON/INPUT/K,M,DWS,DT,DT1,DT2,DT3,TMAX,KLMAX,
DSL,CSL,SPOR,DPSLAG,SMELT,BTEMP,SFUS,TKSL,HMIN,
DINIT,WPELI,PMELT,TINIT,PFUS,TKGAS,DPPEL,
XFEOI,XCARI,XGANGI,XCFE3I,AERL,CRL,AERH,CRH,CRG,
DFE,DFEO,DFE3C,DCAR,DGANG,
TKFEO,TKFE3C,TKCAR,TKGANG,ATKL,ATKH,
EMP,EMS,XRAD,DBEAD,XRBEAD,TKBEAD,CBEAD,WBEAD,EMB,
C1TS,C1TF,C2TS,C2TF,C3TS,C3TF,C4TS,C4TF

1
1
1
1
1
1
1
1
1

COMMON/PROGVAR/TIME,Y,KL,IFLAG,I,RADO,RADI,AREAO,AREAI,
VOL,DW,DIST,DRI,DRO,M1,M11,DMELT,TINT,TT,CPEL,CSH,
TKPEL,DC,DD,DPEL,DSH,DLF,QD,T01,T02,TO3,DWA,TPBINT,
TN2.XP,YP,XM,YM,HTRANS,RSURF,TKSH,DWP,DPELI ,THICK,
CRXN1,CRXN2,CRXN3,CRXN4,CFE,XFEI,XFE3CI,FRCARB,XFE3CR,
XFEO,XFE,XCAR,XFE3C,XGANG,YFEO,YFE,YCAR,YFE3C,YGANG,
TKFE,SPCOND,TKPOR,QRXN,ENTHL,ENTHH,GVOL,GRATE,GRMAX,
WFE,WCAR,WFE3C,XCOAVG,VOLCO,VCOTOT,TGRMAX,NSPF,
ZTD,ZTDP,ZTDS,BDT,BDTB,BDTP,IPS,CPELL,HCONV,HDAMP,
TKPELL,DTK,DTKO,DTKI,VOLIPS,TEMIPS,U

********


SUBROUTINE COMP

**WT DATA**
\[
\begin{align*}
\text{PHI} &= \frac{(C1TF-TO2)/(C1TF-C1TS)}{1} \\
\text{IF(PHI.LT.0.0)PHI} &= 0.0 \\
\text{IF(PHI.GT.1.0)PHI} &= 1.0 \\
\text{WFE3C} &= \text{WFE3CR(II)} \times \text{PHI} \\
\text{WFE} &= \text{WFER(II)} + \left(\frac{167.55}{179.55}\right) \times \text{WFE3CR(II)} \\
\text{WCAR} &= \text{WCARR(II)} + \left(\frac{12.0}{179.55}\right) \times \text{WFE3CR(II)} \\
\text{IF(WCAR.LT.0.0)WCAR} &= 0.0
\end{align*}
\]

**WT FRACTIONS**
\[
\begin{align*}
\text{XFEO} &= \frac{\text{WFEO(II)}}{\text{WTOT(II)}} \\
\text{XCAR} &= \frac{\text{WCAR}}{\text{WTOT(II)}} \\
\text{XFE3C} &= \frac{\text{WFE3C}}{\text{WTOT(II)}} \\
\text{XGANG} &= \frac{\text{WGANG(II)}}{\text{WTOT(II)}} \\
\text{XFE} &= 1.0 - \text{XFEO} - \text{XCAR} - \text{XFE3C} - \text{XGANG}
\end{align*}
\]

**VOL FRACTIONS**
\[
\begin{align*}
\text{DPEL} &= \frac{\text{WTOT(II)}}{\text{VOL}} \\
\text{YFEO} &= \frac{\text{XFEO} \times \text{DPEL}}{\text{DFEO}} \\
\text{YFE} &= \frac{\text{XFE} \times \text{DPEL}}{\text{DFE}} \\
\text{YFE3C} &= \frac{\text{XFE3C} \times \text{DPEL}}{\text{DFE3C}} \\
\text{YCAR} &= \frac{\text{XCAR} \times \text{DPEL}}{\text{DCAR}} \\
\text{YGANG} &= \frac{\text{XGANG} \times \text{DPEL}}{\text{DGANG}} \\
\text{PPOR(II,1)} &= 1.0 - \text{YFEO} - \text{YFE} - \text{YCAR} - \text{YFE3C} - \text{YGANG}
\end{align*}
\]

RETURN
END
**CONTINUE**

I(PS+I-1) = I(PS+I) + AZ2*TEMP(MELT',1).

MASS AT I ASSUMED TO REACH THERMAL EQUILIBRIUM.

NEW SLAG THAT PENETRATED OZ AND PELLET & SLAG.

AV2 = W(LT(MELT),CPEL+V(PL*DSL,CSET(0))

CALL PSPLH

CALL COMP(MELT)

CALL ELEM(MELT)

TOZ = TEMP(MELT',1)

DO 450 WELT = I(PS)+1, K.

IF(I(PS),R,K) = GOTO 450.

TEMP(I(PS) = TEMP(I(PS),1).

**CALC NEW TEMPS DUE TO SLAG PENETRATION.**

I(PS) = TEMP(S, T, MELT), OR. (MILL. GT. K) (GOTO 460

AV2 = W(LT(MELT),CPEL+V(PL*DSL,CSET(0))

CALL PSPLH

CALL COMP(MELT)

CALL ELEM(MELT)

I(PS) = TEMP(I(PS),1).

VOLPS = 4.0 (3.0)*3.1416*(RAD(I(PS).I)**3.0 -

IF(MILL.K)*400.0 460.

IF(NSSP.RK)*400.0 460.

IF(I(PS).TLE)*400.0 460.

**TMPL | SMLT AND SLAG SHELL IS MELTED.**

**SLAG PENETRATION TEST - PENETRATE IP FINAL.**

**STORE PRESENT INTERFACED POSITION**

**INCLUDE COM.POR**

**SUBROUTINE COMPUT**

**SUBROUTINE COMPUT**

*****************************************************************************
CONTINUE
*
********** SPACIAL ELEMENT SCAN LOOP
DO 550 I=1,M
********** INITIALIZE TEST FLAG
IFLAG=0
*** CALC ELEMENT RADII AREAS AND VOL
CALL ELEM(I)
*
********** TEST TO CHOOSE PROPER CALC SUBR
* ****** PELLET INTERIOR ELEMENT
   IF((I.LT.K).AND.(I.LT.M11)) CALL PBODY
   IF(IFLAG.NE.0) GOTO 500
* ****** PELLET SURF W/ SLAG
   IF((I.EQ.K).AND.(M11.GE.K+1)) CALL PSURF
   IF(IFLAG.NE.0) GOTO 500
* ****** PELLET SURF W/O SLAG SHELL : HEATING
   IF((I.EQ.M11).AND.(M11.LE.K).AND.
   1 (TEMP(M11,1).LT.PMELT)) CALL PIH
   IF(IFLAG.NE.0) GOTO 500
* ****** PELLET SURF ELEMENT : MELTING
   IF((I.EQ.M11).AND.(M11.LE.K).AND.
   1 (TEMP(M11,1).GE.PMELT)) CALL PIM
   IF(IFLAG.NE.0) GOTO 500
* ****** SLAG SHELL INTERIOR ELEM
   IF((I.GT.K+1).AND.(I.LT.M11)) CALL SBODY
   IF(IFLAG.NE.0) GOTO 500
* ****** SLAG ADJ TO PELLET INT W/O ADJ SLAG SURF
   IF((I.EQ.K+1).AND.(M11.GT.K+1)) CALL SLIN
   IF(IFLAG.NE.0) GOTO 500
* ****** SLAG SURF ELEMENT
   IF((I.EQ.M11).AND.(M11.GT.K)) CALL SSE
   IF(IFLAG.NE.0) GOTO 500
* ****** ELEMENTS OUTSIDE OF SURFACE
   IF(I.GT.M11) CALL OUTS
   *
500 CONTINUE
*
********** PRINT OUT ELEMENT PROPS
   IF(TIME.LT.Y) GOTO 510
IF(I.EQ.M) Y=Y+1.0
IF((I.EQ.M).AND.(TIME.GE.10.0))Y=Y+4.0
IF((I.EQ.M).AND.(TIME.GE.120.0))Y=Y+5.0
CALL PRINT
CONTINUE

* 

**********CHECK FLAG FOR MISSED OR DOUBLE ROUTINES
IF(IFLAG.LE.0) GOTO 555
CONTINUE
RETURN

555 CONTINUE
WRITE(6,*) 'END IN COMPUT ;ROUTINE # ',IFLAG
STOP
END
***************
SUBROUTINE ELEM
***************

SUBROUTINE ELEM(III)
INCLUDE 'COM.FOR'

*******CALC RAD VOL AREA AND SPACING OF ELEMENTS
RADO=RAD(III,1)
IF(III.NE.1) RADI=RAD(III-1,1)
IF(III.EQ.1) RADI=0.0

AREAO=4.0*3.14*RADO*RADO
AREA1=4.0*3.14*RADI*RADI
VOL=(4.0/3.0)*3.14*(RADO**3.0-RADI**3.0)
DW=RADO-RADI

IF(III.EQ.1) DIST=0.0
IF(III.NE.1) DIST=RADI+(DW/2.0)

*******VOL OF MOVING BOUNDARY
IF(III.EQ.M11) VOL=(4.0/3.0)*3.14*((RAD(M11-1,1)+DEL(1)**3.0-RAD(M11-1,1)**3.0)

*******OUTER AREA OF MOVING BOUNDARY
IF(III.EQ.M11) AREAO=4.0*3.14*(RADI+DEL(1))**2.0

RETURN
END
SUBROUTINE EVOL

********CALC SURF POS AND SHELL THICKNESS
   IF(M1-K) 200,200,210
200 CONTINUE
   RSURF=RAD(M1-1,1)+DEL(1)
   THICK=0.0
   GOTO 220
210 CONTINUE
   RSURF=RAD(M1-1,1)+DEL(1)
   THICK=(RSURF-RAD(K,1))*10.0
220 CONTINUE

********SUM UP GAS VOLS AND RATES FROM ELEMENTS
   GRATE=0.0
   XCOSUM=0.0
   GVOL=0.0
   DO 222 L3=2,K
      GVOL=GVOL+VGAS(L3,1)
      GRATE=GRATE+VRATE(L3,1)+VRATE(L3,2)
      XCOSUM=XCOSUM+(VRATE(L3,1)+VRATE(L3,2))*XCO(L3)
   222 CONTINUE
   IF(GRATE.GT.0.0) XCOAVG=XCOSUM/GRATE
   GRATE=GRATE*60.0

********CALCULATE CONV HEAT TRANSFER COEF
   HCONV=8.64E-3*(GRATE/60.0)**(0.25)

********REMEMBER MAX RATE AND TIME OF OCCURANCE
   IF(GRMAX.LT.GRATE) GOTO 223
   GOTO 224
223 CONTINUE
   GRMAX=GRATE
   TGRMAX=TIME
   HMAX=HCONV
224 CONTINUE

********CALC DAMPENING OF MAX HEAT TRANS COEF
   HDAMP=HMAX*EXP(-(TIME-TGRMAX)/180)

********CHOOSE HDAMP OR HCONV
   HTRANS=HCONV
   IF(HDAMP.GT.HTRANS) HTRANS=HDAMP

*
******MIN STEADY STATE HEAT TRANS
  IF(HMIN.GT.HTRANS) HTRANS=HMIN
*
*
  RETURN
CONTINUE
WRITE(6,*) 'STOP IN EVOL'
STOP
END
SUBROUTINE FDCALC

XP = (DTKO * AREAO * DT) / (DD * DC * VOL * DRO)
XM = (DTKI * AREAI * DT) / (DD * DC * VOL * DRI)
TN2 = TO2 + XP * (TO3 - TO2) - XM * (TO2 - TOI) - QD

RETURN
END
*** SUBROUTINE GRID ***
**********IMPLEMENT RADII CHANGE TO MAINTAIN CONST DENSITY
RAD(1, 2)=RAD(1, 1)
DO 650 L1=2, M
   IF((L1.GT.M).OR.(L1.GT.K))DENSI=DSH
   RAD(L1, 2)=RAD(L1, 1)
650 CONTINUE
DEL(2)=DEL(2)*((RAD(M1, 2)-RAD(M1-1, 2))/(RAD(M1, 1)-
   1 RAD(M1-1, 1)))

******
RETURN
END
SUBROUTINE INIT
INCLUD 'COM.FOR'

**INIT TIME LOOP VARIABLES**
TIME=0.0
Y=0.0
KL=0

**INIT SPACE GRID**
M1=K+1
ZK=K
IPS=K
DWP=(DINIT-DBEAD)/(2.0*(ZK-1.0))
DEL(1)=DWS/5.0
RADI=DEAD/2.0

**INIT ELEM RADII**
DO 100 L4=1,M
IF(L4.LE.K)DW=DWP
IF(L4.EQ.1)DW=DEAD
IF(L4.GT.K)DW=DWS
RAD(L4,1)=RADI+DW
IF(L4.EQ.K) RAD(K,1)=DINIT/2.0
RADI=RAD(L4,1)
100 CONTINUE
RSURF=(DINIT/2.0)
DPELI=WPELI/((1.0/6.0)*3.14*(DINIT**3.0))

**INITIALIZE TEMP IN PELLET**
DO 150 L5=1,K
TEMP(L5,1)=TINIT
150 CONTINUE

**INTERFACE TEMP INITIATION**
TT=TINIT

**INITIALIZE TEMP IN SLAG**
DO 160 L6=K+1,M
TEMP(L6,1)=BTEMP
160 CONTINUE

**INIT COMP AND POROSITY**
XFE3CI=XCFE3I*179.55/12.0
IF(XCFE3I+XCARI.NE.0.0)FRCARB=XCFE3I/(XCFE3I+XCARI)
IF(XCFE3I+XCARI.EQ.0.0)FRCARB=0.0
XFEI=1.0-XFE01-XCARI-XFE3CI-XGANGI
YFEO=DPELI*XFE01/DFEO
YFE=DPELI*XFEI/DFE
YCAR=DPELI*XCARI/DCAR
YFE3C=DPELI*XFE3C/DFE3C
YGANG=DPELI*XGANGI/DGANG
PORINI=1.0-YFE0-YFE-YCAR-YFE3C-YGANG

*****INIT ELEM COMPONENT WTS AND GAS EVOLUTION
DO 162 L6=1,K
CALL ELEM(L6)
WTOTI(L6)=DPELI*VOL
WTOT(L6)=WTOTI(L6)
WFEO(L6)=XFE0I*WTOTI(L6)
WFER(L6)=XFEI*WTOTI(L6)
WFE3CR(L6)=XFE3CI*WTOTI(L6)
WCARR(L6)=XCARI*WTOTI(L6)
WGANG(L6)=XGANGI*WTOTI(L6)
VGAS(L6,1)=0.0
VRATE(L6,1)=0.0
VRATE(L6,2)=0.0
PPOR(L6,1)=PORINI
162 CONTINUE
DO 165 L6=K+1,M
PPOR(L6,1)=0.0
165 CONTINUE
IF(L6.EQ.K+1)PPOR(L6,1)=SPOR

*****PRINT OUT OF INITIAL CONDITIONS
WRITE(6,170) M,K,DWP,DWS,DT1,DT2,DT3,TMAX,KLMAX,
1 NSPF
WRITE(6,175) DBEAD,WBEAD,TKBEAD,CBEAD,XRBEAD,EMB
WRITE(6,180) DSL,CSL,TKSL,SPOR,DPSLAG,SMELT,BTEMP,
1 SFUS,HMIN,TKGAS,EMS,XRAD
WRITE(6,190) DINIT,WPELI,PFUS,PMELT,TINIT,DPELI,EMP,
1 PORINI,DPPEL,ATKL,ATKH
WRITE(6,195) XFEI,YFE,XFE01,YFE0,XCARI,YCAR,XCFE3I,
1 FRCARB,XFE3CI,YFE3C,XGANGI,YGANG
WRITE(6,197) C1TS,C1TF,C2TS,C2TF,C3TS,C3TF,C4TS,C4TF
WRITE(6,198) AERL,CRL,AERH,CRH,CRG
170 FORMAT(/1HA,T50,'PROGRAM GRID INPUT'/
1 1HA,5X,'NUMBER OF TOTAL ELEM ;M = ',I12,
1 T65, 'NUMBER OF PELLET ELEM ;K = ',I12/
1 1HA,5X,'STEP SIZE IN PELLET ;DWP = ',F12.8,
1 T65, 'STEP SIZE IN SLAG ;DWS = ',F12.8/
1 1HA,5X,'TIME STEP SIZE AT START ;DT1 = ',F12.8,
'TIME STEP SIZE #2
5X,'TIME STEP SIZE #3
MAX RUN TIME,S
5X,'MAX # TIME STEPS
SLAG PEN? N=0, Y=1

FORMAT(/1HA,T50,'THERMOCOUPLE PROPS'/
1 HA,5X,'BEAD DIAMETER IN CM ;DBEAD =',F12.8,
1 T65,'BEAD MASS IN G ;WBEAD =',F12.8/
1 HA,5X,'BEAD THERM CONDUCTIVITY ;TKBEAD =',F12.8,
1 T65,'BEAD SPEC HEAT ;CBEAD =',F12.8/
1 HA,5X,'FRACTION HTRANS BY RADIAT ;XRBEAD =',F12.8,
1 T65,'EMMISSIVITY OF BEAD ;EMB =',F12.8)


FORMAT(/1HA,T50,'SLAG AND BATH PROP INPUT'/
1 HA,5X,'SLAG DENSITY ;DSL =',F12.2,
1 T65,'SLAG SPECIFIC HEAT ;CSL =',F12.8/
1 HA,5X,'SLAG THERM CONDUCTIVITY ;TKSL =',F12.8,
1 T65,'SLAG POROSITY ;SPOR =',F12.8/
1 HA,5X,'SLAG PORE DIA ;DPSLAG =',F12.8,
1 T65,'SLAG MELTING TEMP ;SMELT =',F12.2/
1 HA,5X,'SLAG BATH TEMP ;BTMP =',F12.2,
1 T65,'SLAG HEAT OF FUSION ;SFUS =',F12.2/
1 HA,5X,'MIN HEAT TRANS COEF ;HMIN =',F12.8,
1 T65,'GAS THERM COND ;TKGAS =',F12.8/
1 HA,5X,'SLAG EMMISSIVITY ;EMS =',F12.8,
1 T65,'FRAC SURF AREA W/O CONTACT;XRAD =',F12.8)


FORMAT(/1HA,T50,'PELLET PROP INPUT'/
1 HA,5X,'INIT PELLET DIAMETER ;DINIT =',F12.8,
1 T65,'INIT PELLET MASS ;WPELI =',F12.8/
1 HA,5X,'PELLET HEAT OF FUSION ;PFUS =',F12.2,
1 T65,'PELLET MELTING TEMP ;TMELT =',F12.2,
1 HA,5X,'PELLET INIT TEMP ;TINIT =',F12.2,
1 T65,'PELLET DENSITY ;DPELI =',F12.2/
1 HA,5X,'PELLET EMMISSIVITY ;EMP =',F12.8,
1 T65,'INIT PELLET POROSITY ;PORINI =',F12.8/
1 HA,5X,'PELLET POR DIA, CM ;DPPEL =',F12.8,
1 T65,'PELLET LOW TEMP TK ;ATKL =',F12.8/
1 HA,5X,'PELLET HIGH TEMP TK ;ATKH =',F12.8)


FORMAT(/1HA,T50,'INIT PELLET COMPOSITION'/
1 HA,5X.'WT FT IRON ;XFEI =',F12.8,
1 T65,'VOL FT IRON ;YFE =',F12.8/
1 HA,5X,'WT FT FEO ;XFEOI =',F12.8,
1 T65,'VOL FT FEO ;YFEO =',F12.8/
1 1HA.5X,'WT FR CAR
1 T65, 'VOL FR CAR
1 1HA.5X,'WT FR C AS FE3C
1 T65, 'FR OF TOTAL C AS FE3C
1 1HA.5X,'WT FR FE3C
1 T65, 'VOL FR FE3C
1 1HA.5X,'WT FR GANGUE
1 T65, 'VOL FR GANGUE

* *

197 FORMAT(/1HA,T50,'TRANS TEMP RANGES'/
1 1HA.5X,'T START FE3C DISSOLUTION ;C1TS =',F12.2,
1 T65, 'T END FE3C DISSOLUTION ;C1TF =',F12.2/
1 1HA.5X,'T START A>G TRANS ;C2TS =',F12.2,
1 T65, 'T END A>G TRANS ;C2TF =',F12.2/
1 1HA.5X,'T START G>D TRANS ;C3TS =',F12.2,
1 T65, 'T END G>D TRANS ;C3TF =',F12.2/
1 1HA.5X,'START TK INCREASE ;C4TS =',F12.2,
1 T65, 'END TK INCREASE ;C4TF =',F12.2)

* *

198 FORMAT(/1HA,T50,'RXN KINETIC INFO'/
1 1HA.5X,'ACT ENERGY FOR LT RXN ;AERL =',F12.2,
1 T65, 'COEF FOR LT RXN ;CRL =',F12.6/
1 1HA.5X,'ACT ENERGY FOR HT RXN ;AERH =',F12.2,
1 T65, 'COEF FOR HT RXN ;CRH =',F12.6/
1 1HA.5X,'COEF FOR GAS DIFF RXN ;CRG =',F12.6)

* *

RETURN
END
***MAIN PROGRAM***

**INCLUDE 'COM.FOR'**

**MAIN CALLING PROGRAM**

**READ IN DATA**
CALL READ

**INITIALIZE FOR ZERO TIME**
CALL INIT

**CALC HEAT TRANS COEF**
10 CONTINUE
CALL EVOL

**COMPUTE RESULTS FOR NEXT TIME AND PRINT**
CALL COMPUT

**ADJUST GRID SPACING**
CALL GRID

**SHIFT NEW TIME DATA INTO PRESENT TIME ARRAY**
CALL SHIFT

**INCREMENT AND TEST TIME**
KL=KL+1
DT=DT1
IF(TIME.GT.1.0) DT=DT2
IF(TIME.GT.30.0) DT=DT3
TIME=TIME+DT
IF(TIME.GE.TMAX) GOTO 30
IF(KL.GE.KLMAX) GOTO 30
IF(M1.LE.1) GOTO 30
GOTO 10

30 CONTINUE
WRITE(6,*)'END IN MAIN ;KL = ',KL
STOP
END
SUBROUTINE OUTS

INCLUDE 'COM.FOR'

********ELEMENTS OUTSIDE OF MOVING BOUNDARY
TEMP(I,2)=BTEMP
IF(M1-M11) 920,940,930
920 CONTINUE
TEMP(M1+1,2)=BTEMP
GOTO 940
930 CONTINUE
TEMP(M1,2)=SMELT
940 CONTINUE
PPOR(I,1)=0.0
QD=0.0

* IF(IFLAG.NE.0) IFLAG=-1
  IF(IFLAG.EQ.0) IFLAG=8

RETURN
END
SUBROUTINE PBODY

INCLUDE 'COM.FOR'

******PELLET BEAD INTERFACE AND ADJ ELEMENTS

IF(I.LE.2) GOTO 570
GOTO 580
570 CONTINUE

GET ADJ ELEM THERM COND
TO2=TEMP(2,1)
IREM=I
I=2
CALL ELEM(I)
CALL COMP(I)
CALL PTCOND(TO2)
CALL PSPHT
I=IREM
DD=DPEL
IF(I.GT.IPS)DD=DPEL+DSL*PPOR(I,1)
DC=CPEL
DTK=TKPEL

RESET TEMP AND CALC INTERFACE INFO
CALL ELEM(I)
TO2=TEMP(I,1)
RO=(RAD(2,1)-RAD(1,1))/2.0
RI=RAD(1,1)
TPBINT=(TKBEAD*RO*TEMP(1,1)+TKPEL*RI*TEMP(2,1))/
1 (TKBEAD*RO+TKPEL*RI)
SIG=1.36E-12

RADIATION CONTRIBUTION
BDT=(TEMP(2,1)-TEMP(1,1))/(1.0+(RO/TKPEL+RI/TBKEAD)*
1 (4.0*SIG*(TPBINT**3.0)/((1.0/EMB)+(1.0/EMP)-1.0)))
ALP=TKBEAD*RO/(TKBEAD*RO+TKPEL*RI)
BDTB=ALP*BDT
BDTP=BDT-BDTB
IF(I-2) 572,574,580

TEMP OF BEAD
572 CONTINUE
XP=TKBEAD*AREA0*DT/(WBEAD*CBEAD*RI)
XM=0.0
XFO=0.0
XCAR=0.0
XFE3C=0.0
PPOR(I,1)=0.0
XCO(I)=0.0
QD=0.0
TN2=TO2+XP*(1.0-XRBEAD)*(TPBINT-TO2)+XP*XRBEAD*
1 (TPBINT-BDTP-TO2)
TEMP(1,2)=TN2
GOTO 590
*
***** TEMP OF ELEM ADJ TO BEAD
574 CONTINUE
CALL ELEM(I)
CALL PPROP
XP=DTKO*AREA0*DT/(DPEL*CPEL*VOL*(RAD(3,1)-RI)/2.0)
XM=DTK*AREA1*DT/(DPEL*CPEL*VOL*(RO+RI))
QD=QRXN*DT/(DD*DC)
TN2=TO2+XP*(TEMP(3,1)-TO2)-XM*(1.0-XRBEAD)*(TO2-
1 TPBINT)-XM*XRBEAD*(TO2-TPBINT-BDTP)*0.0-QD
TEMP(2,2)=TN2
GOTO 590
580 CONTINUE
*
******** PELLET INTERIOR ELEMENT
TO2=TEMP(I,1)
CALL PPROP
DD=DPEL
IF(I.GT.IPS)DD=DPEL+DSL*PPOR(I,1)
DC=CPEL
DRI=(RADO-RAD(I-2,1))/2.0
*
DRO=(RAD(I+1,1)-RADI)/2.0
IF(I.EQ.M1-1)DRO=(RADO-RADI+DEL(1))/2.0
*
QD=QRXN*DT/(DD*DC)
*
TO1=TEMP(I-1,1)
TO3=TEMP(I+1,1)
*
CALL FDCALC
TEMP(I,2)=TN2
*
********* SET FLAG AND TEST FOR INSTABILITY
590 CONTINUE
IF((TN2.GT.PMELT).OR.(TN2.LT.0.0)) GOTO 600
IF(IFLAG.NE.0)IFLAG=-1
IF(IFLAG.EQ.0)IFLAG=1
**********
RETURN
600 CONTINUE
WRITE(6,*) 'END IN PBODY TN2= ',TN2
STOP
END
* SUBROUTINE PIH *
*********************************************************

SUBROUTINE PIH
INCLUDE 'COM.FOR'

** PELLET INTERFACE HEATING W/O SHELL
T02=TEMP(I,1)
CALL PPROP
DTKO=DTK
DD=DPEL
IF(I.GT.IPS) DD=DPEL+DSL*PPOR(I,1)
DC=CPEL

DRO=(RADO-RADI)/2.0
DRI=(RADO-RAD(I-2,1))/2.0

QD=QRXN*DT/(DD*DC)

TO1=TEMP(I-1,1)
TO3=((DRO*HTRANS*BTEMP)+(TKPEL*TO2))/(TKPEL+HTRANS*DRO)
IF(TO3.LE.SMELT) TO3=SMELT
TT=TO3

CALL FDCALC
TEMP(I,2)=TN2

IF(TN2.GT.PMELT) TEMP(I,2)=PMELT

IF(((TEMP(I,2).GT.BTEMP).OR.(TEMP(I,2).LT.0.0)) GOTO 950
IF(IFLAG.NE.0) IFLAG=-1
IF(IFLAG.EQ.0) IFLAG=3

RETURN
CONTINUE
WRITE(6,*) 'END IN PIH ' TN2= ',TEMP(I,1)
STOP
END
**************
* SUBROUTINE PIM *
**************

* *
SUBROUTINE PIM
INCLUDE 'COM.FOR'
*

********PELLET INTERFACE DURING MELTING
T02=TEMP(I,1)
VOLREM=VOL
VOL=(4.0/3.0)*3.14*(RADO**3.0-RADI**3.0)
CALL PPROP
DD=DPEL
VOL=VOLREM
DLF=PFUS
DMELT=PMELT
*
IF(I.GT.2) DRI=(DEL(1)+RAD(I-1,1)-RAD(I-2,1))/2.0
IF(I.EQ.2) DRI=(DEL(1)+RAD(I-1,1))/2.0
IF(I.EQ.1) DRI=DEL(1)
*
IF(I.EQ.1) T01=PMELT
TT=PMELT
IF(I.NE.1) T01=TEMP(I-1,1)
DWA=DW
*
CALL BOUND
*
IF(DEL(2).LE.0.0) GOTO 1050
GOTO 1060
1050 CONTINUE
DWA=RADI-RAD(I-2,1)
M1=M1-1
DEL(2)=DEL(2)+DWA
TEMP(M1,2)=PMELT
TEMP(M1+1,2)=BTEMP
IF(M1.LT.1) GOTO 1065
IF((DEL(2).LE.0.0).OR.(DEL(2).GT.DWA)) GOTO 1065
1060 CONTINUE
*
IF(IFLAG.LE.0) IFLAG=-1
IF(IFLAG.EQ.0) IFLAG=4
**********
RETURN
1065 CONTINUE
WRITE(6,*) 'END IN PIM ;M1 = ',M1,' DEL(2) = ',DEL(2)
STOP
END
SUBROUTINE PPROP

INCLUDE 'COM.FOR'

*****COORDINATE CALLING OF PELLET PROPS
CALL COMP(I)
CALL PTCOND((TO3+TO2)/2.0)
DTKO=TKPEL
CALL PTCOND((TO2+TO1)/2.0)
DTKI=TKPEL
IF(I.EQ.1PS+1) DTKI=TKPELL
CALL PTCOND(TO2)
DTK=TKPEL
CALL PSPHT
CALL RXN

RETURN
END
SUBROUTINE PRINT

INCLUDE 'COM.FOR'

* PRINT OUTPUT

TEM = TEMP(I,1) - 273.0
TIC = TT - 273.0
TPLUS = TEMP(I,2) - 273.0
TBPC = TBPCINT - 273.0

IF(I.EQ.1) WRITE(6,410) TIME,KL,HTRANS,IPS+1,RSURF,THICK,
1 GVOL.GRATE,XCOAVG
IF(I.EQ.2) WRITE(6,430) RAD(1,1),TBPC
IF(I.EQ.K+1) WRITE(6,430) RAD(K,1),TIC
IF(I.LE.K) WRITE(6,420) I,DIST,TEM,XFEO,
1 XCAR,XFE3C,PPOR(I,1),DC,DTK,ENTHL,
1 ENTHH
IF(I.GT.K) WRITE(6,425) I,DIST,TEM,PPOR(I,1)

FORMAT(1H1.125('*')/1X,
1 5X, 'TIME = ',F12.2,
1 T50, 'TIME ELEM # = ',I12,
1 T95, 'H TRANS COEF = ',F12.8/1X,
1 5X, 'SLAG PEN TO# = ',I12,
1 T50, 'DIST TO SURF = ',F12.8,
1 T95, 'SLAG TH MM = ',F12.4/1X,
1 5X, 'GAS VOL CC = ',F12.2,
1 T50, 'RATE CC/MIN = ',F12.2,
1 T95, 'AVG GAS XCO = ',F12.8/1X/1X,
1 'ELEM #',T13,'POSITION',T27,'TEMP C',T39,'XFE0',T52,'XCAR',
1 T64,'XFE3C',T75,'POROSITY'/1X,125(' - ')/)

FORMAT(1X,18,F12.8,F12.2,4F12.6,2F12.6,2F12.2)

FORMAT(1X,18,F12.8,F12.2,36X,F12.6)

FORMAT(1X.8('*'),T10,F12.8,F12.2)

RETURN

END
SUBROUTINE PSPHT

INCLUDE 'COM.FOR'

********PELLET SPECIFIC HEAT

******INITIALIZE CP EFF DUE TO TRANSFORMATIONS
CRXN1=0.0
CRXN2=0.0
CRXN3=0.0
CRXN4=0.0
RTPI=3.1416**0.5

******SPECIFIC HEATS OF DRI PELLET COMPONENTS

*** ALPHA IRON INCLUDING CURIE TRANS
CFEA=(4.78+(3.327E-3)*TO2+(2.4838E-6)*TO2*TO2)/55.85
IF((TO2.GE.800.0).AND.(TO2.LT.1000.0))CFEA=(54.618
1-0.1176577*TO2+(7.5988E-5)*TO2*TO2)/55.85
IF((TO2.GE.1000.0).AND.(TO2.LT.1020.0))CFEA=(-53.49
1+.066500097*TO2)/55.85
IF((TO2.GE.1020.0).AND.(TO2.LT.1042.0))CFEA=(
1-248.078+.2572727*TO2)/55.85
IF((TO2.GE.1042.0).AND.(TO2.LT.1060.0))CFEA=(
1 465.1684-.42722499*TO2)/55.85
IF(TO2.GE.1060.0)CFEA=(
1 203.1815-.324055*TO2+(1.358209E-4)*TO2*TO2)/55.85

*** GAMMA IRON
CFEG=(5.733+(1.9979E-3)*TO2)/55.85

*** DELTA IRON
CFED=(5.87759+(2.373E-3)*TO2)/55.85

**** PHASE FRACTIONS IN IRON TWO PHASE REGIONS
XAG=(TO2-C2TS)/(C2TF-C2TS)
IF(XAG.LT.0.0)XAG=0.0
IF(XAG.GT.1.0)XAG=1.0
XGD=(TO2-C3TS)/(C3TF-C3TS)
IF(XGD.LT.0.0)XGD=0.0
IF(XGD.GT.1.0)XGD=1.0

**** SPECIFIC HEAT OF IRON
CFE=(1.0-XAG)*CFEA+(XAG-XGD)*CFEG+XGD*CFED

**** SPECIFIC HEAT OF FEO
CFEO=(0.169)+(2.9E-5)*TO2-(9.7E+1)*(TO2**(-2.0))
SPECIFIC HEAT OF GANG
CGANG=(0.227)+(6.13E-5)*TO2-(5.74E+3)*(TO2**(-2.0))

SPECIFIC HEAT OF FE3C
CFE3C=(0.109)+(1.11E-4)*TO2
IF(TO2.GT.463.0)CFE3C=(0.143)+(1.67E-5)*TO2

SPECIFIC HEAT OF CARBON
CCAR=(2.17E-3)+(7.75E-4)*TO2-(2.95E+3)*(TO2**(-2.0))
1-(3.46E-7)*TO2*TO2
IF(TO2.GT.1100.0)CCAR=(0.487)+(8.66E-6)*TO2-(6.3E+4)*
1(TO2**(-2.0))

EFF FE3C & CARBON DISSOLV SPEC HEAT
BD1=(C1TF-C1TS)/4.0
BT1=(C1TS+C1TF)/2.0
XFE3CR=WFE3CR(I)/WTOT(I)
XCARR=WCARR(I)/WTOT(I)
CRXN1=((10217.0/(RTPI*179.55*BD1))*XFE3CR+(12480.0/
1(RTPI*12.0*BD1))*XCARR)*EXP(-((TO2-BT1)/BD1)**2.0)

EFF A>G SPEC HEAT
BD2=(C2TF-C2TS)/4.0
BT2=(C2TS+C2TF)/2.0
BX2=(1185.0-BT2)/185.0
IF(BX2.LT.0.0)BX2=0.0
IF(BX2.GT.1.0)BX2=1.0
BH2=160
CRXN2=(BH2/(RTPI*BD2*55.85))*EXP(-((TO2-BT2)/
1BD2)**2.0)*XFEI

EFF G>D SPEC HEAT
BD3=(C3TF-C3TS)/4.0
BT3=(C3TF+C3TS)/2.0
CRXN3=(200.0/(RTPI*BD3*55.85))*EXP(-((TO2-BT3)/
1BD3)**2.0)*XFEI

NEWMAN-KOPP MEAN SPECIFIC HEAT
CPEL=CFE*XFE+CFE0*XFE0+CCAR*XCAR+CFE3C*XFE3C+CGANG*XGANG
1+CRXN1+CRXN2+CRXN3+CRXN4

ADJUST DENSITY IF SLAG PENETRATES
CPELL=CPEL
IF(I.GT.IPS)CPEL=CPEL+CSL*PPOR(I,1)*(DSL/DPEL)

RETURN
1235 CONTINUE
STOP
END
SUBROUTINE PSURF

INCLUDE 'COM.FOR'

********PELLET SURFACE W/ ADJ SOLID SLAG

*****EVALUATE ADJ SLAG ELEM THERM COND
TO2=TEMP(I+1,1)
CALL STCOND

*****EVALUATE PELLET ELEM PROP
TO2=TEMP(I,1)
CALL PPROP

********DEFINE FICTICIOUS INTERFACE TEMP TO SATISFY BC
RO=(RAD(I+1,1)-RADO)/2.0
IF(M1.EQ.K+1)RO=DEL(1)/2.0
RI=(RADO-RADI)/2.0

TINT=*((DTK*RO)*TEMP(I,1)+(TKSH*RI)*TEMP(I+1,1))/
1 *((DTK*RO)+(TKSH*RI))
TT=TINT

********CALC NEW ELEM TEMP
DD=DPEL
IF(I.GT.IPS)DD=DPEL+DSL*PPOR(I,1)
DC=CPEL

DRO=(RADO-RADI)/2.0
DRI=(RADO-RAD(I-2,1))/2.0
QD=QRXN*DT/(DD*DC)

*******ESTIMATE OF INT TEMP DTEMP DUE TO RADIATION
SIG=1.36E-12
ZTD=((TEMP(K+1,1)-TEMP(K,1))/((1.0*(RO/TKSH+RI/DTK))*(
1 4.0*SIG*(TT**3.0))/((1.0/EMP)+(1.0/EMS)-1.0))))

ALP=DTK*RO/(DTK*RO+TKSH*RI)
ZTDP=ALP*ZTD
ZTDS=ZTD-ZTDP

*******CALCULATE NEW NODE TEMPS
TO1=TEMP(I-1,1)
XXP=DTK*AREA0*DT/(VOL*DD*DC*DRO)
XXM=DTKI*AREA1*DT/(VOL*DD*DC*DRI)

TN2=TO2+XXP*(1.0-XRAD)*(TT-TO2)+XXP*XRAD*(TT-ZTDP-TO2)-
1 XXM*(TO2-TO1)-QD

TEMP(I,2)=TN2
IF((TN2.GT.PMELT).OR.(TN2.LT.0.0)) GOTO 700
IF(IFLAG.NE.0) IFLAG=-1
IF(IFLAG.EQ.0) IFLAG=2
********
RETURN
CONTINUE
700
WRITE(6,*) 'END IN PSURF  TN2=',TN2
STOP
END
SUBROUTINE PTCOND

SUBROUTINE PTCOND(UU)
INCLUDE 'COM.FOR'

********PELLET THERMAL CONDUCTIVITY

*** PORE THERMAL CONDUCTIVITY
TKPOR=((4.115E-12)*DPPEL*(UU**3.0))+TKGAS

*** FRACTION AS GAMMA FE
XAG=(UU-C4TS)/(C4TF-C4TS)
IF(XAG.LT.0.0)XAG=0.0
IF(XAG.GT.1.0)XAG=1.0

*** CHOOSE LOW OR HIGH T TK
TKPEL=(1.0-XAG)*ATKL+XAG*ATKH

********SAVE ORIG PELLET TK

TKPELL=TKPEL

********ESTIMATE TK OF SOLIDS USING KOH & FORTINI
TKSOL=TKPEL*((1.0+11.0*PPOR(I,1))/
1 (1.0-PPOR(I,1)))

********ESTIMATE TK OF PELLET WITH SLAG PENETRATION
*** USING GEOMETRIC MEAN TK
IF(I.GT.IPS)TKPEL=TKSOL**(1.0-PPOR(I,1))*
1 TKSL**PPOR(I,1)

******
RETURN

1250 CONTINUE
STOP
END
SUBROUTINE READ

INCLUDE 'COM.FOR'

READ GRID VARIABLES
READ(5,*)K,M,DWS,DT1,DT2,DT3,TMAX,KLMAX,NSPF

READ SLAG BATH COND AND SHELL PROP VARIABLES
READ(5,*)DSL,CSL,TKSL,SPOR,DPSLAG,SMELT,BTEMP,  
1 SFUS,HMIN,EMS,XRAD

READ PELLET PROPERTIES
READ(5,*)DINIT,WPELI,PMELT,TINIT,PFUS,EMP,DPEL,  
1 ATKL,ATKH

READ PELLET COMPOSITION
READ(5,*) XFE0I,XCARI,XCFE3I,XGANGI

READ PELLET COMPONENT PROPS
READ(5,*) DFE,DFEO,DFE3C,DCAR,DGANG,TKFE0,TKFE3C,  
1 TKCAR,TKGANG,TKGAS

READ REACTION KINETIC INFO
READ(5,*) AERL,CRL,AERH,CRH,CRG

READ TRANSFORMATION TEMP RANGES
READ(5,*) C1TS,C1TF,C2TS,C2TF,C3TS,C3TF,C4TS,C4TF

READ THERMOCOUPLE BEAD PROPS
READ(5,*)DBEAD,WBEAD,TKBEAD,CBEAD,EMB,XRBEAD

WRITE INPUT DATA HEADER
WRITE(6,50)
50  FORMAT(/40X,35('**')/40X,'*',11X,'INPUT DATA',  
    1 11X,'**'/40X,35('**')//)

RETURN
END
SUBROUTINE RXN

INCLUDE 'COM.FOR'

****** PELLET REACTION KINETICS

XPFEO=WFEO(I)/WTOTI(I)
PXPFEO=XPFEO**(2.0/3.0)

****** GAMMA Fe FRACTION

PHI2=(C2TF-TO2)/(C2TF-C2TS)
IF(PHI2.LT.0.0)PHI2=0.0
IF(PHI2.GT.1.0)PHI2=1.0

****** CARBIDE FRACTION

PHI1=(C1TF-TO2)/(C1TF-C1TS)
IF(PHI1.LT.0.0)PHI1=0.0
IF(PHI1.GT.1.0)PHI1=1.0

****** REACTION KINETIC MODELS

RRX1=0.0
IF(TO2.GT.(TINIT+1.0))RRX1=CRL*EXP(-(AERL/
 1 (1.987*TO2)))*PHI1*WTOTI(I)
IF((XFE3C.LE.0.0).OR.(XFEO.LE.0.0))RRX1=0.0

RRX2=CRH*EXP(-(AERH/(1.987*TO2)))*(PXPFEO
1 )*WTOTI(I)
IF((XCAR.LE.0.0).OR.(XFEO.LE.0.0))RRX2=0.0

RRX3=0.0
IF(TO2.GT.(TINIT+1.0))RRX3=CRG*PHI1*WTOTI(I)
IF(XFEO.LE.0.0)RRX3=0.0
IF((XFE3C.LE.0.0).AND.(XCAR.LE.0.0))RRX3=0.0
FRC=0.0
IF((XCAR+XFE3C*0.06683).GT.0.0)FRC=XFE3C*
1 0.06683/(XFE3C*0.06683+XCAR)

****** ELEM GAS EVOL RATES

VRATE(I,1)=(22400.0/(71.85*(2.0-XCO(I))))*
1 (RRX1+RRX3+FRC)
IF(VRATE(I,1).LE.0.0)VRATE(I,1)=0.0
VRATE(I,2)=(22400.0/(71.85*(2.0-XCO(I))))*
1 (RRX2+RRX3*(1.0-FRC))
IF(VRATE(I,2).LE.0.0)VRATE(I,2)=0.0
VGAS(I,2)=VGAS(I,1)+(VRATE(I,1)+VRATE(I,2))*DT

****** RXN ENTHALPIES

ENTHL=((1.0-XCO(I))/(2.0-XCO(I)))*(-94321.0)
1 +(XCO(I)/(2.0-XCO(I)))*(-26771.0)
1  -(1.0/(2.0-XCO(I)))*(5200.0)
1  -(-62941.0)

*  
ENTHH=((1.0-XCO(I))/(2.0-XCO(I)))*(-94321.0)
1  +XCO(I)/(2.0-XCO(I)))*(-26771.0)
1  +(.95)*(979.0)
1  -(1.0/(2.0-XCO(I)))*(12480.0)
1  -(-62941.0)

*  
QRXN=(1.0/(71.85*VOL))*(ENTHL*(RRX1+RRX3*
1  FRCARB)+ENTHH*(RRX2+RRX3*(1.0-FRCARB)))

********GAS COMP BASED ON CARBON GASIFICATION EQUIL
EQCG=10.0**(3.2673-(8820.690/TO2)-(1.208714E-3
1  *TO2)+(0.153734E-6*TO2*TO2)+2.295483*
1  LOG10(TO2))

*  
XCO(I)=((EQCG*EQCG+4.0*EQCG)**0.5-EQCG)/2.0

********COMP SHIFT DUE TO RXN
WFEO(I)=WFEO(I)-(71.85*(2.0-XCO(I))/22400.0)
1  *(VRATE(I,1)+VRATE(I,2))*DT
IF(WFEO(I).LE.0.0)WFEO(I)=0.0

*  
WCARR(I)=WCARR(I)-(12.0/22400.0)*VRATE(I,2)*DT

*  
WFE3CR(I)=WFE3CR(I)-(179.55/22400.0)*VRATE(I,1)
1  *DT

*  
WFER(I)=WFER(I)+(55.85*(2.0-XCO(I))/22400.0)*
1  VRATE(I,2)*DT+(55.85*(3.0+(2.0-XCO(I)))/22400.0)
1  *VRATE(I,1)*DT

******COMP SHIFT DUE TO CARBIDE DISSOLUTION
WFE3C=WFE3CR(I)*PHI1
WFE=WFER(I)+(167.55/179.55)*WFE3CR(I)*(1.0-PHI1)
WCAR=WCARR(I)+(12.0/179.55)*WFE3CR(I)*(1.0-PHI1)
IF(WCAR.LE.0.0)WCAR=0.0
WTOT(I)=WFEO(I)+WFER(I)+WFE3CR(I)+WCARR(I)
1  +WGANG(I)

******

RETURN
END
SUBROUTINE SBODY

INCLUDE 'COM.FOR'

******SOLID ELEMENT IN SLAG BODY

T02=TEMP(I,1)
CALL SPROP
DTKI=TKSH
DTKO=TKSH
DTK=TKSH
DD=DSH
DC=CSH

DRI=(RADO-RAD(I-2,1))/2.0
DRO=(RAD(I+1,1)-RADI)/2.0
IF(I.EQ.M1-1) DRO=(RADO+DEL(1)-RADI)/2.0

QD=0.0

TO1=TEMP(I-1,1)
TO3=TEMP(I+1,1)

CALL FDCALC
TEMP(I,2)=TN2

IF((TN2.GT.SMELT).OR.(TN2.LT.0.0)) GOTO 900
IF(IFLAG.NE.0) IFLAG=-1
IF(IFLAG.EQ.0) IFLAG=7

RETURN

900 CONTINUE
WRITE(6,*) 'END IN SBODY  TN2=',TN2
STOP
END
***************SUBROUTINE SHIFT***************
SUBROUTINE SHIFT
***************SUBROUTINE SHIFT***************
SUBROUTINE SHIFT
INCLUDE 'COM.FOR'

**********MOVE NEW VALUES INTO PRESENT TIME ARRAY
DO 750 L2=1,M
  TEMP(L2,1)=TEMP(L2,2)
  RAD(L2,1)=RAD(L2,2)
  CONTINUE
DO 752 L2=1,K
  VGAS(L2,1)=VGAS(L2,2)
  CONTINUE
DEL(1)=DEL(2)

*******
RETURN
END
SUBROUTINE SLIN

INCLUDE 'COM.FOR'

SLAG ELEMENT ADJ TO PELLET
TO2=TEMP(I,1)
CALL SPROP
DTK=TKSH
DTKI=TKSH
DTKO=TKSH
DD=DSH
DC=CSH

INT TEMP RETAINED FROM PREV STEP IN PSURF
DRI=(RADO-RADI)/2.0
DRO=(RAD(I+1,1)-RADI)/2.0
IF(M1.EQ.K+2)DRO=((RADO-RADI)/2.0)+DEL(1)/2.0
QD=0.0

TO3=TEMP(I+1,1)
CALCULATE NEW NODE TEMP
XXP=DTK*AREA0*DT/(VOL*DD*DC*DRO)
XXM=DTK*AREA1*DT/(VOL*DD*DC*DRI)

TN2=TO2+XXP*(TO3-TO2)-XXM*(1.0-XRAD)*(TO2-TT)-
XXM*XRAD*(TO2-TT-ZTDS)-QD
TEMP(I,2)=TN2

IF((TN2.GT.SMELT).OR.(TN2.LT.0.0)) GOTO 800
IF(IFLAG.NE.0) IFLAG=-1
IF(IFLAG.EQ.0) IFLAG=6

RETURN

END
SUBROUTINE SPROP *

**COORDINATE SHELL PROP CALCS**

PPOR(I,1) = SPOR
DSH = DSL * (1.0 - SPOR)
CSH = CSL
CALL STCOND

RETURN
END
***************
* SUBROUTINE SSE *
***************

SUBROUTINE SSE
INCLUDE 'COM.FOR'

******SLAG SURFACE ELEMENT
T02=TEMP(I,1)
CALL SPROP
DD=DSH
DTK=TKSH
DTKO=TKSH
DTKI=TKSH
DLF=SFUS
DMELT=SMELT

DRI=((RADI-RAD(I-2,1))/2.0)+DEL(1)/2.0
IF(I.EQ.K+1) DRI=DEL(1)/2.0

TO1=TEMP(I-1,1)
IF(M1.EQ.K+1)TO1=TT
QD=0.0

DWA=DW
CALL BOUND

*** SHELL FREEZES FOREWARD 1 ELEMENT
IF(DEL(2).GE.DW) GOTO 1120
GOTO 1140
1120 CONTINUE
M1=M1+1
DWA=RAD(M1-1.1)-RADO
DEL(2)=DEL(2)-DW
TEMP(M1-2)=SMELT

*** INTERPOLATION OF TEMP OF NODAL PT M1-1
RM=RAD(M1-1.1)+DEL(2)/2.0
RM1=(RAD(M1-1.1)-RAD(M1-2.1))/2.0+RAD(M1-2.1)
RM2=(RAD(M1-2.1)-RAD(M1-3.1))/2.0+RAD(M1-3.1)
RM3=(RAD(M1-3.1)-RAD(M1-4.1))/2.0+RAD(M1-4.1)
TM=SMELT
TM2=TEMP(M1-2,2)
TM3=TEMP(M1-3,2)
CC=((TM-TM3)/(RM-RM3))-((TM2-TM3)/(RM2-RM3))
1 (((RM*RNM3)/RM3)-(RM2*RM2-RM3*RM3)/
1 (RM2-RM3))
BB=((TM2-TM3)/(RM2-RM3))-((RM2*RM2-RM3*RM3)/
1 (RM2-RM3))
AA = TM3-RM3*RM3*CC-RM3*BB
TM1 = AA + BB*RM1 + CC*RM1*RM1
TEMP(M1-1,2) = TM1
GOTO 1180

* 1140 CONTINUE
*
*** SHELL MELTS BACK 1 ELEMENT
IF(DEL(2) .LE. 0.0) GOTO 1150
GOTO 1160
1150 CONTINUE
DWA = RADI - RAD(M1-2,1)
M1 = M1 - 1
DEL(2) = DEL(2) + DWA
IF(M1 .EQ. K) DEL(2) = RAD(K,1) - RAD(K-1,1)
TEMP(M1,2) = SMELT
TEMP(M1+1,2) = BTEMP
GOTO 1180
*
1160 CONTINUE
*
*** SHELL INT MOVEMENT WITHIN AN ELEMENT
TEMP(M1,2) = SMELT
*
1180 CONTINUE
*
*** TEST FOR TOO LARGE AN INTERFACE MOVEMENT
IF((DEL(2) .LT. 0.0) .OR. (DEL(2) .GT. DWA)) GOTO 1185
*
*
IF(IFLAG .NE. 0) IFLAG = -1
IF(IFLAG .EQ. 0) IFLAG = 5
******
RETURN
1185 CONTINUE
WRITE(6,*) 'END IN SSE ; DEL(2) TOO LARGE = ', DEL(2)
STOP
END
**************
* SUBROUTINE STCOND 
**************
*
SUBROUTINE STCOND
INCLUDE 'COM.FOR'
*
************SLAG THERMAL CONDUCTIVITY WITH PORES 
*
SPCOND=((4.06E-12)*DPSLAG*(TO2**3.0))+TKGAS
TKSH=TKSL**(1.0-SPOR)*SPCOND**SPOR
*
******
RETURN
END
APPENDIX G

Models of the Effective Thermal Conductivity for Porous Solids

The influence of porosity on the effective thermal conductivity of a porous solid may be estimated from a number of theoretical and empirical models. The upper bound relationship\(^{(86)}\) is predicted using the series conduction model,

\[
k_{\text{eff}} = (1 - e_p)k_m + e_p k_p
\]

where \(e_p\) is the porosity of the material,
\(k_m\) is the thermal conductivity of the substrate,
and \(k_p\) is the thermal conductivity of a porous region.
The lower bound relationship\(^{(86)}\) is predicted from the parallel conduction model,

\[
k_{\text{eff}} = \left\{ \frac{(1 - e_p)/k_m}{(1 - e_p)/k_p} \right\}^{-1}
\]

In these upper and lower bound models, the solid and porous regions are assumed to be oriented in the direction of heat flow, and perpendicular to the direction of heat flow, respectively.

A more conservative set of bounding conditions is obtained by using the Maxwell-Eucken relationship,\(^{(73)}\) which is based on the assumption that one phase in the porous solid is continuous and the other phase is distributed, randomly, within the continuous phase,

\[
k_{\text{eff}} = k_c \frac{1 + 2 e_p \left[ 1 + \frac{k_c}{k_d} \right]}{1 - e_p \left[ 1 - \frac{k_c}{k_d} \right] / \left[ 1 + \frac{k_c}{k_d} \right]}
\]

\(^{(G-3)}\)
where $k_c$ is the thermal conductivity of the continuous phase, and $k_d$ is the thermal conductivity of the dispersed phase.

The conservative upper bound solution is obtained by using the solid substrate as the continuous phase. The lower bound solution is obtained by using the porous region as the continuous phase.

An intermediate prediction can be made by employing the geometric mean formula proposed by Ben-Amoz, \(^{(81)}\) which is based on the assumption that the solids and the pores are randomly interdispersed in the porous material,

\[
  k_{\text{eff}} = k_m (1 - e_p) k_p (G-4a)
\]

This model predicts values for the effective thermal conductivity of a porous solid that lie between the conservative upper and lower bound predictions of the Maxwell-Eucken formula. The formalism is also unique because it is easily expanded for use in multicomponent systems,

\[
  k_{\text{eff}} = \prod_i Y_i k_i^{\text{eff}} \quad \text{(G-4b)}
\]

A number of empirical correlations have also been developed to relate the porosity of a porous solid to its effective thermal conductivity.\(^{(80,86,87)}\) A correlation that is widely accepted for the prediction of the effective thermal conductivity of porous metallic solids is the relationship proposed by Koh and Fortini, \(^{(80)}\)

\[
  k_{\text{eff}} = k_m (1 - e_p)/(1 + ne_p) \quad \text{(G-5)}
\]

\[\]
where \( n \) is a constant which is equal to 11 for sintered metal powders. Equation (G-5) has been shown to hold for different metals, and over a wide range of porosities.
BIBLIOGRAPHY


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(49) J.F. Elliott, M. Gleiser, and V. Ramakrishna: Thermochemistry for Steelmaking, Addison-Wesley, Reading, Ma., 1963.


(88) S. Olsen: University of Trondheim, Norwegian Institute of Technology, Trondheim, Norway, unpublished research, 1982.

BIOGRAPHICAL NOTE

The author was born in Camden, New Jersey on April 23, 1955, and was raised in the neighboring town of Haddon Heights. He graduated from Haddon Heights High School in 1973.

The author enrolled in the College of Engineering at Drexel University and subsequently joined Foote Mineral Company as a Metallurgical Co-op student. He graduated from Drexel University in 1978 with a B.S. degree and an M.S. degree in Metallurgical Engineering.

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