CHAPTER VI

DISCUSSION

The experimental results summarized in Chapter IV are discussed in this chapter. The information on the formation and evolution of gas from DRI is first analyzed through the thermodynamics of carbon-oxygen reactions. Then the data on the transfer of heat to the metallic particles immersed in hot slags are discussed through comparisons made with the results of the simulation model described in Chapter V.

A. Evolution Results

A brief discussion of the constant and variable temperature extractions is given in this section.

1. Constant Temperature

Removal of oxygen from DRI when heated in a capsule of helium is accomplished by carbon or carbon monoxide. The carbon present in DRI may be in form of Fe_3C , free graphite or dissolved in the iron. For HYL and Midrex materials, Fe_3C is reportedly the major constituent. The reduction reactions are thus as follows:

$$Fe_{x}^{0} + y Fe_{3}^{C} = (x+3y)Fe + y CO$$
 (6.1)

$$Fe_{y}O_{y} + y CO = xFe + yCO_{2}$$
 (6.2)

$$CO_2 + Fe_3C = 3Fe + 2CO$$
 (6.3)

A combination of reaction (6.2) with reaction (6.3) also leads to the reduction of DRI with cementite, as is illustrated by reaction (6.1). Reaction (6.3) is endothermic ($\Delta H = 35,240$ cal/mole CO_2^{77}) and is favored by high temperatures, as is shown in Figure 6-1. The amount of water vapor collected during the helium extraction tests was very small and probably entered the capsule as moisture with DRI or with DRI container.

The equilibrium partial pressure of CO in iron-oxygen system at total pressure of 1 atm is shown in Figure 6-1. Because of dissociation of carbon monoxide according to reaction (6.3) iron oxide cannot in theory be completely reduced below about 700°C. The broken lines in Figure 6-1 represent the metastable reduction reactions occurring in the Fe-O-C system. Also as is seen, when temperature rises, the equilibrium CO/CO₂ ratio for production of iron increases.

The partial pressure of CO that is in equilibrium with CO₂ and carbon changes from about zero to one when temperature rises from 500 to 800°C, as shown in Figure 6-1. Comparing with the data given in Tables 4-3 to 4-8, it is seen that these changes are consistent with results of the helium extraction tests. Also, as is seen from the equilibrium Fe-O-C diagram, above 700°C and with CO partial pressures of more than about 0.7, DRI can completely reduce to free iron. The results of helium extractions show that the effect of temperature on removal of oxygen from DRI samples decreases as temperature rises above 700°C.

Below 650°C, magnetite is stable. Between 650 and 700°C, wustite is expected to appear according to the following reactions:

$$Fe_{3}O_{4} + Fe_{3}C = 3Fe + 3''FeO'' + CO$$
 (6.4)



Fig. 6-1 Equilibrium Fe-O-C System at 1 atm (after Elliott, et al. 77).

$$2Fe_{3}O_{4} + Fe_{3}C = 3Fe + 6"FeO" + CO_{2}$$
 (6.5)

The equilibrium partial pressure of CO is 0.4 at 650°C. For Equations (6.4) and (6.5) the total volume of gas can be calculated as a function of the oxygen content of DRI:

$$V_{\rm F} = 2.19 \% 0$$
 (6.6)

where V_E is in cm³/g and %0 is weight percent of oxygen. A comparison is made of the volumes of gas (CO + CO₂) calculated from Equation (6.6) and the values measured during helium extraction of DRI samples in Table 6-1. For samples of higher oxygen contents, the measured volumes of evolved gases are slightly higher than the equilibrium gas volumes. The difference may be due to the reduction of small quantities of Fe₂O₃ to Fe₃O₄ at low temperatures.

2. Variable Temperature

Reactions (6.4) and (6.5) can similarly occur during bomb extraction of DRI. The formation of "FeO" starts at 650°C and will proceed at higher temperatures until the complete conversion of magnetite to wustite is achieved. This is due to the continuous increase of the temperature of DRI. Assuming 50 percent of the exhaust to be CO (cf. Figure 6-1), the total volume of the evolved gas can be computed from the following equation:

$$V_{\rm p} = 2.3 \% 0$$
 (6.7)

The total gas volumes calculated for various DRI samples are given in Table 6-2. The temperatures of the samples up to which these volumes

Table	<u>6-1 Vol</u>	ume of Gas Evolved fr	om DRI at 650°C.
	~	$v_{co} + v_{co}$	2., cm ³ /g
Sample	<u>%0</u>	He Extraction	Equilibrium
В	3.26	10.6	7.1
D	3.12	10.8	6.8
С	2.18	5.0	4.8
G	2.01	4.5	4.4
E	1.92	4.2	4.2
Lump Ore	1.85	4.0	4.0

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Table 6-1 Volume of Gas Evolued from DPT 650°

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Sample	$v_{\rm B}^{\rm , cm^3/g}$	Temp., °C
В	7.7	800
D	7.3	841
С	5.1	791
G	4.7	850
E	4.5	821
Lump Ore	4.3	806

Table 6-2	Calculated Gas Volumes and Corresponding	
·-	Bomb Temperatures.	

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have been evolved are determined from the experimental results and are illustrated in the same table.

The results shown in Table 6-2 indicate that the conversion of magnetite to wustite ends at about 850°C. Above 700°C, the reduction of wustite to pure iron is thermodynamically possible:

$$"Fe0" + Fe_{2}C = 4Fe + C0$$
 (6.8)

$$2"FeO" + Fe_3C = 5 Fe + CO_2$$
(6.9)

The tendency for reactions (6.4) and (6.5) to proceed is however higher than that of reaction (6.8) at high temperatures due to the larger free energy changes. At about 750°C the rate of evolution of gas from DRI materials undergoing bomb extraction reaches a maximum. Above 750°C, although the conversion of Fe_30_4 is favored by high temperatures, the rate of gas evolution decreases due to the decrease in the magnetite content of DRI. A minimum in the gas evolution curves is observed at about 850°C. This corresponds with the temperature at which Fe_30_4 /"Fe0" conversion becomes complete, as shown in Figures 6-2 and 6-3 (cf. Table 6-2).

The reduction of wustite to pure iron is also favored by high temperatures. At about 1000°C, a peak is observed in the rate of evolution of gas. At higher temperatures, although the reduction reactions are thermodynamically possible, the diffusion of reactants controls the rate of reduction of the sample. This rate decreases with increasing progress of reactions and removal of the last traces of oxygen or carbon from DRI. It can be seen from the equilibrium



Fig. 6-2 Gas Evolution from Type C Pellets. Temp. Rate, 250°C/min. Particle Size, 1 and 2 mm.



Fig. 6-3 Gas Evolution from Type F Pellets. Temp. Rate, 250°C/min. Particle Size, 1 mm.

diagram that above 1000°C, the gas evolved is almost pure CO.

a. Effect of Grain Size

The overall thermal conductivity of crushed DRI when charged into an extraction bomb was calculated from Equation (D.7). The fraction of the pores produced between the grains was determined from the difference between the overall density of the crushed charge and the density of DRI. The thermal conductivity of the pores was computed from Equation (D.11). The diameter of the pores was assumed equal to that of the grains. The thermal conductivity of DRI grains was calculated from Equation (E.1). The results for 1 and 2 mm crushed materials of type D are plotted in Figure 6-4. It can be seen that the overall thermal conductivity for 2 mm size grains is higher than that of 1 mm grains. This difference may be responsible for the slight shift of the gas exgraction curves to the higher temperatures described in Section IV.A.2.a.2.

The effects of the change of the overall thermal conductivity of the charge of an extraction bomb on the temperature profile and the rate of extraction of gas are shown schematically in Figure 6-5. The temperature profile γ corresponds to a high conductivity or a low heating rate. The temperature of the charge in this case is the same as that of the thermocouple bead. The associated gas evolution curve is also shown in Figure 6-5. The temperature profile γ can be replaced by β , if the thermal conductivity associated with γ decreases to that of β . The gas evolution curve, however, can be the same, if the rate of extraction of gas is plotted against the mean temperature of the charge. Since the gas evolution curve is plotted against the temperature



Fig. 6-4 Estimated Overall Thermal Conductivity of Type D Pellets of 1 and 2 mm Size.

registered by the thermocouple which is less than the mean temperature of the charge, it is shifted to the lower temperatures. If the temperature profile becomes less uniform (curve α), the gas evolution curve will shift to the lower temperatures even further.

b. Effect of Heating Rate

A slow heating rate favors a more uniform temperature distribution which results in a decrease in the total volume of the gas evolved below the temperature associated with the larger gas evolution peak (1000°C) and an increase in the volume of the gas evolved above that temperature (Figures 4-15 and 14-16). A less uniform temperature profile results in shifting of the gas evolution rate curve to the lower temperatures, as shown in Figure 6-5. Changing the rate of rise of temperature of the sample also affects the rate of reduction of DRI. At very high heating rates the diffusion of reactants through DRI grains may contol the rate of formation of gas and shift the gas evolution rate pattern to that at higher temperatures. A combination of these effects results in a slight shift of the larger gas evolution peak to the right for temperature rate of 1000°C/min in Figures 4-17 and 4-18.

B. Heat Transfer Results

The experimental results of the heat transfer studies are discussed through comparison with the mathematical calculations for heating both inert and DRI particles in hot liquid slags with and without local gas bubbling.



Fig. 6-5 Temperature Profile and Gas Evolution for DRI of Different Thermal Conductivities Increasing from α to γ .

1. Inert Specimen

The growth of the shell of solid slag and the rise of temperature at the center of 1.8 cm diameter nickel sphere when immersed in a bath of hot slag are illustrated in Figures 6-6 and 6-7. The rates of evolution of gas from the specimens are specified. The thickness of the shells of slag and the central temperatures of the specimens determined from the mathematical model described in Chapter V are also plotted in the same diagrams.

Without gas evolution, as is seen, the growth of the shell of slag and the rise of the temperature at the center of the specimen determined experimentally and mathematically both are consistent. The Nusselt numbers employed for these calculations are given in Figure 6-9 in which the contributions of conduction--Equation (5.11)--and initial transient forced convection are included. The latter is assumed to last for 5 seconds during which the corresponding Nusselt number drops linearly from 175 to 0. Since the information available on natural convection--Equation (5.12)--leads to smaller Nusselt numbers, it may be concluded that the short-term conduction is the dominant mechanism for transfer of heat to the particle.

2. Effect of Local Bubbling

An example of the effects of evolution of gas on solidification and melting of slag on a submerged sphere is demonstrated in Figure 6-6. As is seen, the evolution of gas from the specimen shifts the curve to the lower thicknesses. The shifted curve is however almost parallel to the curve for no gas evolution (cf. Figures 4-23, 6-11 and 6-12).



Fig. 6-6 Effect of Gas Evolution on Thickness of Solid Slag on 1.8 cm Dia. Ni Sphere Heated in Slag A. Slag Temp., 1250°C.

This finding indicates that, after the root of the shell freezes, the rate of transfer of heat to the solid-liquid slag interface is almost the same for experiments with and without gas bubbling. It may be concluded that the evolution of gas from the sphere basically affects the thickness of the solid shell at the initial transient period (assumed 5 seconds) during which the root of the shell may grow.

During this period, the evolution of gas accompanied with the plunging effects may generate an enormous amount of violence in the bath. The cold layer of solid slag immediately formed on the sphere can be removed by departing gas bubbles which sweep their way from the gas ports into the liquid (Figure 6-8). Since the particle and its steel tubing support are still cold, the temperature of the gases evolved from the sphere may be substantially less than that of the bulk liquid slag resulting in a low thermal conductivity of the departing gas bubbles which partially shield the exterior of the specimen (Figure 3-10).

The partial removal of the cold slag from around the sphere results in a decrease of the thickness of the shell of slag while the shielding of the particle with gas bubbles has a decreasing or an increasing effect on the rate of transfer of heat into the particle. The overall effect is an increase in the rate of heating of the specimen, as is seen from the calculated curves plotted in Figure 6-7.

The thermal conductivity of the liquid slag as influenced by the rising gas bubbles is estimated from Equation (D.7) and plotted in Figure 6-10. The temperature of the evolving gas is assumed to be the



Fig. 6-7 Effect of Gas Evolution on Rise of Temp. of 1.6 cm Dia. Ni Sphere Heated in Slag A. Slag Temp., 1250°C. Curves for O and 2.5 l/min are displaced 20 and 10 sec to right.





same as the temperature of the wall of the thermocouple well. The gas bubbling data given in Table 3-7 were utilized for these calculations (see Appendix I for estimation of porosity of slag). The results show that below 600°C, the thermal conductivity of the liquid decreases with gas bubbling. Above that temperature, the thermal conductivity of the gas bubbles exceeds that of the liquid slag because of radiation effects and the overall thermal conductivity rises. For large nickel spheres (3 cm diameter) the fraction of the surface area that is shielded by gas bubbles is about 70 percent less than that of the small spheres. The rate of heating of the large spheres must therefore be less sensitive to the shielding effects of gas bubbles.

Although the temperatures at the center of the spheres measured after a long time, when the slope of the heating curves is very small, were found insensitive to sudden changes of the gas flow rate (Figure 4-21) and the heat capacity of the evolved gases is small as compared to the enthalpies absorbed by the sphere, the difference between the measured and calculated heating curves appears to be due to the cooling (or heating) effects of the gas stream on the temperature sensing device. The observed insensitivity might have been due to the heating of the gas stream when passing through the long and hot steel tube used to support the sphere and supply the evolving gas.

A simple calculation of the heat capacity of the evolved gas shows that the rate of transfer of heat to the surface of a small nickel sphere is more than 10 times greater than the total rate of absorption of heat by the stream of gas flowing at 6 ℓ/\min (at slag temperature) to reach the temperature of the bulk (1250°C). For a large sphere under



Fig. 6-9 Overall Nusselt Number for Heating Ni Spheres and DRI Pellets in Liquid Slags with or without Gas Evolution.





Estimated Thermal Conductivity of Liquid Slag Surrounding 1.8 cm Dia. Ni Sphere (cf. Table 3-5 and Appendix I).



Fig. 6-11 Effect of Gas Evolution on Thickness of Slag Shell Frozen on 3 cm Dia. Ni Sphere Heated in Slag B. Slag Temp., 1250°C.

the same conditions, the rate of flow of heat to the particle is more than 30 times greater than that absorbed by the gas.

The growth of shells of slag on 3 cm nickel spheres immersed in liquid slag B at bulk temperatures of 1250 and 1275°C are compared with the calculated thicknesses in Figures 6-11 and 6-12. The Nusselt numbers utilized for calculations are illustrated in Figure 6-9. From the best fit of data, neither the contribution of the steady state natural convection--Equation (5.12)--is present nor that of the forced convection by gas bubbling, Equation (5.14). Using the same Nusselt quantities as were used for heat transfer calculations in absence of gas evolution leads to the best set of results. Hence, short-term conduction is the dominant heat transfer mechanism in this case too.

It was assumed that the removal of the shell of slag due to the evolution of gas occurs during the initial transient period. The change of the average thickness of the slag shell during this period was corrected by a factor inserted into the model which specified the fraction of solid slag that remained on the surface of the particle. For heating of a particle without gas evolution, this fraction is 1. The removal of the cold crust of slag from the surface of the particle can also be expressed in terms of a large initial Nusselt number which can function in the same way as the correction factor does.

The overall effect of the decrease of the thickness of the shell of slag due to the gas evolution is an increase in the rate of heating of the particle, as shown in Figures 6-13 and 6-14. This effect may result in a decrease in the melting time of the particles charged into



'ig. 6-12 Effect of Gas Evolution on Thickness of Slag Shell Frozen on 3 cm Dia. Ni Sphere Heated in Slag B. Slag Temp., 1275°C.





steelmaking slags, as will be discussed later.

3. Formation of Gas

The temperature at the center and the volume of the gases evolved from D-R pellets E and D described in Table 5-2 were calculated from the simulation model and compared with the experimental results, as illustrated in Figures 6-15 and 6-16. The mathematical calculations show a larger thermal lag than is registered by the thermocouple during the measurements. The rapid rise of the temperature of the thermocouple immediately after immersion of the pellet may be due to convective heat transfer from the flowing stream of hot gas that forms at the external layer of the pellet into the thermocouple bead.

When a cold DRI pellet is plunged into a hot bath of slag, the temperature of its surface rises rapidly while, because of the low thermal conductivity of the pellet, its core remains cold (Figure 6-15). A large volume of hot gas may thus form at the areas close to the periphery of the pellet which is sucked into the steel tube used to support the pellet (see Section III.D.2.c and Appendix B for experimental details). This gas can heat up the thermocouple bead as well as the cold core and result in the rapid rise of temperature that is measured by the thermocouple. When the difference between the temperature of the surface and the temperature at the center of the pellet becomes substantially small, the measured temperature approaches the calculated one.

The volumes of the gases evolved from pellets E and D are calculated and compared with the experimental results in Figure 6-16 using the gas evolution data for type E or D as reference (see Section



Fig. 6-15 Rise of Temp. of D-R Pellets E and D Immersed in Slag B (cf. Table 5-2).



Fig. 6-16 Gas Evolution from DRI Pellets E and D when Heated in Slag B (cf. Table 5-2).

V.A). The slight difference between measured and calculated volumes of the evolved gases produced for a short period after immersion may be due to the convective heating of the cold core. The variation of the chemical compositions of the pellets from the mean compositions may also be responsible for further differences between the measured and calculated quantities. Yet, the results are satisfactorily consistent.

The growth of the shell of solid slag on the pellets obtained from model calculations is plotted in Figure 6-17. The initial growth of the solid shell on pellet E is faster than on D, but the maximum thickness of the shells is about the same. Pellet E is a highly metallized Midrex pellet (see Table 4-2), D is a low metallized HYL pellet (see Table 4-1). The density of E is greater than that of D, its porosity less (see Table 5-2). Hence the thermal conductivity of pellet E is greater than that of D. This results in a higher rate of absorption of heat by E and a thicker shell of frozen slag formed on its surface initially.

Since pellet D is less metallized than E, when the temperature is high enough that a substantial quantity of gas is evolved, its heat capacity will exceed from that of E (see Appendix F) resulting in a lower surface temperature (Figure 6-15) and a higher rate of transfer of heat to the surface. The difference in the heat absorped by the pellets is responsible for the slower remelting of the slag shell solidified on pellet D for times greater than 20 seconds after immersion.

After about 60 seconds the shell of solid slag formed on surface





Fig. 6-17 Solid Shells of Slag on Surface of DRI Pellets E and D (cf. Table 5-2).



Fig. 6-18 Sensitivity of Temp. at Center of 1.8 cm Ni Sphere to Changes Specified in Table 6-3.

of pellet E is totally remelted (Figure 6-17). The total removal of the shell results in a rapid rise of the surface temperature of the pellet, as shown in Figure 6-15. Because of the relatively low thermal conductivity of the pellet, however, the response of the center temperature of the particle to this change is not illustrated in the figure.

4. Sensitivity Analysis

The effect of variation of the input parameters of the system on the heating curves and the thickness of the solid shell of slag were determined from the simulation model. The reference conditions and the changes of the parameters to which the results of the model are most sensitive are summarized in Table 6-3. The sensitivity of the results to the specified changes are compared in Figures 6-18 and 6-19. As is seen, 50°C increase in the temperature of the solid-liquid slag interface results in the greatest change of the solid slag shell thickness.

The model was found insensitive to the parameters summarized in Table 6-4 in which the average changes of the slag shell thickness and the center temperature are also given.

E. <u>Conclusions</u>

The conclusions to be drawn from the experimental and calculated results discussed in the previous sections may be summarized as follows: 1. Gas Evolution.

a. The reduction of magnetite to wustite between about 600 to 850°C and that of wustite to iron above 700°C result in the evolution of gas from DRI.

		Quantity	
No.	Property	reference	current
1	Initial temp. of particle, °C	130	230
2	Interfacial resistance between particle and slag, surface fraction isolated	0	0.5
3	Heat of fusion of slag, cal/g	80	120
4	Conductivity of Liq. slag, cal/cm. sec. °C	0.0052	0.0062
5	Plunging transient period, sec.	5	2.5
б	Initial Nu number for plunging	210	315
7	Long-term Nusselt number	3.43	6.86
8	Temp. of bulk liq. slag, °C	1250	1300
9	Solidus temp. of slag, °C	1140	1190

Table 6-3	Changes	of	Conditions	of	the	System	for
Sensitiv		Sensitivity	Ana	lysi	ls.		



Temp.,100°C

Fig. 6-19 Variation of Thickness of Solid Shell Against Changes Specified in Table 6-3.

	Quantity		Percent Increase	
Property	reference	current	thickness	temp.
Porosity of particle, fraction	0.02	0.10	0	0
Pore diameter in particle, cm	0.01	0.10	0	0
Density of particle, g/cm ³	8.29	7.29	-12	3
Density of solid slag, g/cm^3	3.7	4.7	-10	0
Porosity of solid slag, fraction	0.06	0.12	-4	-3
Pore diameter in solid shell, cm	0.02	0.10	3	2
Conductivity of solid slag, cal/cm. sec.°C	0.0059	0.0069	4	0
<pre>Specific heat of solid slag, cal/g. °C</pre>	0.25	0.50	6	-4
Solidus Temp. of slag, °C	1413	1488	7	4.5
Density of liquid slag, g/cm ³	3.6	4.6	0	0
Specific heat of liquid slag, cal/g. °C	0.28	0.56	-3	0

Table 6-4Sensitivity of Shell Thickness and Center Temp.of 1.8 cm Ni Sphere to Changes of Parameters Specified.

b. At about 750°C, the thermodynamics of the reactions favor the $Fe_{3}O_{4}/"FeO"$ conversion dramatically and a maximum in the rate of gas evolution is observed. Since the amount of magnetite is limited in the sample, the evolution of gas because of the reduction of magnetite to wustite decreases above 750°C.

c. Because of the favorable thermodynamics of "FeO"/Fe reduction, a peak in the rate of evolution gas occurs at about 1000°C above which the gas evolution rate drops with increasing progress of reactions and removal of the last traces of oxygen or carbon from DRI.

d. The effect of grain size on evolution of gas from DRI is not considerable. The slight shift of gas rate patterns when DRI grain size changes is due to: (1) change of chemical composition and (2) change of the thermal conductivity of the samples.

e Heating rate does not appreciably affect the evolution of gas from DRI.

2. Heat Transfer.

a. The growth of the shell of solid slag on surface of a particle immersed in liquid slag prevents the rapid rise of temperature of the particle.

b. When the bath of liquid slag is not exogenously mixed, shortterm conduction is the dominant mechanism for transfer of heat to an immersed inert particle.

c. The local evolution of gas from a particle into the slag decreases the thickness of the shell of slag which may freeze immediately after immersion, but does not appear to have a significant influence on the shell thickness or the Nusselt number of the bath long after immersion.

d. The temperature and rate of heating of a particle with gas evolution are greater than those of a particle without gas evolution due to the thinner slag shell formed on the former.

e. The formation of gas in a D-R pellet increases the heat capacity of the pellet and decreases the rate of rise of its temperature (if the produced gas is not allowed to evolve into the bath). The thickness of the slag shell will be greater in this case.