The Reduction of Iron Oxides by Volatiles in a Rotary Hearth Furnace Process: Part III. The Simulation of Volatile Reduction in a Multi-Layer Rotary Hearth Furnace Process

I. SOHN and R.J. FRUEHAN

For reduction of iron oxides by volatiles from coal, the major reductant was found to be H_2, and it can affect the overall reduction of iron oxides. In this study, the reduction by actual volatiles of composite pellets at 1000 °C was studied. The volatile reduction of the hand-packed Fe_2O_3/coal composite pellet as it is devolatilizing out of the pellet was found to be negligible. However, the reduction of iron oxide pellets at the top layer by volatiles from the bottom layers of a three-layer pellet geometry was observed to be about 15 pct. From the morphological observations of partially reduced pellets and the computed rates of bulk mass transfer, volatile reduction appears to be controlled by a mixed-controlled mechanism of bulk gas mass transfer and the limited-mixed control reduction kinetics. Using the reduction rate obtained from the single pellet experiments with pure hydrogen and extrapolating this rate to an H_2 partial pressure corresponding to the H_2 from the volatiles, an empirical relationship was obtained to approximately predict the amount of volatile reduction up to 20 pct.

I. INTRODUCTION

PREVIOUS work with fine powders[1] and single composite pellets by the authors[2] have shown that the reduction by H_2 is extremely complex, and no single mechanism can explain the entire spectrum of reduction. The only realistic conclusion that could be made was a mixed-control mechanism, but even a mixed-control model did not accurately describe the actual reduction mechanism. However, useful empirical reactions rates could be obtained from the reduction curves, and predictions of volatile reduction rich in H_2 could be estimated. Both the fine powders and the single pellets reduced with H_2 seemed to indicate that pore mass transfer is relatively important at the later stages of reduction, beyond 50 pct. However, the reduction of iron oxides by volatiles is limited to less than 40 pct. Thus, pore diffusion is unlikely to be important in the controlling mechanism for reduction by volatiles.

The reduction of 40 g of Fe_2O_3 powders spread over 16.5 g of high volatile (HV) coals shown in a previous publication[2] revealed that volatile reduction can reduce iron oxides to some degree. To determine the possibility of volatile reduction for pellets in multilayers similar to a multilayer rotary hearth furnace (RHF) process, three layers of composite pellets were heated to a temperature of 1000 °C on the top layer, resulting in the gradual release of volatiles from the bottom layers, which are at lower temperatures, to reduce the oxide in the top layer. To distinguish the sole effect of volatiles, the individual reactions involved at each layer were separated. In the final stage of this study, the degree of reduction for these multilayer pellets were predicted using empirical rate equations obtained from single composite pellets reduced with H_2.

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II. EXPERIMENTAL SETUP

To approximately simulate both the heat transfer in an actual RHF where radiation is the dominant heat-transfer mode and the subsequent devolatilization from the bottom layer, a fast-acting infra-red (IR) heater was used. Temperature and weight loss data are acquired at 1 Hz and the IR lamp is controlled by the surface temperature of the pellets in the upper layer using a simple proportional integral derivative (PID) program embedded into LABVIEW* 7.0. A thermal gradient of about 150 °C

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*LABVIEW is a trademark of National Instruments Corp., Austin, TX.

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from top to bottom layer is observed at steady state. Although the RHF operates near 1200 °C ~ 1350 °C, the evolution of volatiles and the reactions with these volatiles for multilayers are expected to occur well below 1000 °C. The Fe_2O_3 and coal chemistry is identical to the PAH and HV coals given in previous publications.[1,2]

To obtain comparable sintering to the Fe_2O_3/coal composite pellets, pure Fe_2O_3 pellets used in the current study were thoroughly mixed with 15 wt pct of Al_2O_3 and rolled into 16-mm to 18-mm pellets. The induration process was subject to similar procedures described in a previous paper.[2] To remove possible water vapor in the system, the empty reactor was preheated to 350 °C before each run. In some cases, the reactive layers were substituted with an inert Al_2O_3 dense ceramic ball (diameter = 1.58 cm).

Cross-sectional observations of partially reduced Fe_2O_3 pellets at 1000 °C for 3000 seconds were done using back scattering electron-energy dispersive spectroscopy (BSE-EDS) to verify the morphology of the reduced product layer.

III. RESULTS AND DISCUSSION

A. Reduction of Composite Pellets During Devolatilization

There have been mixed results in the literature[3–7] regarding volatiles reducing the pellet itself as devolatilization

occurs. The general consensus has been that volatiles do not take part in reducing the pellets. This is due to their short retention time in the pellet.

A schematic of the single reactive layer in the reactor is shown in Figure 1, which was used to determine the possibility of volatiles reducing the pellet. With a single reactive layer at the bottom (L1) and nonreactive layers for the middle (L2) and top (L3), the reduction of a single composite layer (L1) by its own volatiles can be determined. To separate the complex reactions in the bottom layer, each reaction that contributes to the total weight loss must be accounted for. For a Fe_2O_3/coal composite pellet, the total possible weight loss is a combination of devolatilization, fixed car-
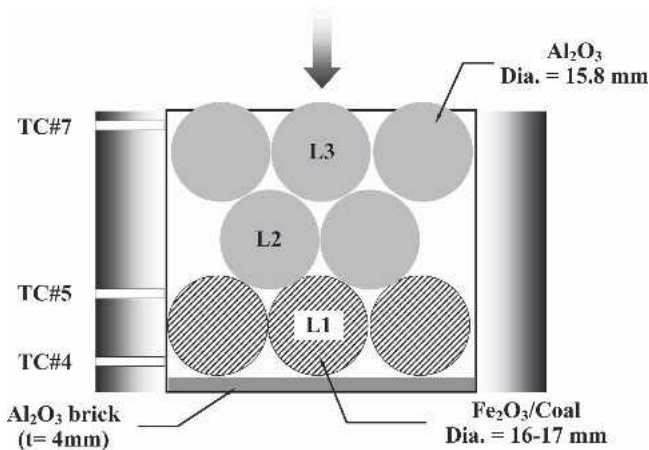

Fig. 1—Volatile reduction in a single reactive layer at the bottom (L1).

Table I. Separation of Individual Reactions for a Single Reactive Layer Composite Pellet

Experiment	Reacting Pellet	Layer	Separation of Individual Reactions
1) PDCL1_AL2_AL3	Fe_2O_3/Ch	BTM	i) FC reduction (FC)
			i) FC reduction (FC)
3) PCL1_AL2_AL3	Fe_2O_3/Co	BTM	ii) Devolatilization (DV)
			ii) Volatile reduction (VR)

P = porous analytical hematite, DC = devolatilized coal, C = coal, A = Al_2O_3 balls.
L1 = layer 1, L2 = layer 2, L3 = layer 3.
Co = coal, Ch = char.

bon reduction, and volatile reduction, of which volatile reduction is the focal point of interest. Using the set of experiments in Table I, the weight loss associated with the devolatilization and volatile reduction could be ascertained.

The individual weights of the composite pellets are given in Table II, and to compare distinctively separate experiments, weight corrections with carbon content must be done.

In Figure 2, a single reactive layer of Fe_2O_3/char composite pellets at the bottom of a three-layer geometry resulted in some weight change when the top layer was heated to 1000 °C. The weight loss observed can be possible only if fixed-carbon reduction occurred, since the oxidation of carbon by the residual oxygen in N_2 was not likely. The temperature profile of the corresponding experiments measured from the walls of the crucible is shown in Figure 3 and revealed that although the top surface temperature of TC#7 reaches 1000 °C in 240 seconds, the temperature at the bottom layer is too low for fixed carbon reduction to occur. However, separate experiments by directly measuring the temperature inside the quartz crucible from top to bottom layer of the pellet during heating indicated that the actual temperature near the surface of TC#5 in Figure 1 can be about 100 °C higher, which is high enough for fixed carbon reduction to be significant.

Therefore, in Figure 2, the weight loss associated with Fe_2O_3/char can be assumed to be fixed carbon reduction. To directly compare the difference between the Fe_2O_3/coal and Fe_2O_3/char composite pellets in Figure 2, the Fe_2O_3/char curve must be compensated by 1.041 (=6.399/6.147) to account for the difference in carbon content shown in Table II. The compensated curve is shown by the dotted line in Figure 2. The difference between the dotted and dashed curves is shown in Figure 4, which corresponds to the sum of the devolatilization and the possible reduction by volatiles.

The volatiles seem to evolve sometime after 240 seconds, and the amount of volatiles for seven pellets layered in a close-packed arrangement was 3.54 g. The total weight loss during the devolatilization and the possible reduction by these volatiles was approximately 3.94 g. However, considering the inherent errors involved with the acquisition of weight and temperature, the reduction of a single layer of hand-packed Fe_2O_3/coal composite pellets by its own volatiles as the devolatilization occurs was found to be negligible.

B. Role of Volatiles for Multilayers of Composite Pellets

A three-layer composite pellet was used to test the possibility of volatile reduction in a multilayer geometry. The

Table II. Individual Weights of the Composite Pellets in Each Layer

Experiment	Reacting Pellet	Layer	Fe_2O_3 (g)	C (g)	VM (g)	Ash (g)
1) PDCL1_AL2_AL3	Fe_2O_3/Ch	BTM	24.590	6.147	0.000	0.601
2) PDCL1_AL2_P15AL3	Fe_2O_3/Al	TOP	29.298	0.000	0.000	0.000
	Fe_2O_3/Ch	BTM	25.678	6.419	0.000	0.627
3) PCL1_AL2_AL3	Fe_2O_3/Co	BTM	25.546	6.399	3.536	0.624
4) PCL1_AL2_P15AL3	Fe_2O_3/Al	TOP	29.595	0.000	0.000	0.000
	Fe_2O_3/Co	BTM	23.846	5.973	3.301	0.583

P = porous analytical hematite, DC = devolatilized coal, C = coal, A = Al_2O_3 balls.
15A = alumina 15 wt pct, L1 = layer 1, L2 = layer 2, L3 = layer 3.
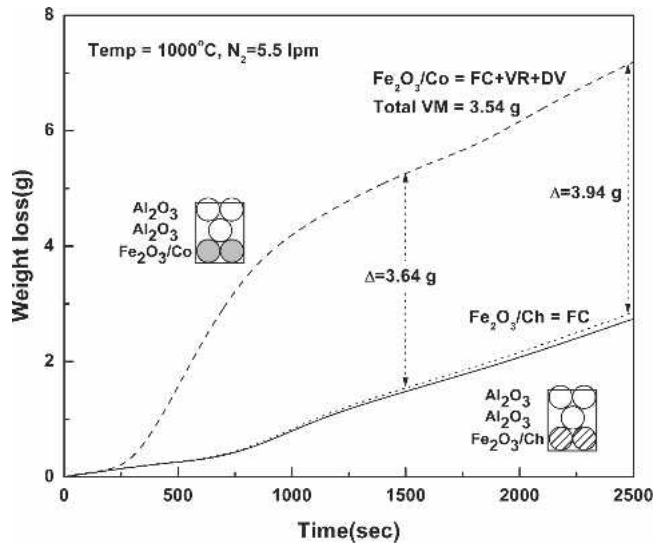Co = coal, Ch = char, VM = volatile matter.

Fig. 2—The weight loss of a single reactive layer of composite pellets placed at the bottom with inert Al_2O_3 pellets at the middle and top layer. Co = coal, Ch = char, FC = fixed carbon reduction, VR = volatile reduction, DV = devolatilization.
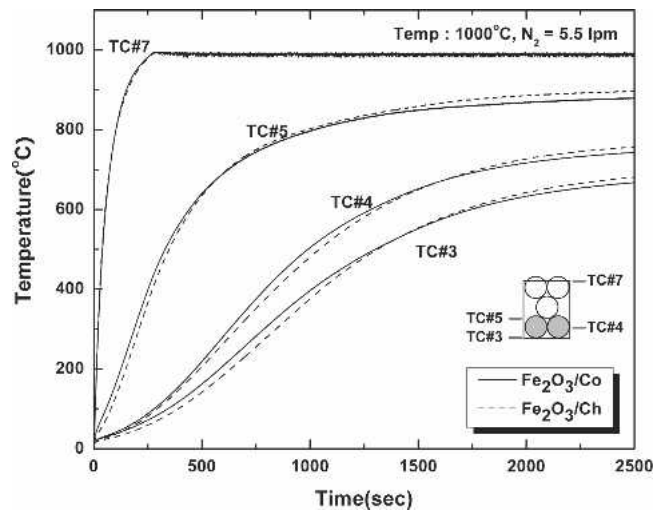

Fig. 3—Temperature profile for single-layer composite pellet for a target temperature of 1000 °C. TC = thermocouple, Co = coal, Ch = char.

Fig. 4—Volatile reduction separated from the Fe_2O_3/coal composite single-layer reduction at 1000 °C.

Fig. 5—Schematic of a three-layer composite pellet and the complex reactions involved in the IR heater. FC = fixed carbon reduction.

schematic of the three layers and the complex set of reactions are shown in Figure 5.

For a multilayer geometry, generally four separate individual reactions take place: evolution of volatiles; reaction of volatiles with the oxides; fixed carbon reduction; and reduction of Fe_2O_3 by CO produced from fixed carbon reduction. These reactions occur in each layer, and a total of 12 separate reactions must be considered for a three-layer geometry. To simplify and isolate volatile reduction instead of using composite pellets for all three layers, the composite pellets of layers 2 and 3 can be substituted with Al_2O_3 and Fe_2O_3 pellets, respectively. By separating the individual reactions according to Table III, the reduction of Fe_2O_3 pellets at the top layer (layer 3) by volatiles evolving from the bottom layer (layer 1) can be determined. By separating each individual reactions involved and by subtracting the results
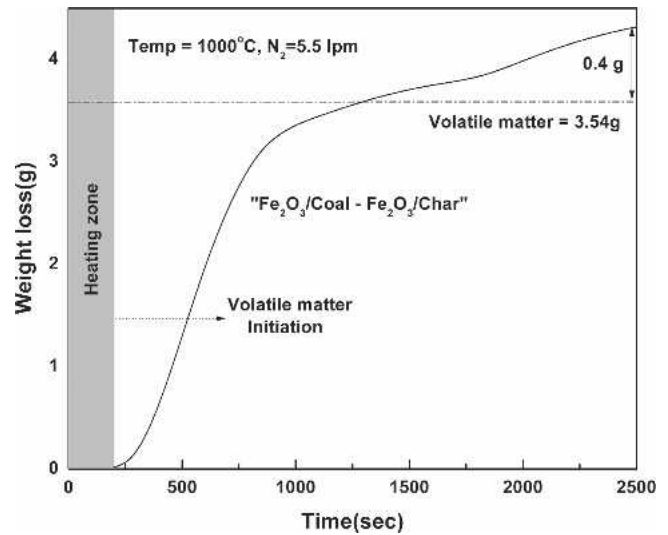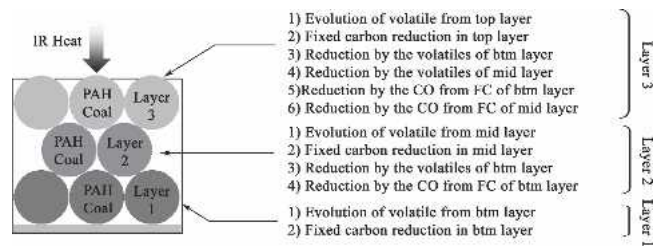
of the experiments [(#4 - #3) - (#2 - #1)], the sole effect of volatile reduction can be determined.

In Figure 6, the weight loss of Fe_2O_3/char composite pellets in layer 1 and inert Al_2O_3 pellets in layers 2 and 3 with N_2 corresponds to the reduction by fixed carbon. Due to the expansion of gases during heating and the effect on the load cell of the balance, separate experiments have given curve 3 to be the initial weight loss corresponding to the initial heating cycle, and beyond that threshold the weight loss associated with fixed carbon reduction occurs. Curve 2 is the compensated curve for the difference in carbon contained in the composite pellet for the Fe_2O_3/char experiment compared to Fe_2O_3/coal experiment in Table III. The 2) PDCL1_AL2_P15AL3 experiment in Figure 7 corresponds to the fixed carbon reduction at the bottom layer and possibly the reduction of Fe_2O_3 at the top layer by the CO gases that are evolved from fixed carbon reduction.

The 3) PCL1_AL2_AL3 experiment consists of two components contributing to the overall weight loss, which are the fixed carbon reduction and the evolution of volatiles from the bottom layer. The 4) PCL1_AL2_P15AL3 experiment has four components: FC reduction at the bottom; reduction of Fe_2O_3 at the top layer by CO evolved from the fixed carbon reduction at the bottom; volatile matter evolution from the bottom; and reduction of Fe_2O_3 at the top layer by the volatiles evolved from the bottom. Similar to the 1) PDCL1_AL2_AL3 and 2) PDCL1_AL2_P15AL3 experiments, to compare the

Table III. Separation of Individual Reactions for a Multilayer Composite Pellet

Experiment	Layer	Reacting Pellet	Separation of Individual Reactions
1) PDCL1_AL2_AL3	TOP	Al_2O_3	i) FC reduction at btm
	MID	Al_2O_3	
	BTM	Fe_2O_3/Ch	
2) PDCL1_AL2_P15AL3	TOP	Fe_2O_3	i) FC reduction at btm
	MID	Al_2O_3	ii) Reduction of top by CO evolved from the btm
	BTM	Fe_2O_3/Ch	
3) PCL1_AL2_AL3	TOP	Al_2O_3	i) FC reduction at btm
	MID	Al_2O_3	iii) VM evolution from btm
	BTM	Fe_2O_3/Co	
4) PCL1_AL2_P15AL3	TOP	Fe_2O_3	i) FC reduction at btm
	MID	Al_2O_3	ii) Reduction of top by CO evolved from the btm
	BTM	Fe_2O_3/Co	iii) VM evolution from btm
			iv) Reduction of top by VM evolved from the btm

Volatile reduction = (#4 - #3) - (#2 - #1)

P = porous analytical hematite, DC = devolatilized coal, C = coal, A = Al_2O_3 balls.
15A = alumina 15 wt pct, L1 = layer 1, L2 = layer 2, L3 = layer 3.
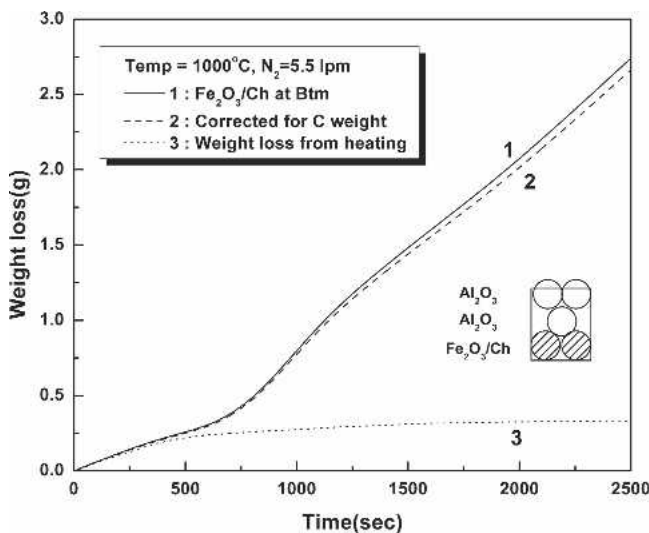Co = coal, Ch = char, VM = volatile matter.

Fig. 6—The weight loss measurements of Fe_2O_3/char at the bottom layer with Al_2O_3 balls at the middle and top for a top surface temperature of 1000 °C. Ch = char.

reduction behavior of these independent experiments, the weight loss measurements must be compensated with the appropriate weight correction factors corresponding to the car-
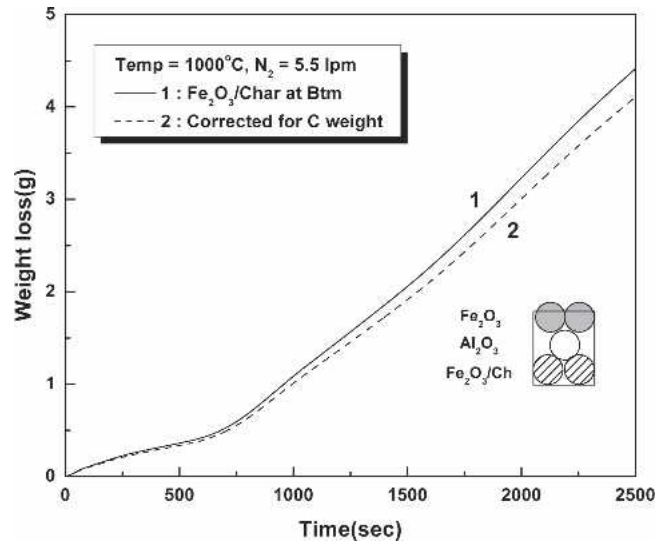

Fig. 7—The weight loss measurements of Fe_2O_3/char at the bottom layer with Al_2O_3 balls at the middle and Fe_2O_3 at the top with a top surface temperature of 1000 °C. Ch = char.
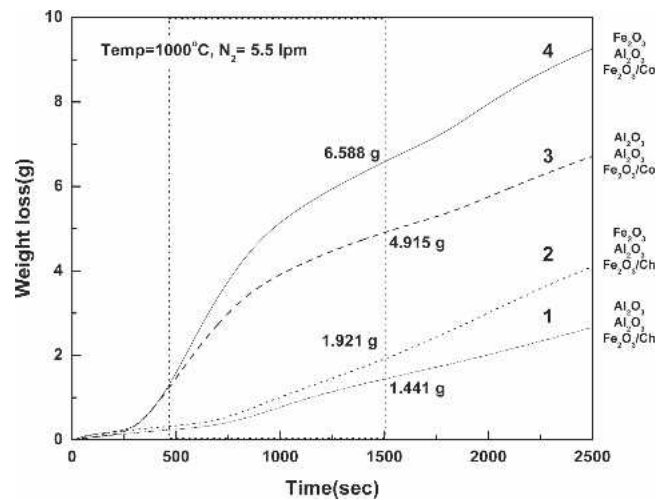

Fig. 8—The weight loss measurements of experiments 1 to 4 corrected for carbon content to the reference carbon content of experiment 4. Co = coal, Ch = char.

bon content of the 4) PCL1_AL2_P15AL3 experiment. The corrected curves are presented in Figure 8.

Using the aforementioned method described in Table III, the sole effect of reduction for a three-layer pellet geometry is shown in Figure 9. Results show that the initiation of volatile reduction starts after 350 seconds, but because of the difference in the superficial weight loss between curves 1 and 2, possibly due to the difference in heating rates, a slight shift in the curve of Figure 10 downwards of about 0.01 is observed. Thus, the dashed line is the baseline for volatile reduction, resulting in about 15 pct reduction for a reaction time of 1200 seconds. During the 1200 seconds of reduction, the initial rate of 2.7×10^{-4} [1/sec] corresponds to the rate when the concentration of hydrogen is comparably higher than at the later stages of reduction due to the rapid evolution of H_2 and lighter hydrocarbons. As the lighter

gases are evolved and consumed, the concentration of hydrogen is subsequently dependent upon the cracking of heavy hydrocarbons (tar), which are slower to react and smaller in concentration, resulting in the decrease from the initial rate of reduction.
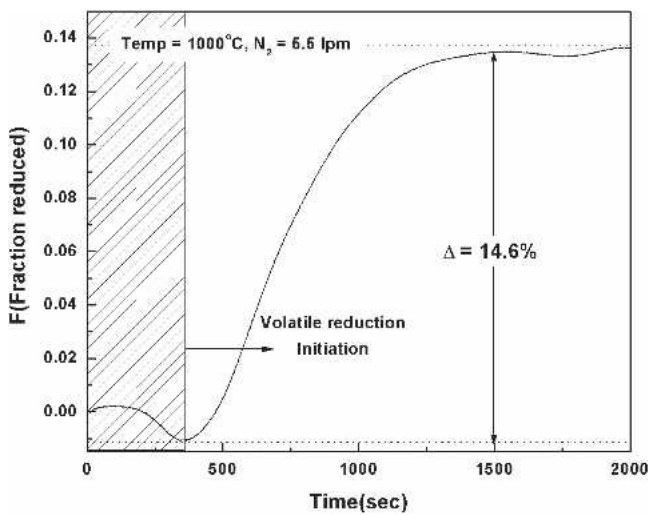

Fig. 9—Sole effect of volatiles in a three-layer geometry at a top surface temperature of 1000 °C.

Beyond 1500 seconds, the fraction reduced is relatively constant since most of the volatiles are evolved from the coal. The slight fluctuation after 1500 seconds is expected, since each independent experiment, although quite comparable, does have some differences in the heating rate and sizes of the pellets. These combined effects could have a slight impact on the final weight loss measurements.

C. Morphology of the Fe_2O_3 Pellet Reduced by Volatiles

From the weight loss measurements of multilayer pellets, the potential for volatiles as a source for reduction was determined. However, it is difficult to distinguish the degree of reduction occurring within the pellet core and near the surface of the pellet when measuring only the total weight loss. Cross-sectional observations of reduced pellets do give useful information on this. However, reduction was not uniform throughout the pellet: the reduced area showed Fe_3O_4, FeO, and even Fe.

Figure 10 shows the partially reduced Fe_2O_3 pellets placed at the top of the three-layer geometry reduced by not only the volatiles evolved from the Fe_2O_3/coal layer at the bottom, but also the CO gas generated from the fixed carbon reduction of Fe_2O_3/coal at the bottom layer. Although the total reaction time was 3000 seconds and the morphological observation includes an additional 21 pct reduction by the evolving CO from the fixed carbon reduction at the bottom
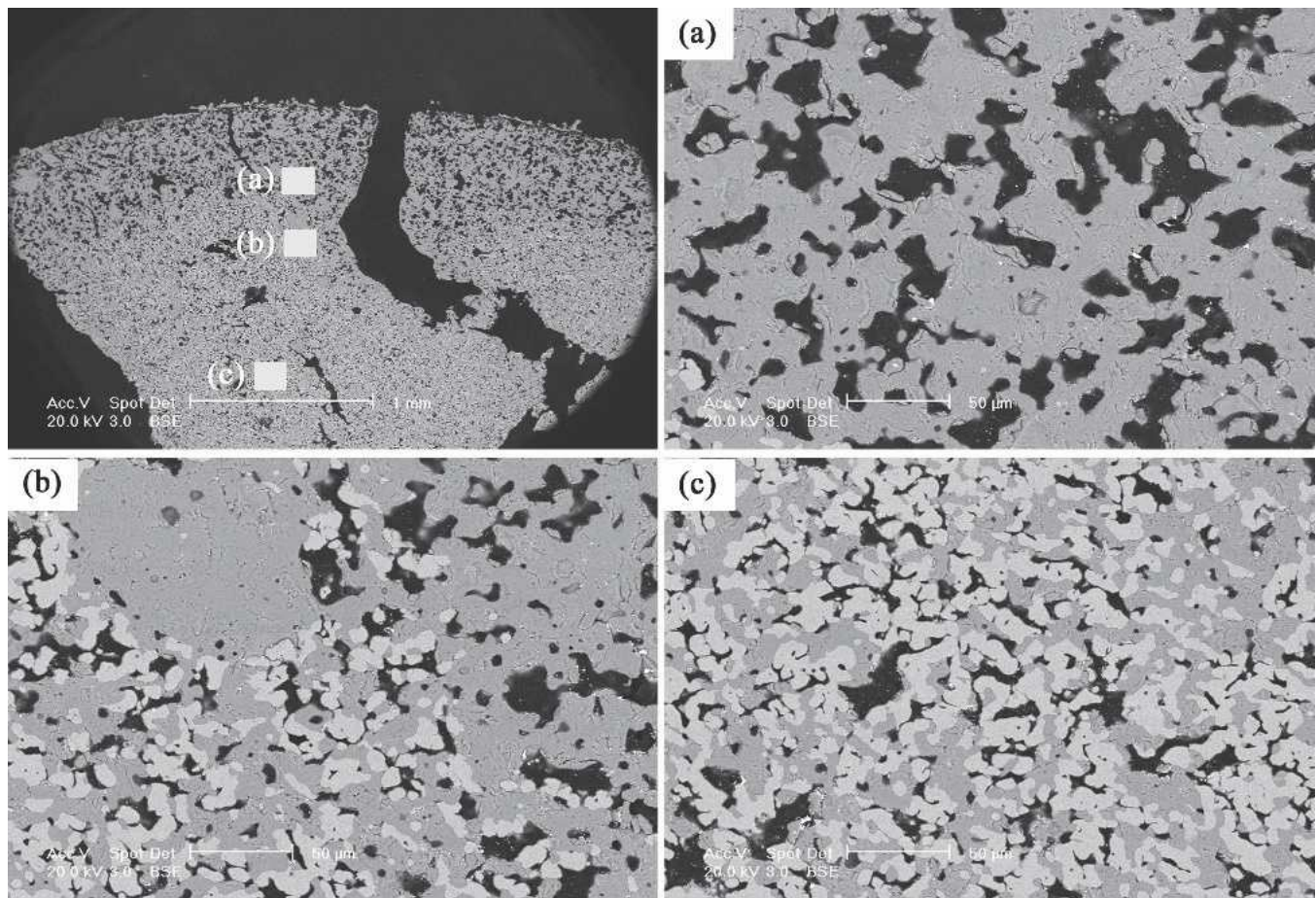

Fig. 10—BSE-SEM of the Fe_2O_3 pellet from the surface toward the core of the pellet (pellet upper portion). Enlarged images of section (a), (b) and (c) is also shown.
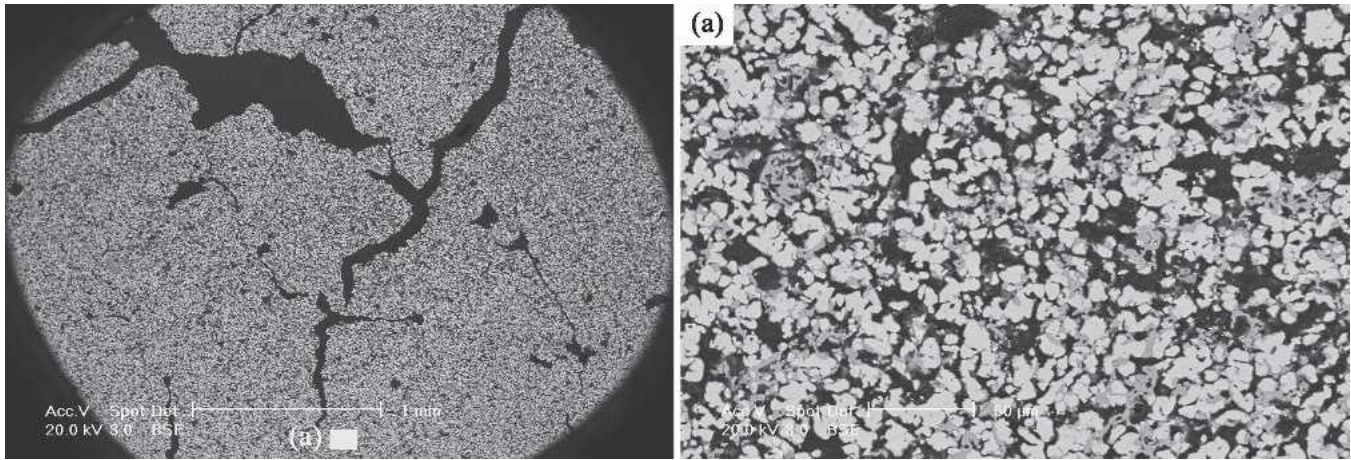
Fig. 11—BSE-SEM of the Fe_2O_3 pellet from the core toward the surface of the pellet (pellet bottom section). Enlarged image of section (a) is also shown.

layers, qualitative information regarding the contribution of volatiles to the reduction morphology of iron oxides can be obtained. The reduced iron oxides show the morphology to be highly porous, with cracks forming for the iron oxides. The formation of cracks and pores seems to be more extensive at the top portion of the pellet near the surface, where the direct impingement of the radiation from the IR heater was occurring.

The upper portion of the pellet in Figure 10 shows a distinct layer near the exterior surface of the pellet that becomes brighter moving toward the core of the pellet. Figure 10(a) shows a highly porous layer where the EDS analysis has given generally uniform composition of O (23 to 24 wt pct) and Fe (76 to 77 wt pct) corresponding to $FeO_{1.042}$ to $FeO_{1.102}$, indicating that some reduction is occurring. Further into the core of the pellet in Figures 10(b) and (c), the layer is less porous, with bright phases dispersed in the matrix. These bright phases were rich in iron compared to the iron oxides observed in Figure 10(a), with the oxygen content less than 0.1 pct, which is negligible.

At the bottom portion of the Fe_2O_3 pellet in Figure 11, the iron phase seems to constitute the majority of the pellet's cross section. Although at the pellet's top section large grains of FeO or Fe_3O_4 were observed sporadically, they were not observed at the bottom portion of the pellet. However, the reduced layer still had small amounts of FeO and Fe_3O_4 oxides dispersed in the majority of existing Fe-rich phases, suggesting the possibility that reduction is controlled by a limited-mixed control.[8] There was a higher overall reduction at the bottom layer compared to the middle and top sections of the pellet. This is expected, since the reducing potential of the gases is higher at the bottom of the pellet than the top, even though the temperature at the top surface is somewhat higher than the bottom. These results are consistent with the reduction morphology of layered powders in a previous publication,[2] where the reduction was higher near the interface of coal and Fe_2O_3 due to the higher reducing potential existing near the coal layer.

D. *Controlling Mechanism of Volatile Reduction*

From the results of the fine powders and single pellet experiments in previous publications,[1,2] pore mass trans-

fer was important at the later stages of reduction (above about 50 pct), but at the initial stages the limited-mixed control is likely to be important. For volatile reduction below 15 pct, the maximum thickness of the product layer is only 0.04 cm, assuming a spherical pellet of 1.65 cm in diameter. Considering that pore mass transfer is a factor only when there is sufficient product layer thickness, it is unlikely that pore mass transfer or conductive heat transfer is important in determining the rate-controlling mechanism of volatile reduction.

Thus, in the reduction range of interest, the role of pore mass transfer through a porous product layer can be neglected. Bulk mass transfer, on the other hand, can have a significant effect on the kinetics according to the detailed calculations below. The flux of product gas away from the sample can be expressed as Eq. [1], with the mass transfer coefficient for natural convection around a sphere given by Eq. [2].[8]

$$J_{H_2O-N_2} = \frac{1}{4\pi \cdot r_o^2} \times \frac{dn_o}{dt} = -\frac{m_{H_2O-N_2}}{RT}\left(P_{H_2O}^S - P_{H_2O}^B\right)$$

$$= -\frac{m_{H_2O-N_2}}{RT}\left(P_{H_2O}^{eq}\right) \qquad [1]$$

$$m_{H_2O-N_2} = \frac{D_{H_2O-N_2}}{d}\left(2 + 0.6\, Re^{1/2}\, Sc^{1/2}\right) \qquad [2]$$

where $m_{H_2O-N_2}$ = the mass transfer coefficient of H_2O through N_2, $P_{H_2O}^S$ = the partial pressure of H_2O at the surface, $P_{H_2O}^B$ = the partial pressure of H_2O in the bulk, $P_{H_2O}^{eq}$ = the partial pressure of H_2O at equilibrium, $D_{H_2O-N_2}$ = the diffusivity of H_2O in N_2, R = the gas constant [82.06 $cm^3 \cdot$ atm/mole $\cdot$ K], d = the diameter of the pellet (1.65 cm), Re = the Reynolds number, and Sc = the Schmidt number. Since the Reynolds number is small for volatile evolution ($Re \approx 0$), the calculated parameters in Table IV can be used in determining the rate of oxygen removal when dominated by bulk mass transfer through a gas boundary layer.

Using Merrick's work on the mathematical calculation of gaseous species in the volatile matter of coals where H_2, CH_4, C_2H_6, and tar are considered,[9] the amount of total H_2 in 9.86 g of HV coals, considering both H_2 and the hydrocarbons, was determined to be 0.241 moles. Since 5.5 lpm of high-purity (HP; 99.998 pct) N_2 is simultaneously introduced into the

Table IV. Parameters for the Calculation of the Bulk Mass Transfer Controlled Rate

$D_{H_2O-N_2}$ (cm^2/sec)	$m_{H_2O-N_2}$ (cm/sec)	Diameter (cm)	$P_{H_2O}^{eq}$ (atm)
3.3	4.0	1.65	0.0182

reactor and about 1200 seconds of reaction time was observed for volatile reduction in Figure 9, the total amount of N$_2$ was 4.91 moles. Because the instantaneous H$_2$ partial pressure cannot be obtained, the average bulk H$_2$ partial pressure calculated to be $\widetilde{P}_{H_2} = P_{H_2}^B = 0.047$ atm was used. Using this H$_2$ partial pressure, the equilibrium water vapor pressure was calculated assuming the FeO/Fe equilibrium. The computed flux for the bulk gas mass transfer controlled reactions was 6.97×10^{-7} (mole/cm$^2 \cdot$sec) and the resulting rate for a 1.65-cm-diameter pellet was 5.92×10^{-6} (mole/sec). Since the initial rate of volatile reduction in Figure 9 is 2.15×10^{-5} (mole/sec), the calculated bulk mass transfer is about one-third the observed rate. The approximate calculations suggest that bulk gas phase mass transfer can act as a significant resistance to the overall reduction.

Along with the bulk gas mass transfer, the role of chemical kinetics must be ignored. At 1000 °C, work with both the fine powders[1] and the single pellets[2] showed that chemical kinetics is a contributing factor to the rate-controlling mechanism below 20 pct. Similar characteristics are expected to occur for volatile reduction. And from the morphological observations of partially reduced oxides by volatiles in Figures 10 and 11, a dispersed mixture of iron oxide phases in the layer of porous product layer indicated a limited-mixed control type of mechanism. Thus, a mixed-control of bulk mass transfer and limited-mixed control is likely to be the controlling mechanism for volatile reduction.

If a mixed-control of bulk mass transfer and limited-mixed kinetics control was rate-controlling, and assuming the receding interface is small so that the radius of the reacting interface(r_i) is comparable to the initial radius(r_o), Eq. [3] can be used.

$$\frac{dn_o}{dt} = -\frac{4\pi \cdot r_o^2}{\left(\dfrac{RT}{k_{lm}} + \dfrac{RT}{m_{H_2O-H_2}}\right)}\left[P_{H_2}^B\right] \quad [3]$$

where k_{lm} = the limited-mixed control rate constant of $\left(k'\rho SD_A^{eff}\right)^{1/2}$ with k' as the apparent rate constant [mole/(cm$^2 \cdot$ sec $\cdot$ moles/cm^3)], ρ = the density of the oxide[g/cm^3], S = the specific surface area (cm^2/g), and D_{eff} = the effective diffusivity (cm^2/sec). With appropriate integrations, Eq. [4] can be derived where the fraction reduced is proportional with time:

$$F = -\frac{4\pi \cdot r_o^2 MW_o}{W_i\left(\dfrac{RT}{k_{lm}} + \dfrac{RT}{m_{H_2O-N_2}}\right)}\left[P_{H_2}^B\right] \times t \quad [4]$$

where MW_o = the molecular weight of oxygen (16 g/mole), W_i = the initial weight of oxygen, and F = the fraction of oxygen removed.

Replotting Figure 9 after removing the heating zone and compensating for the baseline, Figure 12 shows the linear slope of F with respect to time. The initial reduction in region I shows a linear rate of oxygen removal with respect to time,
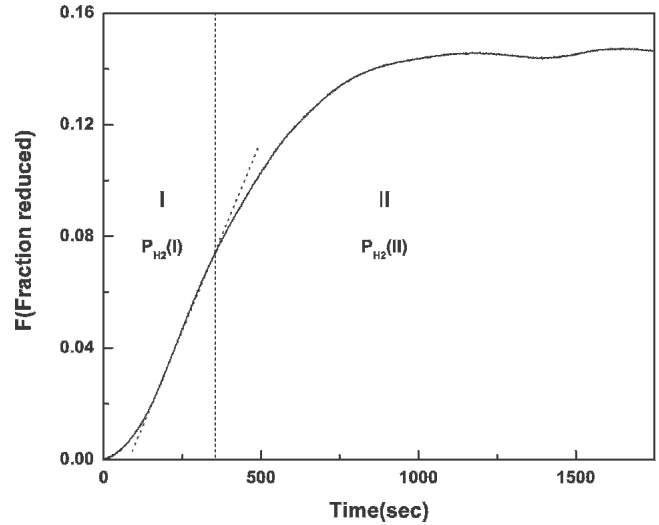

Fig. 12—The fraction of oxygen removed at the top layer of Fe$_2$O$_3$ by volatile reduction compensated for heating time and nonzero baseline. P_{H2}(I) = hydrogen partial pressure in stage I, P_{H2}(II) = hydrogen partial pressure in stage II.

but it decreases in slope after about 8 pct in reduction. The reason for the deviation in linearity with time is expected to be the exhaustion of hydrogen gas in the volatiles. Therefore, it appears that the mixed-control of bulk gas mass transfer and limited-mixed control are the dominant mechanisms for the reduction of iron oxide pellets by volatiles.

For Fe$_2$O$_3$ reduced to FeO at 1000 °C, the equilibrium hydrogen partial pressure is small and can be neglected. Thus, essentially all of the H$_2$ could be used, but to achieve 15 pct reduction by the volatiles, approximately 0.08 moles of H$_2$ was consumed from a possible 0.24 moles of total H$_2$ in volatiles. Therefore, only about 34 pct of the hydrogen was consumed, which indicates that the reduction process by volatiles is not at equilibrium and kinetic modeling is applicable.

E. Prediction of Volatile Reduction

It was found that the volatiles from the bottom layer of a three-layer geometry can reduce the pellet at the top layer by about 15 pct for the present experiment. The work with fine powders revealed useful information to understand the fundamentals of hydrogen reduction and the first-order dependency with H$_2$ partial pressure. By extrapolating the rate of reduction for a single pellet at $P_{H_2}^B = 0.0468$ atm from the reduction curves at $P_{H_2}^B = 1$ atm, the empirical rate equation of Eq. [5] could be obtained.

$$\frac{dF}{dt} = 4.35 \times 10^{-3} \times P_{H_2}(t) \ (1000 °C) \quad [5]$$

Integrating between $t = 0$ to $t = t$ for the fraction reduced, assuming an average hydrogen partial pressure, results in Eq. [6].

$$F = 4.35 \times 10^{-3} \times \widetilde{P}_{H_2} \times t \ (1000 °C) \quad [6]$$

For $\widetilde{P}_{H_2} = P_{H_2}^B = 0.0468$ atm, a reduction degree of 24.4 pct was obtained. This is slightly higher than the observed value of 14.6 pct but is well within the limits of the approximations. Therefore, Eq. [6] can be used to compute the amount

of volatile reduction that can occur in an RHF for the top layer, and since $\widetilde{P}_{H_2}$ is related to the hydrogen in the coal, coals with greater concentrations of hydrogen will have more reduction by the volatiles. If the alumina in the middle layer of a three-layer geometry is substituted with Fe_2O_3/coal composite pellets, some of the hydrogen from the middle layer may add to the reduction. Since the average weight of Fe_2O_3/coal composite pellets is 5 g, the total amount of volatiles in the second layer with six pellets is 2.94 g; this constitutes about 0.207 moles of H_2, resulting in the increase of the average hydrogen partial pressure to $\widetilde{P}_{H_2} = 0.084$ atm. This in turn increases the driving force by about two times, and higher reduction of the upper layer should occur. Thus, with sufficiently high concentrations of hydrogen in coals, volatile reduction can be a significant source of reduction.

IV. CONCLUSIONS

In this study, the role of volatiles in the reduction of iron oxide coal composite pellets was investigated. The following were obtained:

1. The reduction of composite pellets during the devolatilization was found to be negligible. However, the reduction of iron oxides at the top layer from volatiles evolving from the bottom layer was significant, and the possibility of volatile reduction in multilayers for the RHF was demonstrated.
2. The partially reduced layer showed mixed phases of iron oxides dispersed in the matrix of the reduced layer, indicating the importance of the limited-mixed control. The mechanism of volatile reduction at the early stages was found to be a mixed-control of bulk gas mass transfer and limited-mixed kinetic control.
3. Using the empirical rate equation from the single-pellet experiments, approximate prediction could be made with regard to the amount of reduction by volatiles in an RHF process.

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