The Influence of Carbon Deposition on the Reduction Kinetics of Commercial Grade Hematite Pellets with CO, H$_2$, and N$_2$

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Experimental measurements are reported on the rate at which commercial grade, low silica hematite pellets react with a gas mixture consisting of CO, H$_2$, and N$_2$ over the temperature range 500 °C to 1200 °C. Systems of this type are of considerable practical interest, both regarding the operation of direct reduction processes and ironmaking in the blast furnace. The results of the work may be summarized as follows: No carbon deposition was found when operating the system above 900 °C and in the absence of CO gas. When operating the system below 900 °C carbon deposition occurred, which in effect prevented the normal conversion from reaching completion. The maximum rate of carbon deposition was found to occur between 500 °C and 600 °C. In general hydrogen (in the presence of CO) tended to promote carbon deposition, while the presence of nitrogen appeared to retard the deposition process. When the reaction process was being carried out below 900 °C with CO + H$_2$ gas mixtures, the reduction process occurred simultaneously with carbon deposition. At lower temperatures, say around 500° to 600 °C, the deposition process dominated, while at the higher temperatures, and particularly at a high hydrogen content of the reactant gas, the reduction process was dominant. The structural examination of the partially reacted specimens has shown that the carbon deposited was found primarily in the form of elemental carbon rather than cementite. Furthermore, X-ray analysis of the free pellet surface has indicated that iron was present in the carbon deposit phase. The practical industrial implications of these findings are discussed in the paper.

I. INTRODUCTION

THE purpose of this investigation is to examine the rate at which commercial grade hematite pellets react with CO, CO$_2$, and H$_2$ mixtures over the temperature range 500 °C to 1000 °C, which corresponds to the region where carbon deposition onto the solid surface may accompany the reduction process. Problems of this type are of obvious technological interest, because of their relevance to both the direct reduction processes used for sponge iron production and also to the operation of the iron blast furnace.

In direct reduction systems carbon deposition may be desirable under certain circumstances; but in any case it would be helpful to define the precise conditions under which such carbon deposition would take place at sufficiently fast rates to have an influence on the overall operational characteristics of the system. Under other circumstances carbon deposition may inhibit the reduction process and may thus be undesirable.

The decomposition of CO and attendant carbon deposition may also be thermodynamically feasible in the iron blast furnace.

Regarding previous work, the reduction kinetics of hematite pellets with various reducing gases has been extensively studied and will not be reviewed here.[1,2,3]

The rate of carbon deposition from CO/CO$_2$ mixtures has been studied by numerous investigators, including Schenck et al.,[1] Turkdogan and Vinters,[2] and others.[3-6]

It is noted that most of these researchers studied carbon deposition kinetics onto metallic iron surfaces, which

have been prepared either by direct reduction or by some other means.

There appears to be general consensus among the investigators that the range of gas compositions and temperatures over which carbon deposition occurs does indeed correspond to that defined by thermodynamic considerations. However, the actual rate at which carbon deposition occurs was found to be markedly influenced by both the nature of the solid iron surface (composition and mode of preparation) and the possible impurity content of the gas.[1,2] Furthermore, there appears to be general acceptance of the views, first put forward by Schenck,[1] that the formation of an iron phase which would act as a catalyst is a necessary pre-condition of extensive carbon deposition. Furthermore, Haas et al.[3] and Gaballah et al.[4] found that even small quantities of hydrogen have led to a dramatic increase in the carbon deposition rate. Another interesting point should be noted, that as suggested by Turkdogan, on carbon deposition onto iron most of the carbon could be converted into cementite, and since cementite would not be a catalyst for the decomposition of CO, this could inhibit or at least hinder further carbon deposition.

The practical conditions under which carbon deposition may take place in oxide reduction systems are, of course, rather more complex than studied in most of the previously cited investigations, because in industrial practice carbon deposition may occur simultaneously with the actual reduction process. It is this particular system that we are seeking to examine in the present study.

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II. EXPERIMENTAL

The experimental arrangement used employed the conventionally used procedure for studying the reaction of single solid pellets with a reactant gas.[7] A hematite pellet was

suspended from one arm of a recording balance in a tubular Marshall furnace. The pellet was brought to temperature in a nitrogen stream and was then reacted with a CO, H_2, N_2 mixture of predetermined composition, which was supplied at a fast enough linear velocity so that external mass transfer did not constitute a rate limiting step. The progress of the reaction was continuously monitored. The range of temperatures and gas compositions studied is summarized in Table I.

These kinetic measurements were complemented with the structural characterization of the unreacted and the partially reacted specimens, using scanning electron microscopy, X-ray analysis, mercury porosimetry, and BET surface area determination. The solid reactants used were commercial grade, low silica pellets, the composition of which is given in Table II.

III. RESULTS

Before presenting the experimental results it is thought worthwhile to define the thermodynamic equilibrium conditions that characterize the system. This is done in Figure 1 showing a plot of the equilibrium partial pressures of the gas phase with the various solid phases present.

Two sets of curves are shown[8] which define the phase equilibria between iron and iron oxide phases with water vapor and hydrogen (full line), on the one hand, and the phase equilibria between the iron and the iron oxides phases with carbon monoxide and carbon dioxide on the other (— — — — lines). The second set of curves shows the Fe-O-C-H system. Also shown, with the broken lines, are the equilibria corresponding to $H_2/H_2O/CO/CO_2$ mixtures, with iron and the iron oxide phases. It is seen that the lower the temperature, the lower is the fractional oxygen removal required from the wustite, before the appearance of the iron phase. Figure 2 shows the equilibrium gas composition, as

a function of temperature,[9] for a unit carbon activity and for a total pressure of one atmosphere for a system containing carbon, oxygen, and hydrogen with initially unity for the value of the ratio CO/H_2.

The following reactions were considered in calculating these equilibria:

$$C + H_2O \rightleftarrows CO + H_2$$

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

$$C + 2H_2 \rightleftarrows CH_4$$
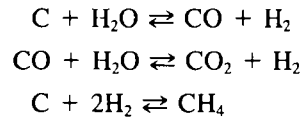
These reactions include the

$$2CO \rightleftarrows C + CO_2$$

component of the system.

Fig. 1—Equilibrium diagram Fe-O-H, Fe-O-C, and Fe-O-C-H system.
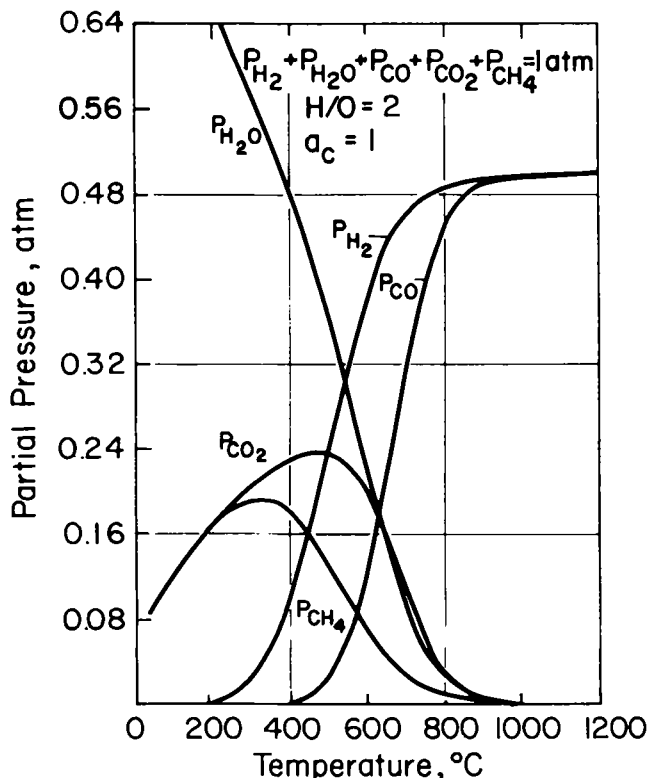
Fig. 2—Equilibrium gas composition of the C-H-O phases as a function of temperature.

Table I. The Temperature Range and the Gas Composition Covered by the Experiments

Temperature, °C	Gas Composition
600 to 1234	Pure H_2 and CO
600 to 1234	$H_2 \cdot CO$ = 75 pct:25 pct
600 to 1234	$H_2 \cdot CO$ = 50 pct:50 pct
600 to 1234	$H_2 \cdot CO$ = 25 pct:75 pct
500	Pure H_2 and CO
500	H_2:CO = 75 pct:25 pct
500	H_2:CO = 50 pct:50 pct
500	H_2:CO = 25 pct:75 pct

	H_2	CO	N_2
700	50 pct	0 pct to 50 pct	50 pct to 0 pct
700	0 pct to 50 pct	50 pct	5 pct to 0 pct

Table II. Chemical and Physical Characteristics of the Commercial Low Silica Pellets

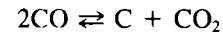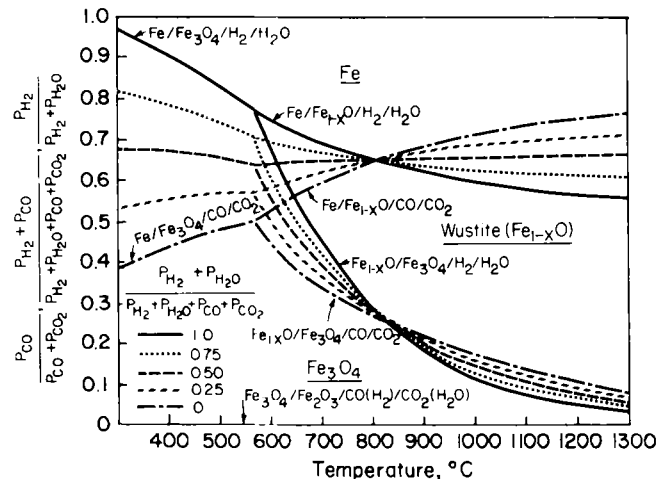| Fe	SiO_2	Al_2O_3	CaO	MgO	Mn	P	S
67.55	2.68	0.29	0.19	0.19	0.009	0.009	0.005

Tumble test: $+\frac{1}{4}''$ 97.2 pct, -28 mesh 2.2 pct
Compression strength (mean): 445 Kg
Porosity: 50 to 60 pct
Sintering temperature: 1260 °C

Inspection of Figure 2 shows that carbon deposition may indeed take place, due to the decomposition of the CO, at temperatures below about 900 °C. Furthermore, from the standpoint of thermodynamics, the formation of CH_4 would also be possible.

In the following Figures 3 to 10 we shall show a selection of the kinetic measurements, given on a plot of X, the fractional weight loss against time. In this context X has been defined as the ratio: actual weight loss/theoretical weight loss, corresponding to the removal of all the oxygen associated with the iron from the pellets.

As will be seen subsequently, that while this fractional weight loss is an inambiguous quantity in the case of iron oxide reduction, its use will become problematic when iron oxide reduction and carbon deposition occur simultaneously.

Figure 3 shows the reduction kinetics of commercial grade hematite pellets with hydrogen at temperatures between 605 °C and 1234 °C. These data will represent a reference rate to which the other reduction measurements will be compared.

Figure 4 shows the behavior of the system, when reacted with a gas mixture consisting of 75 pct H_2 and 25 pct CO. It is seen that above about 900 °C the reaction appears to proceed to completion quite rapidly; furthermore, no visual evidence of carbon deposition has been found for these systems. In contrast for operation below 900 °C the fractional weight loss was found to reach a maximum at some intermediate time and then the pellet appeared to gain weight.

This behavior is readily explained by the fact that reduction and carbon deposition were likely to occur simultaneously and eventually a stage was reached when the rate of carbon deposition exceeded that of the reduction process.

An extreme case of this behavior was exhibited by the curve corresponding to 600 °C. The reproducibility of the data is illustrated by the two duplicate runs corresponding to 700 °C.

Figures 5 to 7 depict similar plots, but illustrating the effect of gas composition. In essence these plots show a similar behavior in that carbon deposition is avoided above about 900 °C, but that significant carbon deposition has been observed in all the cases when the temperature is allowed to fall below 900 °C. The detailed analysis of these curves is difficult, because several processes were found to
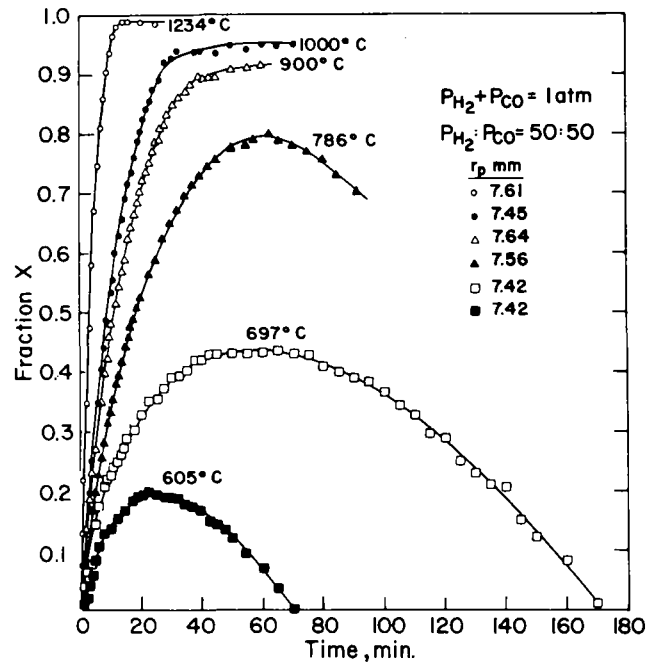

Fig. 4—The apparent fractional weight loss of a commercial low silica hematite pellet reacted by a 75 pct H_2 as a function of time.
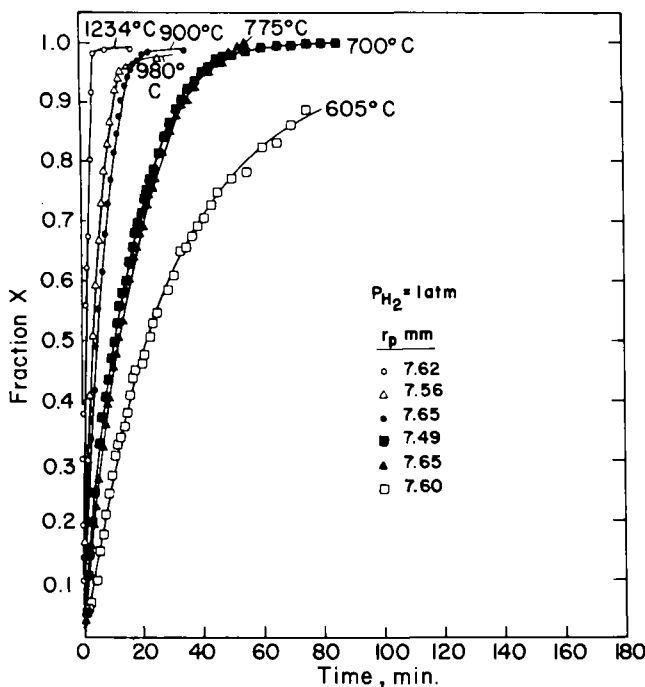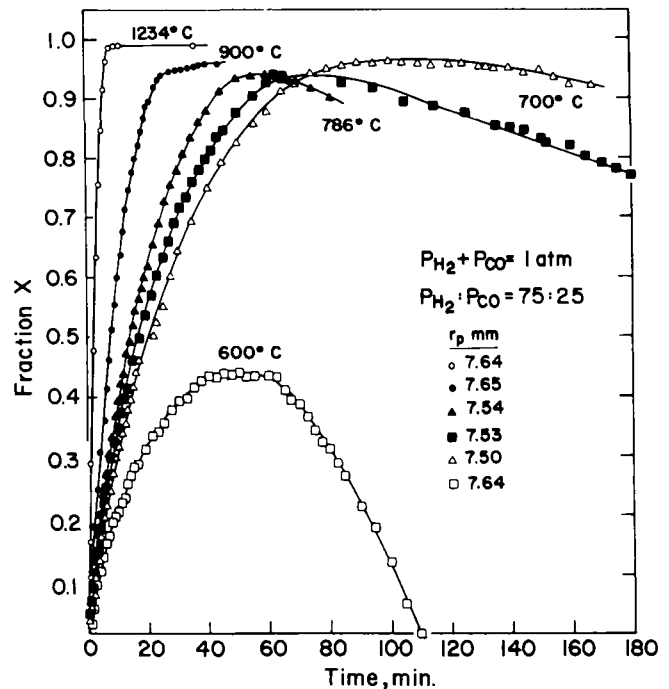

Fig. 5—The apparent fractional weight loss of commercial low silica hematite pellet reacted by 50 pct H_2, 50 pct/CO mixture as a function of time.
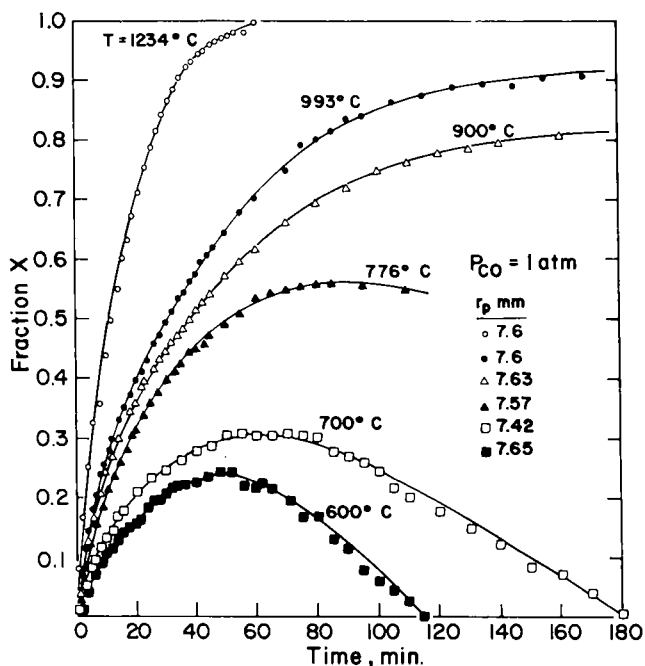

Fig. 3—Fractional reduction of a commercial low silica hematite pellet by pure H_2 as a function of time.

Fig. 6—The apparent fractional weight loss of a commercial low silica hematite pellet reacted by 25 pct H_2, 75 pct CO mixture, as a function of time.
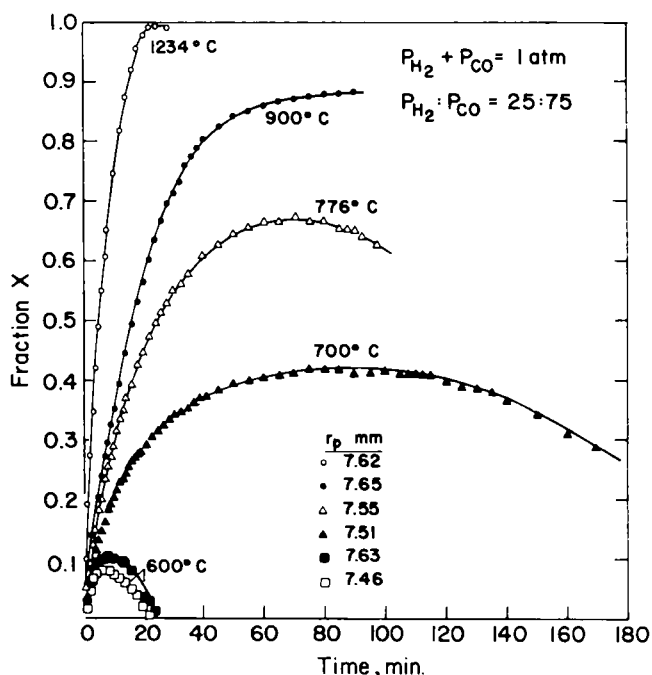

Fig. 7—The apparent fractional weight loss of a commercial low silica hematite pellet reduced by pure carbon monoxide, as a function of time.

occur simultaneously, namely, the reduction of the oxides with CO and with H_2 which would result in a weight loss and the decomposition of the CO on the solid surface, which would result in a weight gain. In addition, the reaction between the solid oxides and the solid carbon may also take place.

Examination of these plots shows the limiting types of behavior for all these cases. At the higher temperatures, say 700 to 800 °C, the reduction of the oxides appears to have taken place first to a significant extent, to be followed by

carbon deposition. For runs at the lower temperatures, however, say at around 600 °C, significant carbon deposition appears to have taken place even at low fractional weight loss levels. The initially rapid rates of carbon deposition observed at the low temperatures (*i.e.*, at 600 °C) may be explained by the fact that the range of nonstoichiometry of wustite is very small under these conditions, so that an iron phase may be readily formed. Inspection of the curves also indicates that once carbon deposition has taken place to a significant extent, this will greatly reduce the rate at which the reduction process may proceed.

A comparison of Figures 4 to 7 indicates that for the conditions examined carbon deposition occurs at the highest rate for a gas composition of about 25 pct H_2 and 75 pct CO. The precise gas composition at which the maximum rate of deposition will occur has not been defined as a result of this work, but for a CO + H_2 mixture this is likely to be at finite H_2 levels between 0 to 25 pct H_2 content.

Figure 8 depicts the reaction characteristics at 500 °C for various H_2/CO gas compositions. It is seen that the reaction proceeds in the normal, expected manner with hydrogen. The remarkable feature of all these runs is that for the conditions considered, when the reactant gas contains appreciable amounts of CO, only very low levels of iron oxide reduction may be obtained. It is of interest to note that the actual rate of carbon deposition is enhanced by the addition of hydrogen.

It should be remarked here that since wustite is unstable below 570 °C, in the runs carried out at 500 °C an iron phase must have formed very early, which could then act as a catalyst for the decomposition of the carbon monoxide.

Since the hydrogen content of the reactant gas appeared to have an important effect on the rate of CO decomposition,
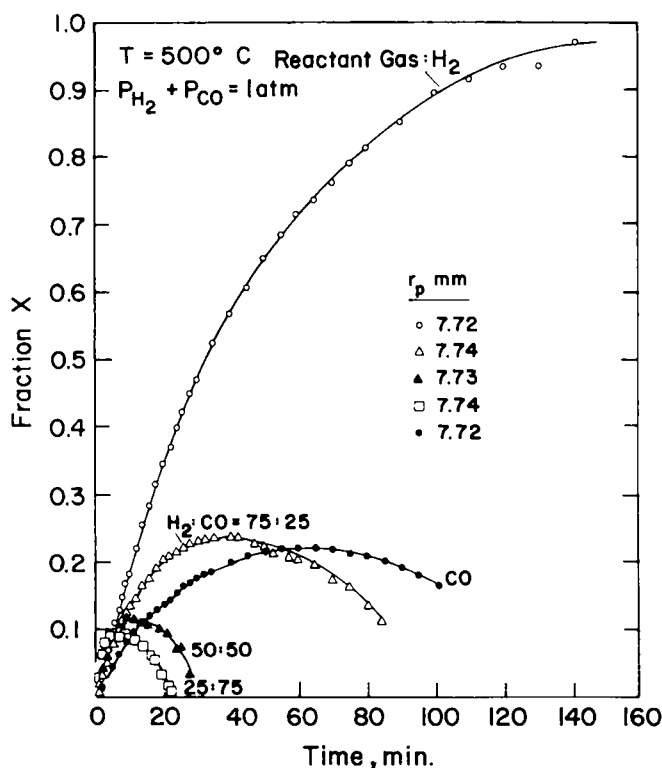

Fig. 8—The apparent fractional weight loss of a commercial low silica hematite pellet at 500 °C reacted by H_2/CO mixture as a function of time.

it may be of interest to examine this aspect of the problem in some more detail.

Figure 9 shows a plot of the fractional weight loss, X, against time, for a constant value of $P_{CO} = 0.5$ atm but for various hydrogen partial pressures (using a mixture of H_2, CO, and N_2 at a total pressure of 1 atm).

The results shown here clearly illustrate the complexity of the system. The runs corresponding to 0.3 and 0.1 atmosphere partial pressures of hydrogen indicate the dual role of hydrogen in both enhancing the reduction rates in the early stages of the process and then enhancing the rate of carbon deposition for longer times. These results also indicate that the presence of nitrogen may reduce the rate of carbon deposition.

It should be remarked that on carrying out the reduction process with a 50 pct CO, 50 pct N_2 mixture, no carbon deposition has been observed.

Figure 10 shows a plot of the conversion against time for a fixed value of $P_{H_2} = 0.5$ atm and examining the effect of

the CO partial pressure (using a mixture of H_2, CO, and N_2 at a total pressure of 1 atm). It is seen that up to about 20 pct CO, the carbon monoxide content of the gas does not influence the rate of carbon deposition. However, once the CO content of the gas is increased beyond this value, carbon deposition will occur rapidly.

Structural Considerations

Table III shows the variation of some physical characteristics of the hematite pellets on reduction with hydrogen at 1234 °C.

It is seen that very marked structural changes were found to occur during the reaction; more specifically, the total pore volume has increased dramatically and there has also been a significant increase in the total surface area.

On examining the behavior of partially reduced pellets, X-ray analyses have shown that for an average pellet oxygen content of 28 pct, magnetite and hematite phases were
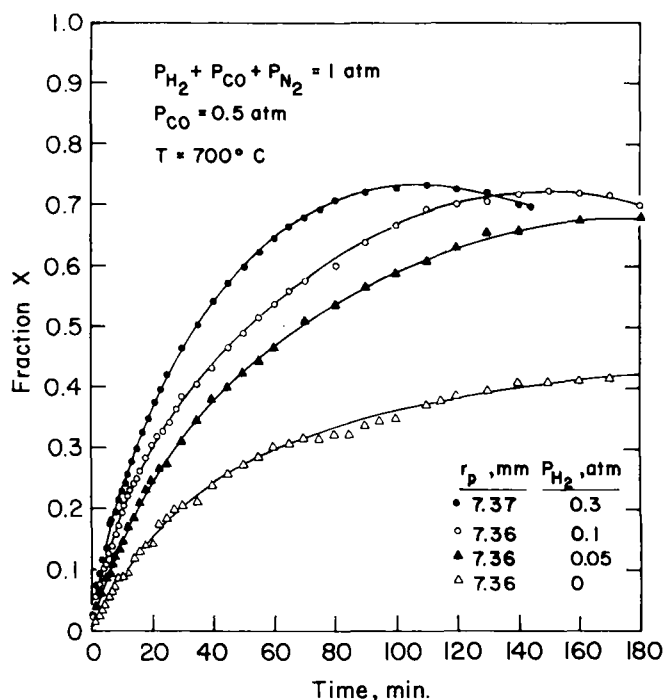

Fig. 9—The influence of hydrogen content on the fractional weight loss at 700 °C reacted by a $H_2/CO/N_2$ mixture at a constant carbon monoxide partial pressure.
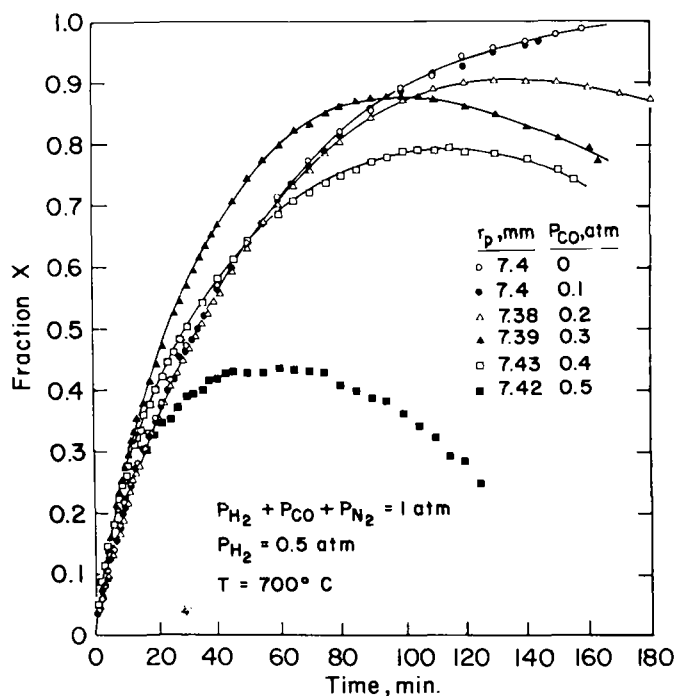

Fig. 10—The influence of carbon monoxide content on the fractional weight loss at 700 °C reacted by a $H_2/CO/N_2$ mixture at a hydrogen partial pressure.

Table III. Specific Surface Area, Pore Characteristics, Density, and Porosity of the Commercial Low Silica Hematite Pellets and also Partially Reduced Pellets with Reduction by H_2 at 1234 °C

	Specific Surface Area m^2/g	Total Pore Area m^2/g	Total Pore Volume cm^3/g	Average Pore Diameter μm	Bulk Density g/cm^3	Apparent Density g/cm^3	Porosity Pct
hematite pellet	0.07	0.0543	0.0399	2.9410	3.9600	4.7032	15.8
pellet reduced 18.87 pct	0.14	0.0931	0.1471	6.3158	2.7106	2.7106	39.87
32.2 pct	0.33	2.7715	0.1435	0.2070	2.7801	4.6245	39.89
42.62 pct	0.11						
61.2 pct	0.17	0.089	0.1751	7.8719	2.7569	5.3295	48.27
97.7 pct	0.16	0.2038	0.2470	4.8474	2.4657	6.3064	60.90

present. At a 23 pct oxygen content, wustite, magnetite, and hematite were found, while at an oxygen content of 16.4 pct iron, wustite, carbon, and cementite were present.

It should be noted that much of the carbon that has been deposited onto the outer surface of the partially reduced pellets was in a porous, not strongly adhering form, which could be readily removed. This carbon could be quickly reoxidized, especially when the pellets were warm. Carbon deposition under such circumstances would simply entail the loss of valuable reducing gas and would have no technological merit.

Figure 11 shows scanning electromicrographs of the outer surface of pellets reduced with hydrogen at 1000 °C, 800 °C, and 600 °C. It is seen that the lower the temperature of reduction, the more porous is the appearance of the outer surface layer.

Figure 12 shows the corresponding photomicrographs for reduction with pure CO at 1243, 900, and 776 °C. It is readily seen that carbon deposition had taken place for reduction at 776 °C.

Figures 13(a) and (b) show scanning electromicrographs of the outer surface of pellets which have been reduced with (50 pct H$_2$, 20 pct CO, and 30 pct N$_2$) and 50 pct H$_2$ and 50 pct CO, respectively.

The significant difference in the morphologies of the carbon deposited, as seen in Figure 13 and those previously given in Figure 12(c), are readily apparent. It should be noted, furthermore, that Figures 11, 12(a), and 12(b) depict sponge iron, while Figures 12(c), 13(a), and 14(b) testify to the existence of graphite at the outer surface.

Figure 13(c) shows an X-ray map of the system which has been previously presented in 13(b). It is noted that the iron phase seen is ferromagnetic and it is in the form of iron rather than cementite. It is likely that this iron must have diffused from the interior onto the surface (the X-ray could not detect the sponge iron some 1 mm below the surface). If cementite had been present this would have reacted with the hydrogen to form methane, as suggested by Haas et al.[3]

Let us summarize the semi-quantitative picture that has been formed as a result of the experiments that have been described in this paper, as sketched in the following Figures 14 and 15.

Figure 14 shows schematically the course of hematite reduction and carbon deposition that one would expect for reaction, say, at 700 °C with a (75 pct) CO + (25 pct) H$_2$ gas mixture.

Three curves are shown: the fractional reduction of hematite, the fraction of iron formed, and the overall fractional
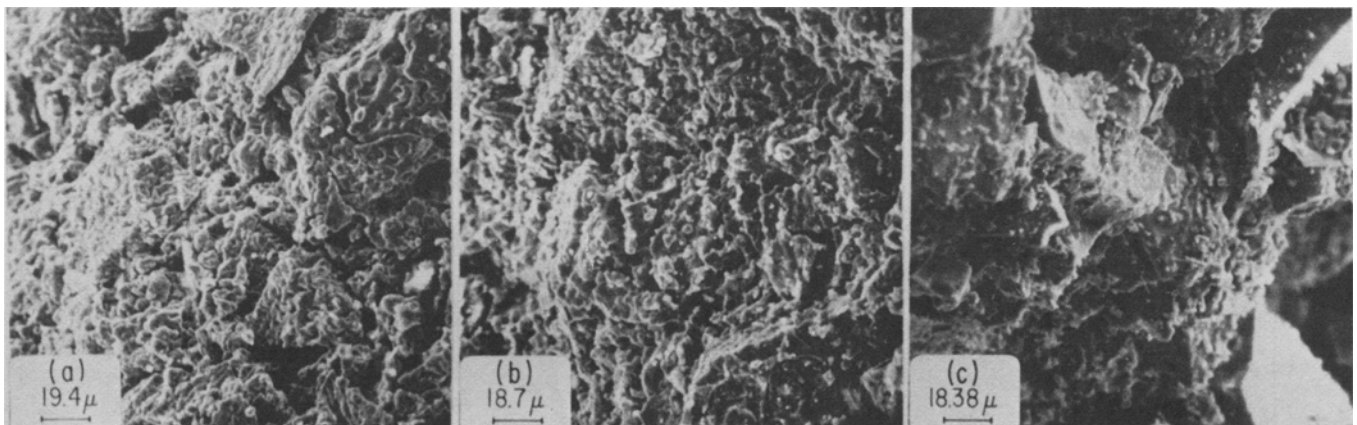

Fig. 11 — Micrographs showing the structure of the outer surface of the pellets reduced in H$_2$ at: (a) 1000 °C, (b) 800 °C, and (c) 600 °C.
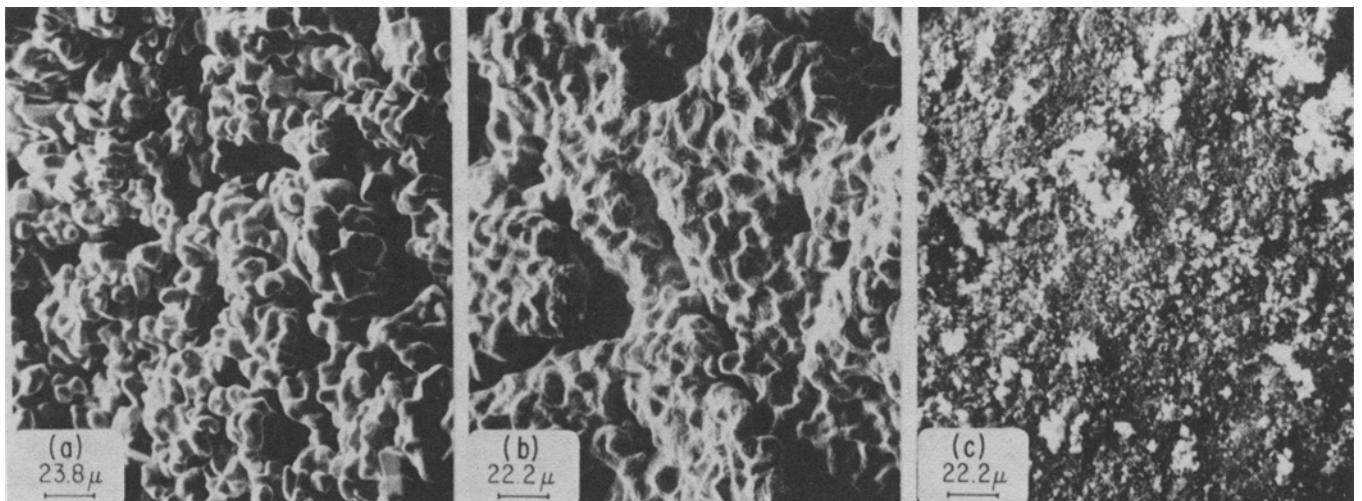

Fig. 12 — The structure of the outer surface of the pellets reduced in CO at: (a) 1234 °C, (b) 900 °C, and (c) 776 °C.
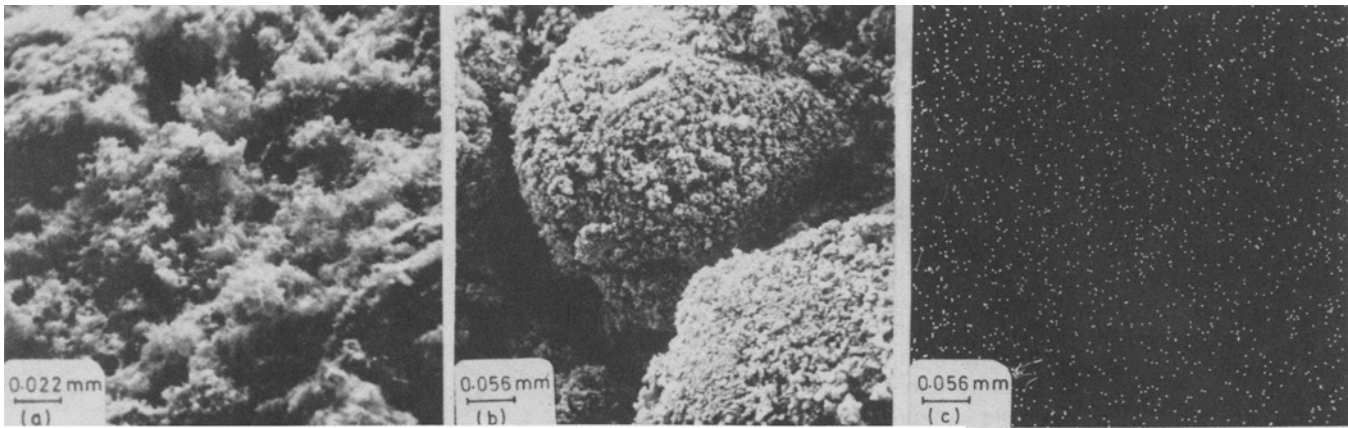
Fig. 13- -(a) The morphology of the pellet surface after partial reduction at 700 °C by a gas mixture consisting of 50 pct H_2, 20 pct CO, and 30 pct N_2. (b) The surface morphology resulting on reduction at 700 °C with a gas mixture consisting of 50 pct H_2 and 50 pct CO. (c) X-ray map of the iron phase corresponding to Fig. 14(b).
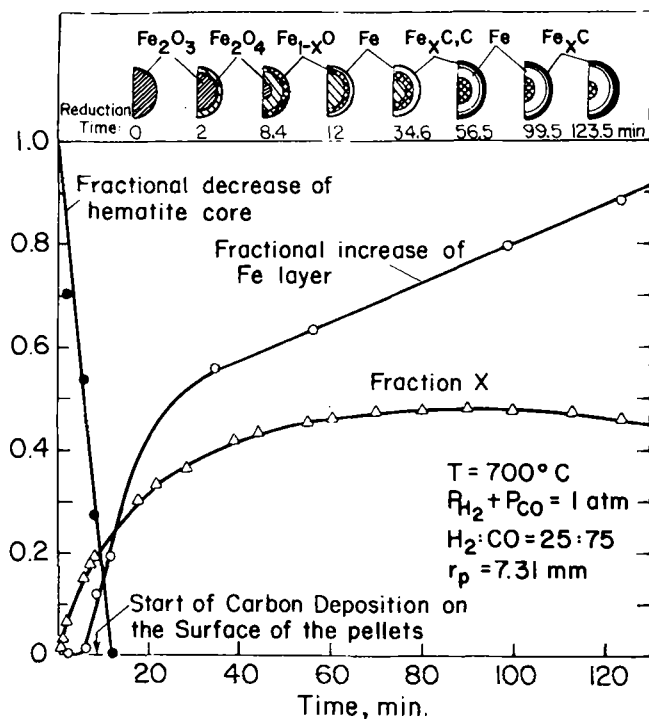

Fig. 14 —(a) The mechanism of reduction by a 25 pct H_2, 75 pct CO mixture at 700 °C. (b) The fractional decrease of the hematite core, and the growth of the Fe-layer as a function of time.

Fig. 15— Schematic sketch showing how the weight of the pellet would change with time for various conditions. (R_{red} = rate of reduction; R_c = rate of carbon deposition.)

reduction. It is seen that the hematite is very readily converted into magnetite. For the present case all the hematite has been converted after about 12 minutes. During that time some iron will have been produced and hence the conditions for carbon deposition have been met. The case for iron formation is promoted by the fact that at 700 °C the range of nonstoichiometry for wustite is quite narrow, as shown in Figure 1. (At yet lower temperatures iron would be even more readily formed, facilitating more rapid carbon deposition.)

Returning to Figure 14, for subsequent times one observed both the progressive growth of the iron layer and extensive carbon deposition. As far as the total "nominal fractional weight loss" is concerned, this is reflected in
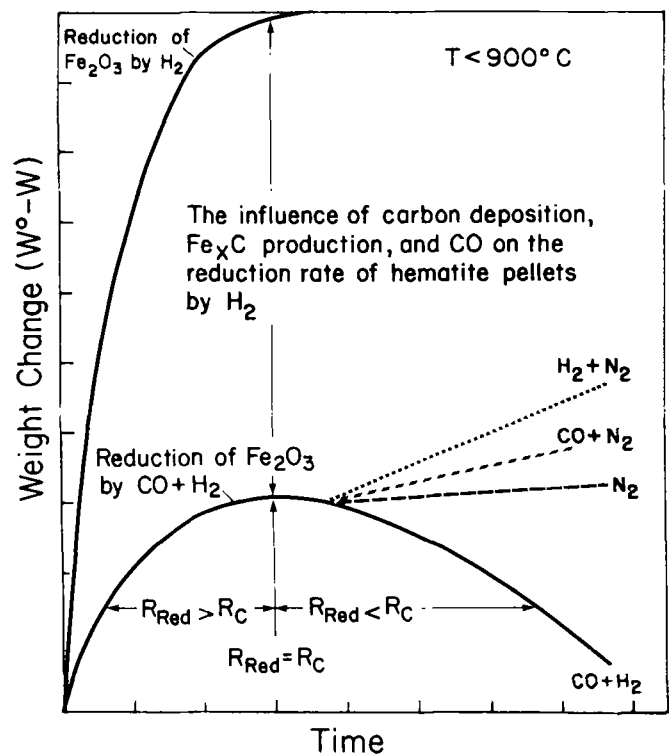
an apparent plateauing of the fractional reduction curve. (In some cases X could actually decrease with time.) The continued carbon deposition may be explained by the fact that iron is likely to diffuse onto the outer surface, providing a continued catalytic effect; this postulate has been verified experimentally; see Figure 13(c).

Figure 15 is a map depicting the possible course of the reaction on a plot of the apparent fractional weight loss X against time, for various gas compositions, below 900 °C.

The upper curve shows the course of reduction with hydrogen, which, as expected, goes rapidly to completion. The lower family of curves represents the reduction process, if carried out using a mixture of CO and H_2, and has three

distinct regions. During the initial stage reduction occurs, with an attendant weight loss, which may be accompanied by carbon deposition, toward the latter part of this initial period. During the second stage the rate of reduction and carbon deposition would proceed at comparable rates, resulting in a plateau.

Subsequently, several possible scenarios may be envisioned.

(i) If one were to continue reacting the pellet with the same hydrogen CO mixture, then there would be a decrease in the apparent fractional weight loss which, as seen in the previously shown Figure 14, would correspond to both continued reduction and carbon deposition, but with carbon deposition proceeding at a faster rate, in terms of weight/unit time. It should be remarked here that the presence of hydrogen would actually promote carbon deposition.

(ii) If on reaching the conditions corresponding to the plateau, the gas composition were changed to CO + N_2, then reduction would continue to occur, albeit at a somewhat reduced rate, while carbon deposition may be suppressed.

(iii) If one were to pass pure nitrogen over the system on reaching the plateau, no carbon deposition would take place, but some additional conversion would occur due to the reaction between the solid carbon and the solid iron oxides.

(iv) Finally, if pure hydrogen or a mixture of hydrogen and nitrogen were made to react with the pellet, then conversion would proceed, albeit at a somewhat reduced rate compared to the reaction with pure hydrogen. This reduction would be attributable to two factors: (a) reduced conversion driving force regarding hydrogen and (b) additional barrier to diffusion through the porous iron, due to the presence of the carbon deposit.

Finally, it is of interest to examine the effect of the gas composition on the relative values of the initial rates at which the pellets react—at a range of reaction temperatures.

This is done in Figure 16, showing a plot of

$$\left(\frac{dX}{dt}\right)_{CO+H_2}\bigg/\left(\frac{dX}{dt}\right)_{CO}$$

against the gas composition.

It is of interest to note that while the reaction would proceed faster with pure hydrogen than with pure CO, the apparent enhancement is rather less than what has been found in the diffusion controlled regime[10] (2 to 4-fold enhancement as opposed to an 8 to 11-fold enhancement).

The curves drawn for reaction at 500 °C and at 600 °C show relatively sharp maxima in the region of 25 pct H_2 and 75 pct CO. It is of interest to note that these maxima correspond to the conditions where we found the most rapid rate of carbon deposition. One may speculate that the local maxima in the reduction rate may be associated with the instability of the wustite phase at the lower temperatures.

The somewhat irregular nature of the initial rate curves appears to be consistent with the findings of other investigators,[4] and would seem to underline further the complexity of this reaction system.

IV. DISCUSSION

In the paper experimental measurements are reported on the rate at which commercial grade hematite pellets react with a gas mixture consisting of CO, H_2, and N_2 under
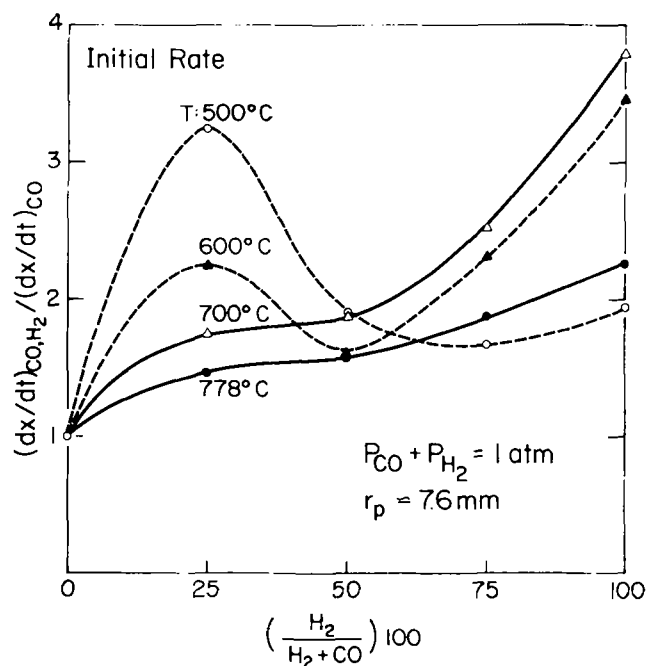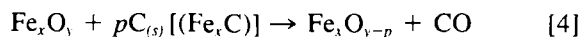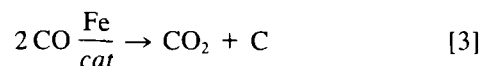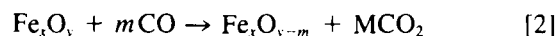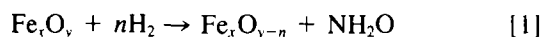

Fig. 16—Plot of the ratio: initial rate of conversion with a gas mixture/initial rate of conversion with pure CO.

conditions where carbon deposition, due to the decomposition of CO, may accompany the reduction process.

Systems of this type are of considerable practical interest in the operation of various "direct reduction" processes and possibly also, regarding the operation of iron blast furnace.

This system is thought to be very complex, because the following individual chemical reactions have to be considered in the interpretation of the rate data:

$$Fe_xO_y + nH_2 \rightarrow Fe_xO_{y-n} + NH_2O \qquad [1]$$

$$Fe_xO_y + mCO \rightarrow Fe_xO_{y-m} + MCO_2 \qquad [2]$$

$$2CO \xrightarrow[cat]{Fe} CO_2 + C \qquad [3]$$

$$Fe_xO_y + pC_{(s)}[(Fe_xC)] \rightarrow Fe_xO_{y-p} + CO \qquad [4]$$

It is noted that reactions (i), (ii), and (iv) would result in a weight loss for the sample, while reaction (iii) would cause a net weight gain.

A large number of experimental runs have been carried out, studying the effect of the gas composition and the temperature on the rate of reaction, and these kinetic measurements have been complemented by the structural characterization of the partially reacted specimens.

The findings of this study may be summarized as follows:

(1) When operating the system above 900 °C or when carrying out the reduction with pure hydrogen (hydrogen, nitrogen mixtures), the reduction process could be brought to completion.

(2) When operating the system with gases containing CO and H_2, below 900 °C carbon deposition has been observed which in effect prevented the reduction process from reaching completion. In some extreme cases no net weight gain has been observed.

(3) Regarding the effect of temperature, the maximum rate of carbon deposition was found to occur between 500 to 600 °C.

(4) Regarding the effect of gas composition over the range examined a gas mixture containing 25 pct H_2 and 75 pct CO gave the maximum rate of carbon deposition.

At a constant CO partial pressure hydrogen tended to promote carbon deposition, while nitrogen had a hindering effect.

(5) The structural examination of the partially reacted specimens has shown that the carbon deposited was found primarily in the form of elemental carbon, rather than cementite. X-ray analysis of the free surface indicated that iron was present in the carbon deposit phase.

Due to the complexity of the reaction system no quantitative kinetic models have been put forward. However, the following qualitative picture is suggested to account for the general observed behavior of the system.

It is thought that provided the thermodynamic conditions are met for the decomposition of the CO to give carbon and CO_2, during the initial stages of the reaction the reduction process tends to dominate, because the presence of an iron catalyst is thought to be necessary in order for the carbon deposition to occur at high rates.

Once an iron phase is formed, carbon deposition will proceed and it will be a question of a balance between the rate of reduction and the rate of carbon deposition. It is generally believed that these processes take place in parallel, although the deposition of a carbon layer will necessarily hinder the access of the reducing gas.

Two additional points ought to be amplified here. One of these is that when the hydrogen content of the reducing gases is high, then reduction may be more important than carbon deposition. In contrast, when the CO content of the reducing gases is high, carbon deposition may overwhelm the reduction process. The presence of hydrogen is thought to aid the decomposition of CO and in particular as reducing gas containing 25 pct H_2 and 75 pct CO tended to provide for the maximum rate of carbon deposition.

The other important point to be made here is that since wustite is unstable below 570 °C and has a very limited permissible composition range just above this temperature, iron is likely to form early on during the reduction process, the catalytic effect of which could permit very rapid rate of carbon deposition. Indeed, the fastest rates of carbon deposition were observed between 500 to 600 °C.

In closing, some comments should be made on the technological implications of these findings.

While the fact that carbon deposition may occur in the course of the reduction of hematite with CO + H_2 mixtures below about 900 °C has been known for a considerable time, it is thought that the present paper has contributed potentially useful information regarding the actual rates of this carbon deposition, compared to the rates of the reduction process.

An obvious consequence of the findings reported in the paper is that in operating DR systems employing pellets, great care has to be taken whenever the temperature of the system falls below about 900 °C, because carbon deposition may take place at quite high rates, depending on the gas composition and on the particular temperature.

While DR systems are normally operated above 900 °C, this critical temperature range will be covered, both during the preheating (prereduction) and the cooling of the pellets.

If one seeks to minimize carbon deposition or at least keep this within bounds, it would seem to be very important to design the DR systems such that the residence time of the pellets in these crucial regions is appropriately controlled.

Carbon deposition in the prereduction stage could be particularly unhelpful because the finely divided carbon could prevent the access of the reducing gas.

Carbon deposition in the cooling section could be beneficial to some extent, by providing additional carbon source in the subsequent smelting process. However, excessive carbon deposition in the form of a loosely adhering layer would merely correspond to a loss in the yield of the reducing gas.

The final point that should be made is that the rate of carbon deposition seems to be quite sensitive to the gas composition. At present most DR systems employ a reducing gas mixture derived from natural gas, the composition of which is controlled by the operation of the reformer. If alternative gas sources were to be contemplated (e.g., using coal gasification), the higher CO content of these gases could drastically alter the carbon deposition characteristics of the reactant gas mixture.

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