The Modeling of Hematite Reduction with Hydrogen Plus Carbon Monoxide Mixtures:

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Part I. The Behavior of Single Pellets

On the assumption of shrinking core behavior, a mathematical model was developed for representing the reduction of hematite disks with a mixture of hydrogen and carbon monoxide. In the model, experimentally measured values were used for the porosity, and the effective pore diffusivities were calculated from pseudo binary formulas. Literature data were used for the activation energies of the reactions, while the preexponential factors were obtained by data fitting. The model was found to provide a good means for representing experimental measurements of Szekely and El-Tawil (1976), both with regards to the effect of temperature and gas composition.

SCOPE

Direct reduction processes for the production of sponge iron are gaining widespread acceptance (Miller, 1972). In many of these processes, ferric oxide pellets are made to react with a mixture of hydrogen and carbon monoxide in a countercurrent moving-bed arrangement. The understanding of the rate at which single pellets react is a necessary prerequisite of the modeling of such systems. While the reduction of iron oxides with pure carbon monoxide or pure hydrogen has been extensively studied (von Bogdandy and Engell, (1971), the reduction kinetics with carbon monoxide plus hydrogen mixtures is virtually unexplored, except for some very limited data by Turkdogan and Vinters (1973) and some preliminary measurements reported by Szekely and El-Tawil (1976).

The purpose of the paper is the development of a mathematical model for the reduction of ferric oxide pellets with hydrogen/carbon monoxide mixtures in the regime where the overall rate is largely controlled by pore diffusion. This model is intended to represent the effect of pellet size, temperature, and gas composition on the overall rate of reaction and should form the necessary first step in the modeling and optimization of moving-bed systems in industrial use.

CONCLUSIONS AND SIGNIFICANCE

With the assumption of shrinking core behavior, a mathematical model was developed for representing the reduction of hematite disks with a hydrogen-carbon monoxide mixture over the temperature range 800° to 900°C. In the model, experimentally measured values were used for the porosity, and the pore diffusion coefficients were predicted from known relationships for pseudo binary diffusion. The activation energies for the individual reactions were obtained from the literature, while the preexponential factors were obtained by data fitting, using measurements of Szekely and El-Tawil (1976) with pure carbon dioxide and pure hydrogen. The theoretically predicted rates of reaction, or times required to attain a given conversion, were found to be in good agreement with measurements over the range of concentrations and temperatures examined. In particular, it was found that the higher the hydrogen content of the reducing gas, the faster was the overall rate of reaction; however, the dependence of the reaction rate on the hydrogen content was not linear. The principal significance of the work is the development of a mathematical model for the reaction of hematite disks, with hydrogen-carbon monoxide mixtures, which is capable of representing experimental measurements and which can form the starting point for the modeling and optimization of industrial systems. No such model has been available up to the present.

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In recent years, there has been a growing interest in the development of 'direct reduction' processes as alternatives to the conventional blast furnace-steelmaking sequence for the production of steel (Bollinger, 1975; Miller, 1972).

In many variants of these direct reduction processes, hematite (ferric oxide) pellets are made to react with a carbon monoxide-hydrogen mixture such as the MIDREX, ARMCO, and PUROFER Systems in a countercurrent moving-bed arrangement, and the resulting solid product is a porous iron pellet, sometimes called sponge iron (McGannon, 1971). In principle, the operation of these moving-bed systems is quite straightforward and should be readily modeled with the ultimate objective of defining the optimal processing conditions, for example, of the inlet gas composition, the inlet temperature, and the like. However, no such modeling equations or attempts at optimization have been published in the open literature.

The work to be described in these two papers was undertaken with the ultimate goal of developing a mathematical model for a system in which hematite pellets are reduced with a carbon monoxide plus hydrogen mixture in a moving-bed arrangement with the view of defining the conditions for the optimal operation.

In the present Part I we shall develop a model for the behavior of single pellets, and the predictions will be compared with actual measurements. The modeling and optimization of the moving-bed system are described in Part II.

PREVIOUS WORK

The obvious industrial importance of iron oxide reduction by carbon monoxide or hydrogen stimulated a great deal of attention during the past two decades. This earlier work has been reviewed in the texts by Bogdandy and Engell (1971) and by Szekely, Evans, and Sohn (1976). Particularly noteworthy papers on hematite reduction have been written by McKewan (1964), Spitzer et al. (1966 *a*, *b*), Warner (1964), and Turkdogan (1971-1972).

On the basis of more recent work (Turkdogan, 1971-72; Sohn and Szekely, 1973), it is generally accepted that the reaction of a porous solid with a gas may be divided into the following regimes:

1. When the overall rate is controlled by chemical kinetics (for example, at low temperatures and for small particles), the pellet reacts at a spatially uniform rate and there are no macroscopic gradients in solids or gaseous composition within the pellet.
2. In contrast, for large particles and at high temperatures (that is, when the overall rate is limited by pore diffusion), the reacted and the unreacted portions of the solid pellet are divided by a sharp interface; this behavior is often termed shrinking core or topochemical.
3. Finally, there exists an intermediate between these two extremes where the reaction zone is of finite thickness.

The reaction of hematite pellets with reducing gases (such as hydrogen or carbon monoxide) conforms to this general pattern but is rather more complex, because the reaction proceeds in a stepwise manner:

$$\underset{\text{hematite}}{Fe_2O_3} \rightarrow \underset{\text{magnetite}}{Fe_3O_4} \rightarrow \underset{\text{wustite}}{FeO} \rightarrow \underset{\text{iron}}{Fe}$$

No comprehensive model has yet been developed for representing the reduction of hematite to iron through these intermediates for the general case (that is, when the reaction front is diffuse so that both chemical kinetics and pore diffusion play an equally important role in determining the overall rate), although individual aspects of this problem have been studied. In particular, Spitzer, Philbrook, and Manning (1966*a*, *b*) have formulated a very comprehensive description of the stagewise reduction of hematite in the region where the topochemical or the shrinking core assumption is appropriate.

It is stressed that all this previous work has been done using either pure hydrogen or pure carbon monoxide as the reducing agent. The behavior of gas mixtures, and in particular the effect of gas composition on the reduction kinetics, has received very limited attention in the open literature, notwithstanding the obvious practical importance of these systems. Notable exceptions are some limited measurements by Turkdogan and Vinters and preliminary measurements by Szekely and El-Tawil, (1976) on the reduction kinetics of hematite disks with carbon monoxide plus hydrogen mixtures over the temperature range 750° to 900°C. Both these authors found that for isothermal conditions, the higher the hydrogen content of the reducing gas mixture, the faster was the rate of reaction.

Our understanding of the rate of gaseous reduction of hematite may be summarized by stating that a good qualitative understanding exists of the factors that govern the reduction kinetics when a single reducing gas is employed; moreover, a proven, quantitative model is available for the whole reduction sequence, for conditions when the shrinking core or topochemical assumption is appropriate. No models have been reported describing the reduction kinetics with a carbon monoxide plus hydrogen mixture, although some preliminary experimental measurements are available. Since the ultimate objective of the work is the development of a mathematical representation of the reduction process which can be readily used for modeling the behavior of moving-bed systems, we shall select the simplest model that is consistent with measurements over the range of variables encountered in industrial operating practice.

Under industrial conditions, the reduction process is carried out at high enough temperatures (and for large enough particles) so that the shrinking core or topochemical asymptote is being approached for most conditions.

For this reason the model to be developed here will be based on the generalization of the shrinknig core concepts to operation with a reducing gas mixture. The predictions based on the model will then be compared with measurements reported by Szekely and El-Tawil (1976).

FORMULATION

The reduction of iron oxides with hydrogen or carbon monoxide is a reversible process, and the equilibrium conditions are well established (Mackenzie, 1963). Higher temperatures favor the reduction with hydrogen, while the converse is true for the reaction with carbon monoxide.

In the statement of the kinetic model we shall follow the treatment developed by Philbrook, Spitzer, and Manning assuming shrinking core type of behavior; that is, the pellet is assumed to reduce topochemically at three advancing interfaces: hematite/magnetite, magnetite/wustite, and wustite/iron. This reduction pattern is shown schematically in Figure 1 for a single hematite pellet. The advancing fronts are specified by the effective interface radii $x^{(t\text{-}s)}$ drawn from the center of the sphere to the inner boundary of the adjacent product phases, t and s. The removal of oxygen occurs at these three advancing interfaces inside the hematite particle which proceeds through the following steps:

1. Transport of gaseous reactant from the bulk gas phase to the outer surface of the particle.
2. Diffusion of the gas through the porous iron layer to the iron/wustite interface.
3. A portion of the gas reacts with wustite to form iron and a gaseous product.
4. The balance of the gas diffuses through the porous wustite layer to the wustite/magnetite interface.

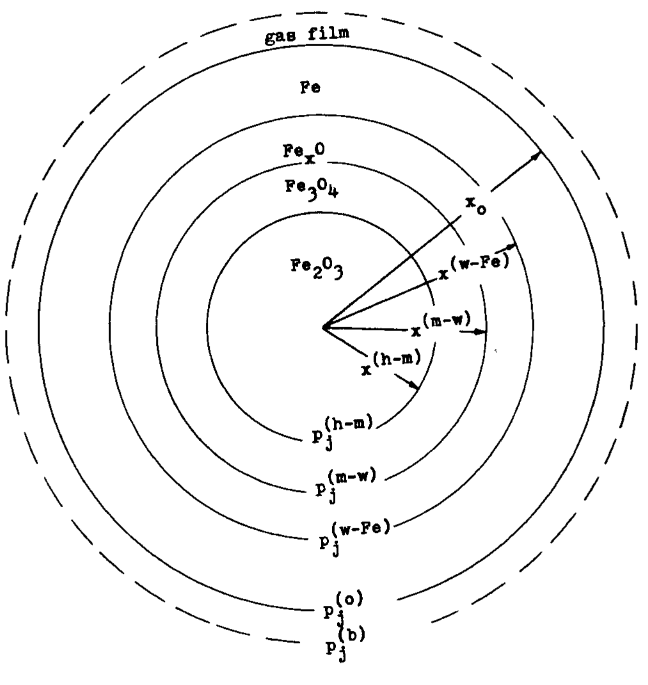

Fig. 1. Schematic representation of the three interface model.

5. A portion of the gas reacts with magnetite to form wustite and a gaseous product.
6. The balance of the gas diffuses through the porous magnetite layer to the surface of the unreacted oxide core, the magnetite/hematite interface.
7. Chemical reaction of the gas with hematite to form magnetite and a gaseous product.
8. Outward transport of the gaseous product follows an opposite pattern.

Each step offers resistance to the overall reduction, but, as we stressed earlier, the topochemical assumption is appropriate only when pore diffusion constitutes the principal resistance.

In representing the reduction process with a carbon monoxide plus hydrogen mixture, which is a generalization of the previous work, in addition to the above stated assumptions we shall consider that

1. The rate of reduction at any reaction interface may be calculated by summing the contributions of the reactions due to hydrogen and carbon monoxide with the oxide. These reactions are assumed to proceed independently.
2. Catalytic effects may be neglected.
3. The effect of the water gas reaction, namely, $H_2 + CO_2 \rightleftarrows H_2O + CO$, may also be neglected.
4. The diffusion process through the pores may be represented in terms of an effective binary diffusion coefficient, corresponding to that of the diffusing component and the gas mixture.

Strictly speaking, all these assumptions constitute over simplifications, the assessment of which has to be done a posteriori by comparing the predictions based on the model with measurements. Since the ultimate objective is the development of a suitable practical model for representing a moving-bed system, agreement with measurements, over a range of operating conditions, is thought to be an appropriate criterion.

The rate of reduction of the hematite is then determined by summing the rates of reaction of the three interfaces. Each interface moves at a rate determined by the specific rate constant $k_r^{(t\text{-}s)}$ for the surface reaction (gas-solid) from t species to s species, that is, hematite to magnetite, magnetite to wustite, wustite to iron, and by the partial pressures of gas species $p_A^{(t\text{-}s)}$ and $p_B^{(t\text{-}s)}$ present at the interfaces as shown in Figure 1, where A is the reactant gas and B is the product gas. For reversible, first-order kinetics, the gas-solid reaction of each reduction step can be expressed as

$$\begin{aligned}&\text{Solid }(t) + \text{Reactant Gas (A)}\\ &\qquad\qquad \rightleftarrows \text{Solid }(s) + \text{Product Gas (B)}\\ &\qquad (H_2/CO) \qquad\qquad\qquad (H_2O/CO_2)\end{aligned}$$

There are three equations identical in form which describe the advancing fronts:

$$\frac{dx^{(t\text{-}s)}}{d\theta} = \frac{1}{\rho_t \phi^{(t\text{-}s)}(1-\epsilon_t)RT_s} \left\{ k_{r,CO}^{(t\text{-}s)} \left[p_{CO}^{(t\text{-}s)} - \frac{P - p_{CO}^{(t\text{-}s)}}{K_{e,CO}^{(t\text{-}s)}} \right] + k_{r,H_2}^{(t\text{-}s)} \left[p_{H_2}^{(t\text{-}s)} - \frac{P - p_{H_2}^{(t\text{-}s)}}{K_{e,H_2}^{(t\text{-}s)}} \right] \right\} \quad (1)$$

where

t-s: h m
m-w
w-Fe

with the initial conditions

$$\text{at} \quad \theta = 0, \quad x^{(h\text{-}m)} = x_o, \quad x^{(m\text{-}w)} = x_o, \quad x^{(w\text{-}Fe)} = x_o$$

The rate of movement of each interface toward the center of the pellet is the sum of the contributions from carbon monoxide and hydrogen reacting with the oxide at that interface.

The key step in the use of the modified three-interface model is the calculation of $p_A^{(t\text{-}s)}$ and $p_B^{(t\text{-}s)}$ using the quasi steady state approximation (Bischoff, 1963; Luss, 1968; Ishida and Shirai, 1970); $p_A^{(t\text{-}s)}$ and $p_B^{(t\text{-}s)}$ can be calculated (Spitzer et al., 1966*a* and *b;* Tsay, 1975), and the expressions for the interfacial partial pressures in terms of the known bulk phase partial pressures $p_A^{(b)}$ and $p_B^{(b)}$ are given as

$$p_A^{(w\text{-}Fe)} = p_A^{(b)} - \left[\frac{R_{F,A} + R_{s,A}^{(Fe)}}{\Omega_c \left[R_{F,A} + R_{s,A}^{(Fe)}\right] + \dfrac{\Omega_d \left[R_{F,B} + R_{s,B}^{(Fe)}\right]}{K_e^{(w\text{-}Fe)} K_e^{(m\text{-}w)} K_e^{(h\text{-}m)}} + 1} \right] \cdot \left[\Omega_c p_A^{(b)} - \frac{\Omega_d}{K_e^{(w\text{-}Fe)} K_e^{(m\text{-}w)} K_e^{(h\text{-}m)}} p_B^{(b)} \right] \quad (2)$$

$$p_B^{(w\text{-}Fe)} = p_B^{(b)} + \left[\frac{R_{F,B} + R_{s,B}^{(Fe)}}{R_{F,A} + R_{s,A}^{(Fe)}} \right] \cdot \left[p_A^{(b)} - p_A^{(w\text{-}Fe)}\right] \quad (3)$$

$$p_A^{(m\text{-}w)} = p_A^{(w\text{-}Fe)} - \left[\frac{R_{s,A}^{(w)}}{\Omega_a R_{s,A}^{(w)} + \dfrac{\Omega_b R_{s,B}^{(w)}}{K_e^{(m\text{-}w)} K_e^{(h\text{-}m)}} + 1} \right]$$

$$\left[\Omega_a p_A{}^{(\text{w-Fe})} - \frac{\Omega_b}{K_e{}^{(\text{m-w})} K_e{}^{(\text{h-m})}} p_B{}^{(\text{w-Fe})} \right] \quad (4)$$

$$p_B{}^{(\text{m-w})} = p_B{}^{(\text{w-Fe})} + \left(\frac{R_{s,B}^{(\text{w})}}{R_{s,A}^{(\text{w})}} \right) \cdot [p_A{}^{(\text{w-Fe})} - p_A{}^{(\text{m-w})}] \quad (5)$$

$$p_A{}^{(\text{h-m})} = p_A{}^{(\text{m-w})} - \left(\frac{R_{s,A}^{(\text{m})}}{R_{s,A}^{(\text{m})} + R_I^{(\text{h-m})} + \frac{R_{s,B}^{(\text{m})}}{K_e{}^{(\text{h-m})}}} \right) \cdot \left[p_A{}^{(\text{m-w})} - \frac{p_B{}^{(\text{m-w})}}{K_e{}^{(\text{h-m})}} \right] \quad (6)$$

$$p_B{}^{(\text{h-m})} = p_B{}^{(\text{m-w})} + \left(\frac{R_{s,B}^{(\text{m})}}{R_{s,A}^{(\text{m})}} \right) \cdot [p_A{}^{(\text{m-w})} - p_A{}^{(\text{h-m})}] \quad (7)$$

where

$$\Omega_a = \frac{1}{R_I^{(\text{m-w})}} + \frac{1}{R_{s,A}^{(\text{m})} + R_I^{(\text{h-m})} + \frac{R_{s,B}^{(\text{m})}}{K_e{}^{(\text{h-m})}}} \quad (8)$$

$$\Omega_b = \frac{K_e{}^{(\text{h-m})}}{R_I^{(\text{m-w})}} + \frac{K_e{}^{(\text{m-w})}}{R_{s,A}^{(\text{m})} + R_I^{(\text{h-m})} + \frac{R_{s,B}^{(\text{m})}}{K_e{}^{(\text{h-m})}}} \quad (9)$$

$$\Omega_c = \frac{1}{R_I^{(\text{w-Fe})}} + \frac{\Omega_a}{\Omega_a R_{s,A}^{(\text{w})} + \frac{\Omega_b R_{s,B}^{(\text{w})}}{K_e{}^{(\text{m-w})} K_e{}^{(\text{h-m})}} + 1} \quad (10)$$

$$\Omega_d = \frac{K_e{}^{(\text{m-w})} K_e{}^{(\text{h-m})}}{R_I^{(\text{w-Fe})}} + \frac{\Omega_b K_e{}^{(\text{w-Fe})}}{\Omega_a R_{s,A}^{(\text{w})} + \frac{\Omega_b R_{s,B}^{(\text{w})}}{K_e{}^{(\text{m-w})} K_e{}^{(\text{h-m})}} + 1} \quad (11)$$

$$R_{F,j} = \frac{RT_s}{k_{m,j} 4\pi x_o{}^2}, \quad j = \text{A, B} \quad (12)$$

$$R_{s,j}^{(\text{Fe})} = \frac{RT_s}{D_{\text{eff},j}^{(\text{Fe})}} \cdot \frac{[x_o - x^{(\text{w-Fe})}]}{4\pi x^{(\text{w-Fe})} x_o} \quad (13)$$

$$R_{s,j}^{(\text{w})} = \frac{RT_s}{D_{\text{eff},j}^{(\text{w})}} \cdot \frac{[x^{(\text{w-Fe})} - x^{(\text{m-w})}]}{4\pi x^{(\text{m-w})} x^{(\text{w-Fe})}} \quad (14)$$

$$R_{s,j}^{(\text{m})} = \frac{RT_s}{D_{\text{eff},j}^{(\text{m})}} \cdot \frac{[x^{(\text{m-w})} - x^{(\text{h-m})}]}{4\pi x^{(\text{h-m})} x^{(\text{m-w})}} \quad (15)$$

$$R_I{}^{(t\text{-s})} = \frac{RT_s}{k_r{}^{(t\text{-s})} 4\pi [x^{(t\text{-s})}]^2} \quad (16)$$

The fractional reduction of the hematite pellet is defined as the weight fraction of the available oxygen originally present which is removed and expressed in terms of the effective interface radii at any time instant by

$$F = \frac{1}{x_o{}^3} \{x_o{}^3 - [x^{(\text{w-Fe})}]^3 + \phi^{(\text{h-w})} [[x^{(\text{w-Fe})}]^3 - [x^{(\text{m-w})}]^3] + \phi^{(\text{h-m})} [[x^{(\text{m-w})}]^3 - [x^{(\text{h-m})}]^3]\} \quad (17)$$

PARAMETER ESTIMATION

In order to predict the behavior of a given system, numerical values have to be assigned to the various parameters appearing in the model.

In the present case, the objective is to select the parameters for representing a series of measurements reported by Szekely and El-Tawil (1976) on the reduction of hematite disks (circumferential face of which was coated by a ceramic) with carbon monoxide, hydrogen, and carbon monoxide-hydrogen mixtures over the temperature range 800° to 900°C.

The experimental conditions for this work are summarized in Table 1. As discussed in earlier publications (Szekely, 1974), certain parameters, such as the pore diffusivities and the gas phase mass transfer coefficients, may be readily estimated; moreover, data have been reported in the literature (Spitzer, 1966) regarding the activation energies of the various reaction steps.

Thus the following were adopted for evaluating the parameters in the governing equations.

The pore diffusivities, porosities, and the external mass transfer coefficients were determined by procedures, to be described below. The frequency factors for the various reactions, three for each gaseous reactant, were estimated with the aid of a data fit from measurements obtained with the pure gaseous components, namely, hydrogen and carbon monoxide reactions.

The actual procedure employed for estimating these quantities is outlined.

Interphase Mass Transfer

At the high Reynolds numbers ($N^R{}_e > 20$), gas film mass transfer posed a negligible resistance. Thus, differences across the external film in concentration were assumed negligibly small.

Porosities of Shell Layers

From the stoichiometry of the consecutive reduction steps, assuming no volume change, the following equations were used to estimate the porosities of the intermediate product layers

$$\epsilon_{\text{Fe}} = 1 - (1 - \epsilon_h) \frac{2\rho_h}{\rho_{\text{Fe}}} \quad (18)$$

$$\epsilon_w = 1 - (1 - \epsilon_h) \frac{2\rho_h}{\rho_w} \quad (19)$$

$$\epsilon_m = 1 - (1 - \epsilon_h) \frac{2\rho_h}{3\rho_m} \quad (20)$$

Effective Diffusivities

Because of the relatively large pore size (2 to 5μ) found experimentally in the reduced layers, the rate of Knudsen diffusion was found to be at least ten times faster than molecular diffusion, so that in

TABLE 1. SAMPLE PROPERTIES AND REDUCTION CONDITIONS OF SZEKELY AND EL-TAWIL'S EXPERIMENTAL WORK (1975)

Type of hematite: reagent grade powder (Baker Chemical Co.)
Diameter of pressed disks: 2.86 cm
Thickness of pressed disks: 1 + cm
Void fraction of disks: 0.6 ± 0.02
Shape of sample: ceramic coated unidirectional disks
Gas flow rate: 18 l/min at room condition
Diameter of tubular furnace: 5 cm
Reduction temperature: 800°, 850°, and 900°C
Pressure: 1 atm
Gas composition: various compositions of H_2-CO mixtures
Mean pore diameter: 2 to 5μ

TABLE 2. THE CALCULATED EFFECTIVE BINARY DIFFUSIVITIES FOR THE FOLLOWING GAS COMPOSITION

y_{CO}: 50%, y_{CO_2}: 20%, y_{H_2}: 20%, y_{H_2O}: 10%

Temperature (°C)	$D_{CO\text{-}m}$ (cm²/s)	$D_{CO_2\text{-}m}$ (cm²/s)	$D_{H_2\text{-}m}$ (cm²/s)	$D_{H_2O\text{-}m}$ (cm²/s)
800	2.244	1.748	6.315	2.412
850	2.427	1.892	6.822	2.601
900	2.616	2.040	7.342	2.797
950	2.810	2.193	7.874	2.999
1 000	3.011	2.350	8.419	3.207

the calculation of the effective binary diffusivity, the effect of Knudsen diffusion was neglected.* The effective binary gas diffusivity is defined as

$$[D_{12}^{(b)}]_{eff} = D_{12}^{(b)} \frac{\epsilon}{\tau} \qquad (21)$$

For the hydrogen, water, carbon monoxide, carbon dioxide gas mixture considered here, the effective diffusivity of one component with respect to the multicomponent system was approximated by (Reid and Sherwood, 1966)

$$D_{1m} = \frac{(1-y_1)}{\sum_{j=2}^{n} (y_j/D_{1j})} \qquad (22)$$

where y_l is the mole fraction of the diffusing component, y_j is the mole fraction of component j, and D_{lj} is the binary gas-diffusion coefficient for l and j. Table 2 shows the calculated diffusivity of each component with respect to the multicomponent system of a specific composition.

Based on the work of Turkdogan (1971) and Szekely and El-Tawil (1976), the tortuosity τ appearing in Equation (21) was estimated as 2.

In practice the fractional reduction F_{exp} is obtained from weight loss measurements as follows:

$$F_{exp} = \frac{W_o - W}{W_o X_{O_2}} \qquad (23)$$

where W_o is the weight of original sample, W is the weight of sample at any given time, and X_{O_2} is the original weight fraction of oxygen in the sample. The experimental data points F_{exp} with respect to time are compared with the model data points F_m obtained from Equations (1) to (17). The objective function of the minimization problem is then formulated as

$$I = \text{Minimize} \left[\sum_{i=1}^{n} \lambda_i \, (F_{exp,i} - F_{m,i})^2 \right] \qquad (24)$$

where λ_i is the weight factor (or penalty constant) of the i^{th} discrete point, and there are n total points to be fit.

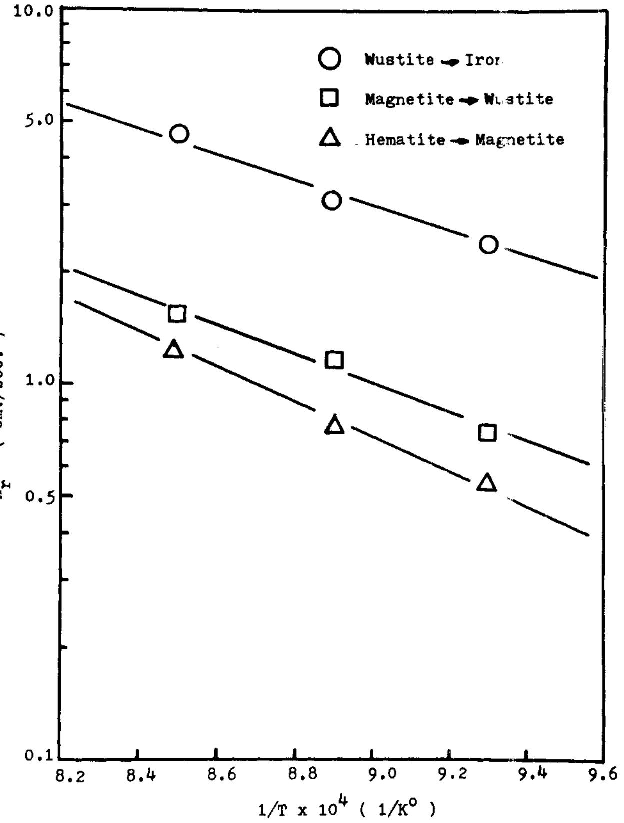

Fig. 2. Plot of the reaction rate constants against the reciprocal temperature for the reduction of hematite with hydrogen.

The experimental fractional reduction curves, that is, fraction of total available oxygen reduced vs. time, of hematite disks reduced by hydrogen and carbon monoxide, respectively, at reduction temperatures of 800°, 850°, and 900°C are employed in the parameter estimation procedures using Equation (24) with the effective diffusivities predetermined. Hence, there are only three parameters, $k_r^{(w\text{-}Fe)}$, $k_r^{(m\text{-}w)}$, and $k_r^{(h\text{-}m)}$, to be estimated for each gas. The Arrhenius type of rate expression is generally assumed applicable for gas-solid reactions. The activation energies of each reduction step from hematite → magnetite → wustite → iron may be obtained from the literature and are given as

for carbon monoxide reduction (Miller, 1968; Trushenski et al., 1974)

$\Delta E^{(w\text{-}Fe)}$ = 16.6 kcal/g-mole
$\Delta E^{(m\text{-}w)}$ = 17.6 kcal/g-mole
$\Delta E^{(h\text{-}m)}$ = 27.2 kcal/g-mole

for hydrogen (Warner, 1964*a*; Nabi and Lu, 1968)

$\Delta E^{(w\text{-}Fe)}$ = 15.2 kcal/g-mole
*$\Delta E^{(m\text{-}w)}$ = 17.0 kcal/g-mole
$\Delta E^{(h\text{-}m)}$ = 22.0 kcal/g-mole

By knowing $\Delta E^{(t\text{-}s)}$ and the estimated $k_r^{(t\text{-}s)}$, the preexponential factor $k_o^{(t\text{-}s)}$ can be determined.

At each specified reduction temperature, a set of $k_r^{(t\text{-}s)}$ of the three consecutive reduction steps was determined by the parameter estimation procedures for the pure hydrogen and the pure carbon monoxide cases separately. The plots of ln $k_r^{(t\text{-}s)}$ vs. $1/T$ are shown in Figures 2 and 3. For each specified reduction step, this graph ln $k_r^{(t\text{-}s)}$ vs. $1/T$ has a slope of $-\Delta E^{(t\text{-}s)}/R$. By adjusting a line with the slope of known value given by the above values of $-\Delta E^{(t\text{-}s)}$ to give the best fit of the three data points, that is, at temperatures of 800°, 850°, and 900°C, a solid line is drawn, as shown in the figure, from which the average value of $k_o^{(t\text{-}s)}$ of the specified reduction step is then determined. The values of the $k_o^{(t\text{-}s)}$ thus obtained are summarized in Table 3.

It may be worthwhile to recapitulate what was done here. Of the parameters appearing in the rate expressions, the pore diffusivities were calculated independently from an expression for a pseudo binary diffusion coefficient, which was then corrected for the known porosity and tortuosity of the solid matrix. Regarding the reaction rate

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* While this procedure was reasonable in the present case, there may be many other instances where allowance has to be made for Knudsen diffusion.

* Assumed data not found in the literature.

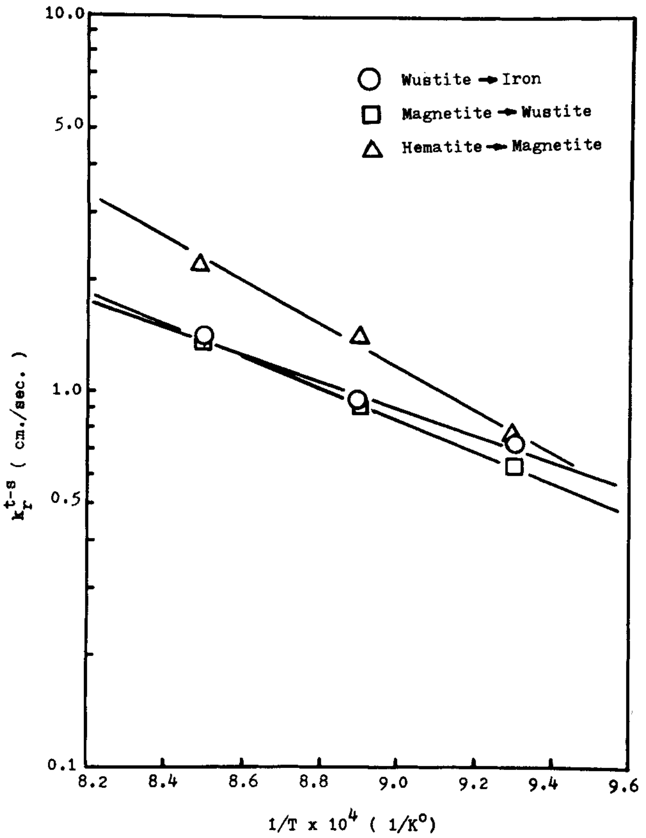

Fig. 3. Plot of the reaction rate constants against the reciprocal absolute temperature for the reduction of hematite with carbon monoxide.

Table 3. Kinetic Constants of Individual Reduction Steps

$$k_r^{(t\text{-}s)} = k_o^{(t\text{-}s)} \exp\left[\frac{-\Delta E^{(t\text{-}s)}}{R\,T_s}\right]$$

For CO-hematite reactions,

$[k_o^{(h\text{-}m)}]_{CO} = 2.7 \times 10^5$ cm/s
$[k_o^{(m\text{-}w)}]_{CO} = 2.5 \times 10^3$ cm/s
$[k_o^{(w\text{-}Fe)}]_{CO} = 1.7 \times 10^3$ cm/s
$[\Delta E^{(h\text{-}m)}]_{CO} = 27.2$ kcal/g-mole
$[\Delta E^{(m\text{-}w)}]_{CO} = 17.6$ kcal/g-mole
$[\Delta E^{(w\text{-}Fe)}]_{CO} = 16.6$ kcal/g-mole

For H_2-hematite reactions,

$[k_o^{(h\text{-}m)}]_{H_2} = 1.6 \times 10^4$ cm/s
$[k_o^{(m\text{-}w)}]_{H_2} = 2.3 \times 10^3$ cm/s
$[k_o^{(w\text{-}Fe)}]_{H_2} = 3.0 \times 10^3$ cm/s
$[\Delta E^{(h\text{-}m)}]_{H_2} = 22.0$ kcal/g-mole
$[\Delta E^{(m\text{-}w)}]_{H_2} = 17.0$ kcal/g-mole
$[\Delta E^{(w\text{-}Fe)}]_{H_2} = 15.2$ kcal/g-mole

constants, the activation energies for the various reaction steps were taken from the literature, while the frequency factors (three for each gaseous reactant) were obtained by a data fit of the measurements carried out with the pure reactants, namely, pure hydrogen and pure carbon monoxide. These measurements were then used to predict the kinetic behavior of gas mixtures.

It should be noted, moreover, that since pore diffusion constituted the principal overall resistance, the actual data fitting of the frequency factors did not play an overwhelming role in matching the predictions with the measurements.

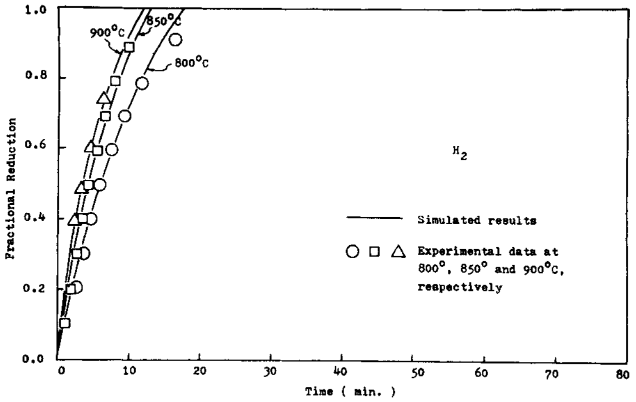

Fig. 4. Comparison of the measurements with the theoretical predictions for the reduction of hematite with hydrogen.

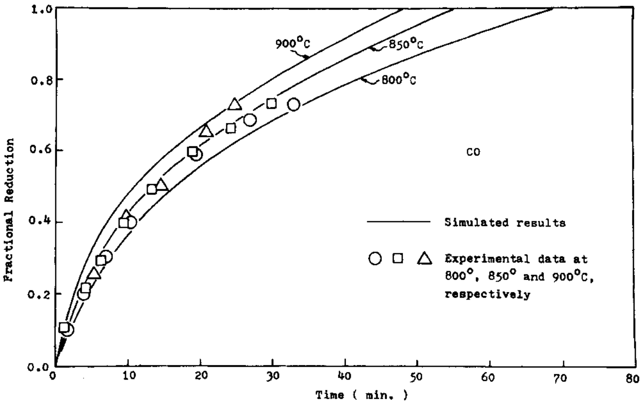

Fig. 5. Comparison of the measurements with the theoretical predictions for the reduction of hematite with carbon monoxide.

COMPARISON OF THE PREDICTIONS WITH MEASUREMENTS

The ultimate test of the appropriateness of the model is its ability to predict the experimentally determined relationships between conversion and time, at various temperatures and gas compositions.

Figures 4 and 5 show a comparison between the experimentally measured and the theoretically predicted conversion vs. time plots for pure hydrogen and pure carbon monoxide as the reducing agents, respectively. It is seen that there is reasonable agreement between measurements and predictions over the temperature range examined. It is noted that the reaction with hydrogen as the reducing agent proceeds much faster (say about five times faster) than reaction with carbon monoxide. This finding is consistent with the results reported by Kawasaki (1962).

A much more critical test of the model and of the assumptions made in its development is its ability to predict the fractional reduction as a function of time for various gas mixtures.

Figures 6, 7, and 8 show plots of the time required to attain a certain fractional reduction as a function of the gas composition for various temperatures. The experimental measurements are denoted by the individual data points, while the theoretical predictions are given by the continuous lines.

It is seen that the mathematical model proposed in the paper is capable of predicting quantitatively the effect of both the gas composition and temperature on the time required to attain a specified degree of reduction. It is noted that the experimental data points exhibit some scatter, but there appears to be no systematic deviations between measurements and predictions.

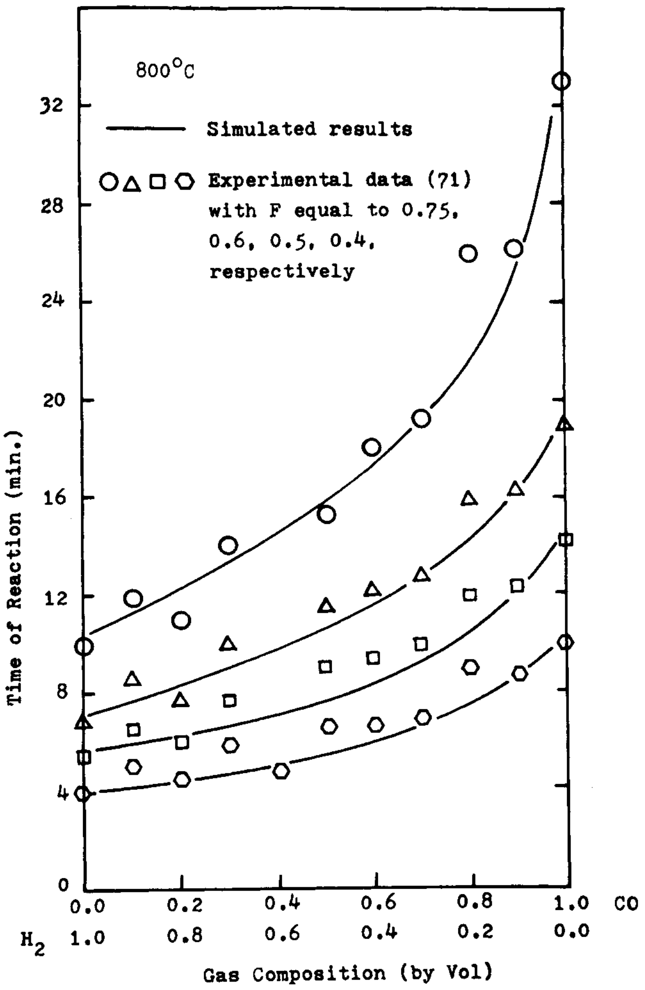

Fig. 6. **Comparison of the measurements with predictions for CO + H_2 mixtures on a plot of the time required to attain a given extent of reaction against the gas composition at 800°C.**

It is noted, moreover, that while the rate of reaction is strongly dependent on the gas composition (the higher the hydrogen content of the reducing gas, the faster the reaction), this relationship is markedly nonlinear.

The following additional remarks may be appropriate at this stage. The trend shown by the experimental points in Figures 6, 7, and 8 is very similar to the findings reported by Turkdogan and Vinters (1973), albeit for a single temperature. It would seem, therefore, that the model could be used for representing these measurements. Justification for the shrinking core representation adopted in the paper has been presented by Szekely and El-Tawil (1976) for the data points that were modeled; moreover, Turkdogan and Vinters (1973) also suggested shrinking core type of behavior in the tentative interpretation of their results.

CONCLUDING REMARKS

By assuming shrinking core or topochemical behavior, a mathematical model was proposed for representing the reduction of hematite disks with hydrogen and carbon monoxide mixtures, within the temperature range 800° to 900°C.

In the development of the model, experimentally measured values were used for the porosity, and the pore diffusion coefficients were predicted from known relationships for pseudo binary diffusion.

The activation energies for the reaction components were obtained from the literature, and the preexponential factors were obtained by data fitting, using measurements for the pure components.

The theoretically predicted rates of reaction (or times required to attain a given conversion level) were found to be in very good agreement with the experimental measurements, both with regard to the effect of temperature and to the effect of gas composition.

The principal objective of the work was the development of a simple model, which is consistent with experimental measurements, for subsequent use in the modeling of a moving-bed system. Thus, the model is not thought to represent an important contribution to the theory of iron oxide reduction but rather a building block for the modeling and optimization of industrial scale systems.

Nonetheless, the predictions of the model are consistent with the basic premise that the overall rate was predominantly controlled by pore diffusion, where the molecular diffusion component was dominant. It follows that the marked dependence on gas composition may be ascribed to the strong influence of the hydrogen content of the mixture in the pseudo binary diffusion coefficient, as shown in Equation (22).

Having shown reasonable agreement with measurements, the model provides a sound basis for representing the moving-bed system to be discussed in Part II. It has to be stressed, nevertheless, that the data fitting were carried out for the particular hematite material and experimental conditions reported by Szekely and El-Tawil. When applying the model for representing data for other types of hematite and at other operating conditions, one should ascertain that the shrinking core approximation is appropriate, and it may also be necessary to readjust the kinetic rate constants used in the model.

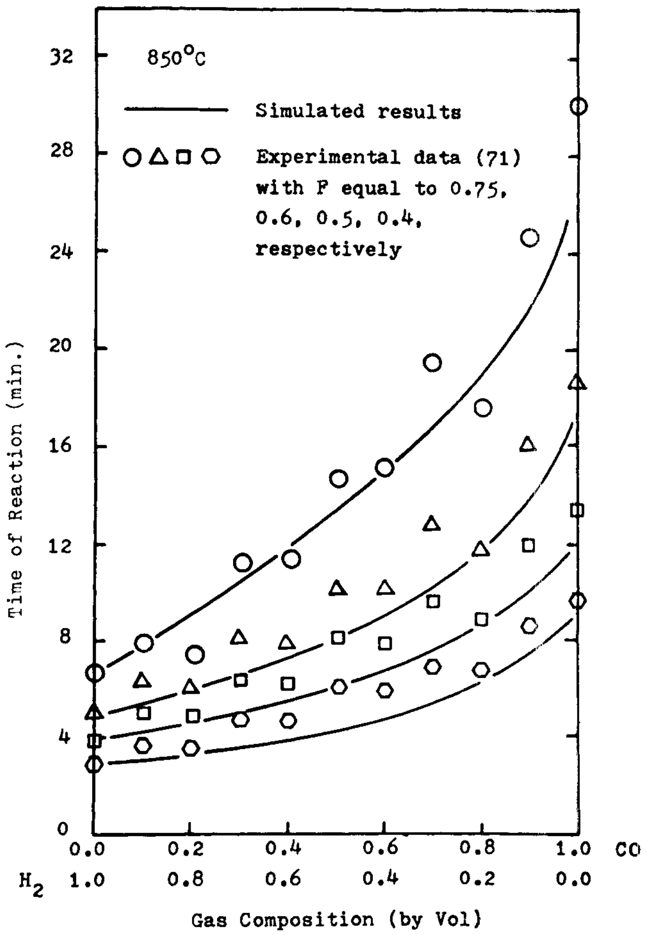

Fig. 7. Comparison of the measurements with predictions for CO + H_2 mixtures on a plot of the time required to attain a given extent of reaction against the gas composition at 850°C.

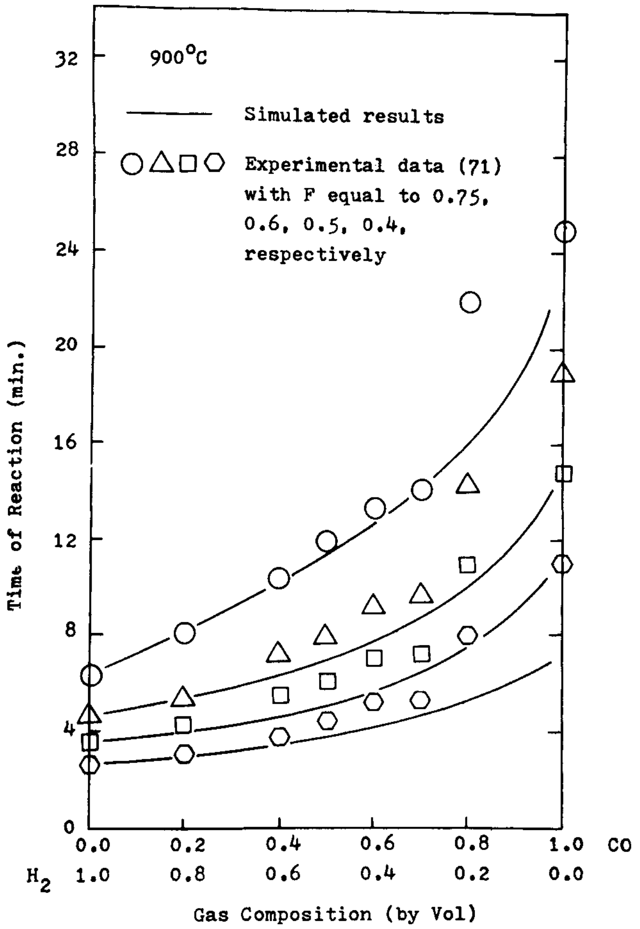

Fig. 8. Comparison of the measurements with predictions for CO + H_2 mixtures on a plot of the time required to attain a given extent of reaction against the gas composition at 900°C.

NOTATION

D_{12} = binary diffusivity, cm²/s
D_{eff} = effective diffusivity, cm²/s
D_{im} = diffusivity of component i in multicomponent system, cm²/s
$D^{(b)}$ = bulk gas diffusivity, cm²/s
$\Delta E^{(t\text{-}s)}$ = activation energy of reaction from t species to s species, kcal/g-mole
F = fractional reduction defined as the weight fraction of oxygen removed with respect to total available oxygen in original hematite pellet, dimensionless
$k_o{}^{(t\text{-}s)}$ = preexponential factor of rate constant for reaction from t to s species, cm/s
$k_r{}^{(t\text{-}s)}$ = specific rate constant for reaction from t to s species, cm/s
$K_e{}^{(t\text{-}s)}$ = equilibrium constant for reaction from t to s species, dimensionless
$p_j{}^{(b)}$ = partial pressure of gas component j in bulk phase, atm
$p_j{}^{(o)}$ = partial pressure of gas component j at surface of the pellet, atm
$p_j{}^{(t\text{-}s)}$ = partial pressure of gas component j at the interface, t-s, atm
P = atmospheric pressure, atm
R = gas constant
T_s = solid temperature, °K
x_o = pellet size in radius, cm
$x^{(t\text{-}s)}$ = effective radius of interface between t and s species, cm
y_i = molar fraction of gas component i, dimensionless

Greek Letters

ϵ_t = void fraction of t phase, dimensionless
ρ_t = true molar density of t species, gmole/cm³
$\phi^{(t\text{-}s)}$ = oxygen density change from t to s species, $\phi^{(\text{h-m})} = 0.333$, $\phi^{(\text{m-w})} = 0.832$, $\phi^{(\text{h-w})} = 0.888$, $\phi^{(\text{w-Fe})} = 1.00$, O atom/gmole t
θ = time, s
τ = tortuosity, dimensionless

Subscripts

h = hematite
m = magnetite
w = wustite
Fe = iron

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Part II. The Direct Reduction Process in a Shaft Furnace Arrangement

A mathematical model was developed for the direct reduction of hematite carried out in a countercurrent moving packed bed, and the process was simulated on a CDC 6400 computer. The response of the model to changes in the various process variables was investigated, and it was found that there is an optimum gas inlet composition (hydrogen-carbon monoxide) for a given set of operating conditions. In addition, an optimum gas inlet temperature was revealed for cases where pure carbon monoxide was used as the reducing gas. The feasibility of side stream injection of reducing gas was studied. The calculations showed that there are certain ranges of operating conditions for which the injection of a hot side stream is advantageous. This study represents the first reported simulation of direct reduction process having carbon monoxide-hydrogen gas mixtures as a reducing medium.

SCOPE

This work represents the first published study of the direct reduction of ferric oxide pellets in a nonisothermal shaft reactor using carbon monoxide plus hydrogen gas mixtures. The kinetic model for the reduction process, developed and verified experimentally in Part I, forms the basis of the reactor model and lends credibility to the simulation results. The system response to operating changes and the discovery of optimal inlet gas compositions, temperatures, etc., should be of interest to the industrial practitioner.

CONCLUSIONS AND SIGNIFICANCE

A mathematical model for the direct reduction process carried out in a countercurrent moving bed using carbon monoxide plus hydrogen mixtures was developed and the response of the model to changes in the various process variables determined. The results show that there exists an optimum inlet gas composition (carbon monoxide-hydrogen) which shifts in response to changes in the other operating conditions. For carbon monoxide-hematite systems, especially those cases using small gas feed rates, there also exists an optimum gas inlet temperature. The feasibility of side stream injection of reducing gas was studied. It was found that there are only certain ranges of operating conditions for which the injection of a side stream would be desirable.

The results of this work suggest several areas in which further optimization studies should be made in order to improve the operation of commercial direct reduction processes.

The projected demands for steel in the coming years coupled with the changing economics in the steel industry strongly support the need for prereduced iron as feedstock (Mackenzie, 1963; Lownie and Barnes, 1972; J. R. Miller, 1972; Pitt, 1973*a-b*). The development of widely accepted prereduction technology is therefore important. More than fifty techniques have been developed for the direct reduction of iron ore, but few have developed beyond the pilot plant stage (McGannon, 1971). In the literature a large number of kinetic studies on a single particle placed in a given environment have been reported over the last 20 yr (see Part I for a discussion of these). However, few attempts have been made to analyze the behavior of metallurgical shaft reactors where the gaseous reduction of hematite takes place. Previous studies on these packed-bed reactors include the work of Barner (1963) and Yagi et al. (1971), who studied isothermal reactors, and the work of Yagi (1974) on nonisothermal reactors. These authors made use of an unreacted shrinking core model (single interface model) to simulate the reduction process. Spitzer et al. (1968) simulated the process in a countercurrent moving packed bed under isothermal conditions by em-