

ON THE DIRECT REDUCTION OF IRON ORE IN ROTARY KILN

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Abstract

An analysis of direct reduction process in the isothermal zone of a rotary kiln has been made. The analysis results in four simultaneous ordinary differential equations and one algebraic equation relating the fraction of total oxygen remaining in iron ore, the fraction of total carbon gasified, partial pressures of carbonmonoxide, carbondioxide and nitrogen inside the charge bed as a function of time.

The numerical solution of equations shows that upto 90% reduction, the rate of reduction is practically constant and it depends on the following parameters: size of ore particles, reactivity of solid fuel, the ratio of iron oxide to carbon in the charge and the fraction of reactor volume occupied by the charge. For a particular reactivity of solid fuel, particle size of ore and the fraction of reactor volume occupied by the charge, the production rate increases with the increase in the ratio of carbon to iron oxide in the charge till the latter reaches a critical value, when further increase of the ratio does not effect the production rate appreciably. This critical ratio of carbon to iron oxide in the charge increases with the decrease in the particle size of ore and with the increase in the reactivity of solid fuel but it is practically independent of fraction of reactor volume occupied by the charge. The analysis further shows that the production rate can be increased by increasing the amount of charge per unit reactor volume, using solid fuel of higher reactivity and by decreasing the particle size of iron ore.

THE EXPERIMENTAL investigations on the direct reduction of iron ore by different grades of solid fuel in nitrogen atmosphere^{1,2} suggests that the reduction proceeds according to following chain of reactions:

$\text{Fe}_n\text{O}_m + m\text{C} = n\text{Fe} + m\text{CO}$ (the starting reaction)

$m\text{CO} + \text{Fe}_n\text{O}_m = n\text{Fe} + m\text{CO}_2$ (reduction by gas) 1(a)

$m\text{CO}_2 + m\text{C} = 2m\text{CO}$ (gasification reaction) 1(b)

Once a sufficient pressure of carbonmonoxide has been built up by the reaction (1), further reduction takes place by the reaction 1(a) followed by the generation of carbonoxide by 1(b)

and the overall rate of reduction was found to be primarily dependent on the rate of reaction 1(b). On the other hand, from the experimental results on the reaction between the mixtures of finely powdered graphite and hematite under vacuum of 5×10^4 torr. Yen³ concluded that the rate of reduction is determined by the diffusion of iron ions in the oxide phase. Moreover, the reduction rate observed by Yen was much less compared to that observed by Baldwin¹ and Kohi².

Remembering that at a total pressure of 5×10^4 Torr the rate of reaction 1(b) which is proportional to the concentration of carbondi-

oxide⁴ is extremely low, it can be concluded that for the industrial processes of direct reduction the mechanism suggested by Yen is of little importance.

In the rotary kiln where the charge containing iron ore and solid fuel is exposed to an atmosphere of carbondioxide and nitrogen, the reduction must be taking place in the following sequence: (i) the formation of carbonmonoxide according to reaction 1(b) followed by (ii) the reduction of iron oxide by carbonmonoxide, reaction 1(a). Based on the above mentioned two reactions, an analysis of the reduction process in the isothermal zone of the rotary kiln has been made.

ANALYSIS:

Assuming that the charge bed is homogeneous and there is no concentration gradient for the gaseous species inside the charge bed, the concentration of carbonmonoxide and carbondioxide inside the charge bed of volume 'v' can be written as:

$$\rho_g v \frac{dp_{CO}}{dt} = v \cdot \dot{r}_{CO} - a \dot{N}_{CO} \quad \dots (2)$$

$$\rho_g v \frac{dp_{CO_2}}{dt} = v \cdot \dot{r}_{CO_2} + a \dot{N}_{CO_2} \quad \dots (3)$$

where,

$$\dot{r}_{CO} = -2W_C \frac{df_C}{dt} + W_O \frac{df_O}{dt} \quad \dots (4)$$

$$\dot{r}_{CO_2} = -W_O \frac{df_O}{dt} + W_C \frac{df_C}{dt} \quad \dots (5)$$

Let the fluxes of carbonmonoxide and carbondioxide be related by the expression

$$\dot{N}_{CO} = -(1-x)\dot{N}_{CO_2} \quad \dots (6)$$

where x is an unknown quantity.

From the definition,

$$\dot{N}_{CO} = K_g^{CO} \rho_g (p_{CO} - p_{CO}^b) + p_{CO} (\dot{N}_{CO} + \dot{N}_{CO_2} + \dot{N}_{N_2}) \quad \dots (7)$$

Assuming that the flux of nitrogen is zero (this assumption is rigorously valid only in the steady state) it follows from equations (6) and (7),

$$\dot{N}_{CO} = \frac{K_g^{CO} (p_{CO} - p_{CO}^b)}{1 - x p_{CO}} \cdot \rho_g \quad \dots (8)$$

$$\dot{N}_{CO_2} = - \frac{K_g^{CO} (p_{CO} - p_{CO}^b)}{1 - x p_{CO}} \cdot (1-x) \rho_g \quad \dots (9)$$

Again, the flux of nitrogen being zero,

$$x = \frac{K_g^{N_2} (p_{N_2}^b - p_{N_2})}{K_g^{N_2} (p_{N_2}^b - p_{N_2}) p_{CO} + K_g^{CO} (p_{CO} - p_{CO}^b) p_{N_2}} \quad \dots (10)$$

The partial pressure of nitrogen inside the charge bed, p_{N_2} , is given by

$$p_{N_2} = p_T - p_{CO} - p_{CO_2} \quad \dots (11)$$

since the total pressure, p_T , inside the charge bed and above it are equal.

Substituting the values of $\dot{r}_{CO}$, $\dot{r}_{CO_2}$, $\dot{N}_{CO}$ and $\dot{N}_{CO_2}$

in equation (2) & (3) and simplifying

$$\rho_g v \frac{dp_{CO}}{dt} = -2W_C \frac{df_C}{dt} + W_O \frac{df_O}{dt} - \frac{a}{v} \left\{ K_g^{CO} (p_{CO} - p_{CO}^b) + K_g^{N_2} \frac{p_{CO}}{p_{N_2}} (p_{N_2}^b - p_{N_2}) \right\} \rho_g \quad \dots (12)$$

$$\rho_g v \frac{dp_{CO_2}}{dt} = W_C \frac{df_C}{dt} - W_O \frac{df_O}{dt} + \frac{a}{v} \left\{ K_g^{CO} (p_{CO} - p_{CO}^b) + K_g^{N_2} \frac{p_{CO} - 1}{p_{N_2}} (p_{N_2}^b - p_{N_2}) \right\} \rho_g \quad \dots (13)$$

The rotary kiln being a horizontally placed cylindrical reactor, the surface area of the charge exposed to the atmosphere of oxidising gases is related to the fraction of reactor volume occupied by the charge by the relation

$$\frac{a}{v} = \frac{2 \sin \theta / 2}{r f_g R_k} \quad \dots (14)$$

where θ is given by

$$2\theta f_g = \theta - \sin \theta \quad \dots (15)$$

Rate of Oxygen Removal:

Since in the rotary kiln the reduction of iron ore takes place topochemically⁵, the rate of oxygen removal from a single iron ore particle can be expressed as:

$$-\frac{dO}{dt} = \frac{P_g D}{4\pi x_0} \cdot \frac{P_{CO} - P_{CO_2}/K_e}{\frac{D}{x_0} + f_0^{-1/3} - 1 + \frac{D}{x_0 K} f_0^{-2/3}} \quad \dots (16)$$

where,

$$\frac{1}{\theta} = \frac{1}{D_{CO}} + \frac{1}{D_{CO_2} \cdot K_e}$$

$$\frac{1}{\alpha} = \frac{1}{K_{CO}} + \frac{1}{K_{CO_2} \cdot K_e}$$

$$D_{CO}^1 = \ell \cdot D_{CO} / r$$

$$D_{CO_2}^1 = \ell \cdot D_{CO_2} / r$$

and K_e is the equilibrium constant for the reduction reaction under consideration.

If the charge bed is composed of iron ore particles of uniform size, at any time the fraction of total oxygen removed from a single particle is equal to the fraction of

of total oxygen removed from the charge bed. Hence,

$$-\frac{df_0}{dt} = \frac{3 \rho_g D}{\rho_0 x_0^2} \cdot \frac{P_{CO} - P_{CO_2}/K_e}{\frac{D}{x_0} + f_0^{-1/3} - 1 + \frac{D}{x_0 K} f_0^{-2/3}} \quad \dots (17)$$

Rate of Carbon Gasification:

For temperature upto 1100°C, the rate of carbon gasification from a single particle of any solid fuel can be written as⁴

$$-\frac{dc}{dt} = 4 \pi x_c \rho_g D_{CO_2} \left\{ P_{CO_2} - P_{CO_2}^e \right\} \quad \dots (18)$$

where,

$$\gamma = (\lambda \coth \lambda - 1) / 1 + \frac{D_{CO_2}^{11}}{x_c \cdot K_{CO_2}} (\coth \lambda - 1)$$

$$\lambda^2 = \frac{k_v \cdot x_c^2}{D_{CO_2}^{11}}$$

If $\lambda \ll 1$, as is the case for a normal rotary kiln process, the equation (18) simplifies to

$$-\frac{dc}{dt} = \rho_g k_v (P_{CO_2} - P_{CO_2}^e) \quad \dots (19)$$

then the rate of carbon gasification from the charge bed can be calculated by the equation

$$-\frac{df_c}{dt} = \frac{3 \rho_g k_v}{\rho_c} (P_{CO_2} - P_{CO_2}^e) \quad \dots (20)$$

Initial conditions

At any time, the fraction of total oxygen removed from the charge in the isothermal portion of the rotary kiln can be obtained by solving equations (11), (15), (17) & (20) along with the initial condition

$$\begin{aligned} \text{at } t = 0, f_0 &= f_c = 1 \\ P_{CO} &= 0 \\ P_{CO_2} &= .21 \end{aligned} \quad \dots (21)$$

Since in actual practice most of the reduction takes place in the isothermal zone of the rotary kiln at a temperature of about 1000°C, equation (21) expresses approximately the values of various parameters inside the charge bed at the entrance of the isothermal reduction zone.

Results and discussion

The reported values of the apparent specific reaction rate constants for the reduction of hematite to iron by CO⁶⁸ and carbon gasification reactions^{4,9,10} vary over a wide range. For the present calculation the value reported by Taniguchi⁶.

$$k = \exp (6.3568 - 6877.8/RT) \text{ Cm/Sec} \quad \dots (22)$$

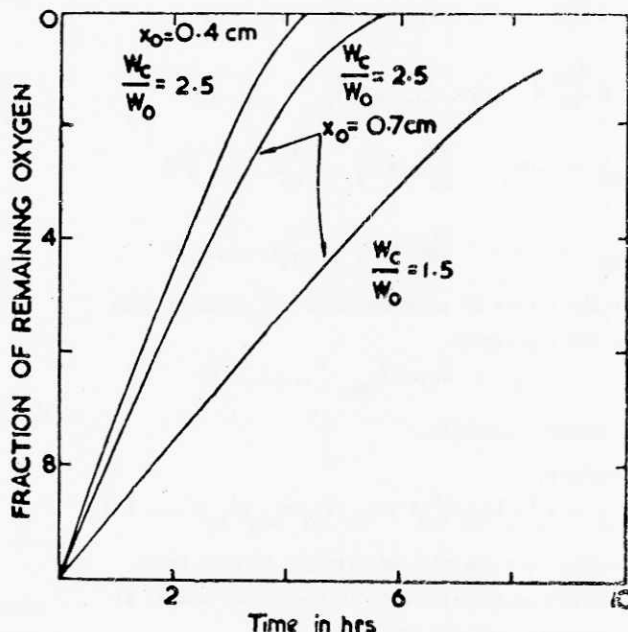


Fig. 1 Effect of particle size and W_c/W_0 on the rate of oxygen removal $f_s = 0.2$, $K_c = .4 \times 10^{14} \text{ Sec}^{-1}$

for the reduction of iron ore and that by Hedden
 $k_v = k_c \exp (-86000/RT) \text{ Sec}^{-1} \dots (23)$
 for the gasification were used. The pre-exponential factor, K , in equation (23) were found to vary⁴ between $.4 \times 10^{12}$ to $.4 \times 10^{14}$ for different grades of fuel.

Although the diffusivity of a gaseous species in a multicomponent mixture of gases depends both on the composition of mixture and the species of gases present, for the convenience of calculation diffusivities are assumed to be independent of the above mentioned factors. The mass-transfer coefficients, k_{co} and k_{o_2} , were calculated assuming the value of Sherwood number to be two, i.e., there is no net flow of gases inside the charge bed, and k_g^{CO} and $k_g^{N_2}$ were calculated by Gilliland Sherwood equation.

$$K_g = .023 (Re)^{0.81} (Sc)^{0.44} \frac{Di}{2Rk} \dots (24)$$

To solve equation (17) the equilibrium constant K_e for the reaction



was used since during the reduction of hematite to iron the oxygen removal takes place at Fe/FeO interface. Calculations were carried out at 1000° C only.

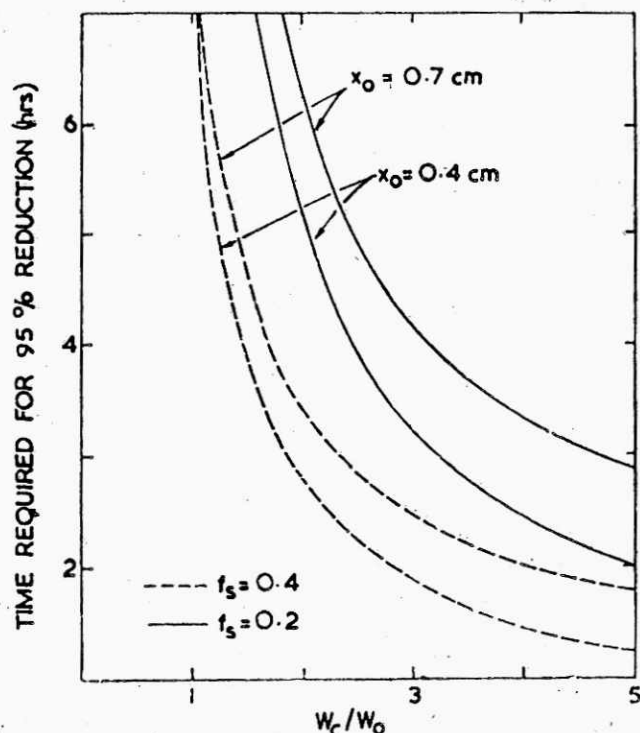


Fig. 3 Effect of particle size, W_c/W_o and f_s on the time required for 95% reduction. $K_c = .4 \times 10^{14} \text{ Sec}^{-1}$

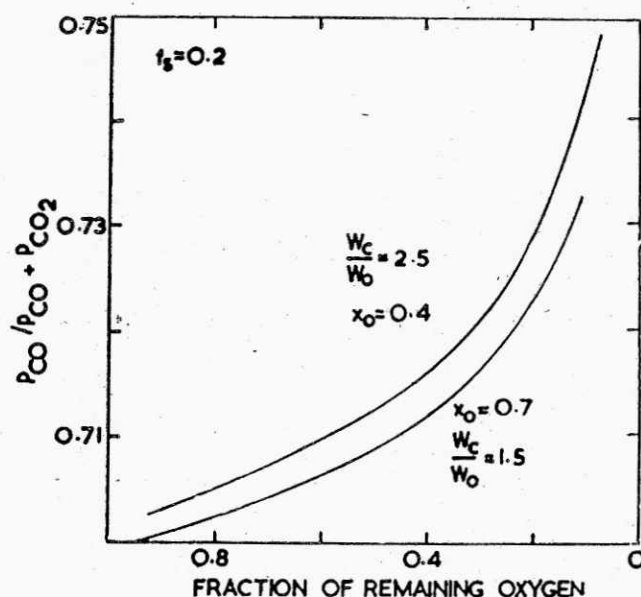


Fig. 2 Effect of particle size of ore and W_c/W_o on the reducing potential of gas inside the charge bed, $K_c = .4 \times 10^{14} \text{ Sec}^{-1}$

Figure(1) shows that the rate of oxygen removal by oxygen is practically constant upto 90% reduction. As the reduction proceeds due to the increase in both the resistance to reaction [denominator in equation (17)] as well as the driving force for reduction. $P_{co}-P_{co_2}/K_e$ (Figure 2) the rate of reaction remains practically unaltered. However, if the ratio of carbon to iron oxide in the charge is small the reduction may not be complete due to the deficiency of carbon (lowest curve in fig.1)

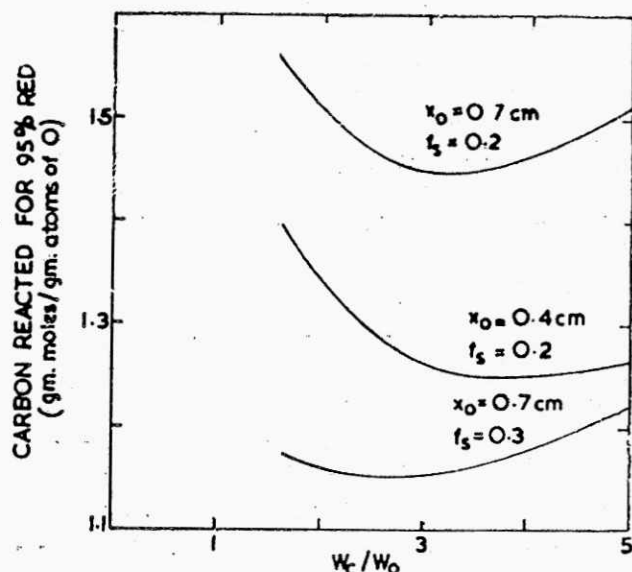


Fig. 4 Effect of W_c/W_o , f_s and the particle size on the amount of carbon consumed for 95% reduction. $K_c = .4 \times 10^{14} \text{ Sec}^{-1}$

It can be noted from figure 3 the time required for a given percentage of reduction can be reduced by increasing the amount of charge per unit reactor volume. the ratio of carbon to iron oxide in the charge and by charging smaller iron ore particles. Remembering that a/v is inversely related to f_s , equation (14), the effect of the amount of charge per unit reaction volume on the time required for 95% reduction can be easily explained.

Figure 4 shows that the amount of carbon consumed for a given percentage of reduction is also dependent on the particle size of ore, fraction of reactor volume occupied by the charge and the ratio of carbon to iron oxide in the charge. Since with the increase in W_c/W_o the amount of carbon gasified per unit time increases while the time required for given percentage of reduction decreases, the total carbon gasified for a given percentage of reduction passes through a minima when plotted against W_c/W_o . The figure 4 further points out that amount of carbon consumed for a given percentage of reaction is more than that required from the stoichiometry.

The production rate per unit charge bed volume may be defined as $W_{op}/100t_p$ where t_p is the time required for 'p' percent reduction. Obviously, the factors which influence t_p or W_o will influence the production rate. It can be noted from figure 5 that with the increase of W_c/W_o which affects both t_p as well as W_o the production rate increases till the former reaches a critical value beyond which it has practically no influence on the production rate. This critical value of W_c/W_o increases with the increase of the reactivity of solid fuel and with the decrease of particle size of ore but it is practically unaffected by the change in the fraction of reactor volume occupied by the charge. The figure 5 further shows that the production rate can be increased by charging fuels of higher reactivity, reducing the particle size of ore and increasing f_s .

Conclusion

(i) In the isothermal zone of a rotary kiln, the rate of reduction is practically independent of time upto 90% reduction.

(ii) The amount of carbon required for a given percentage of reduction is more than that required from the stoichiometric consideration.

(iii) The production rate can be increased by increasing the amount of charge per unit reactor volume, by charging fuels of high reactivity and charging iron ores of smaller size.

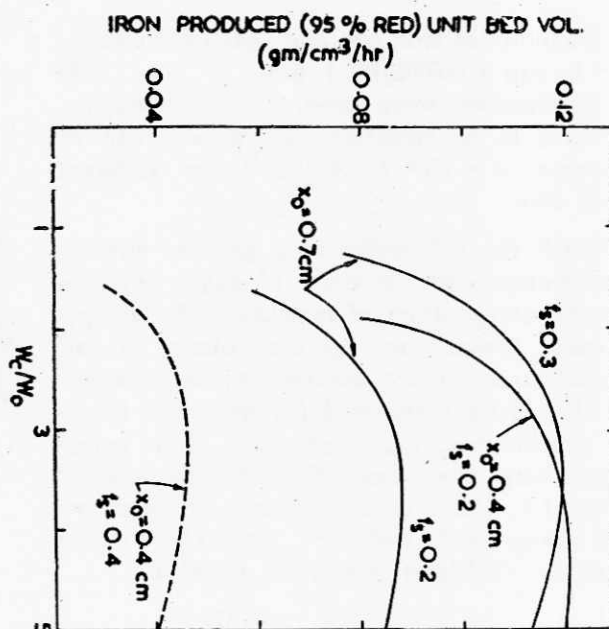


Fig. 5 Effect of W_c/W_o , particle size of ore f_s and the reactivity of solid fuel on the amount of 95% reduced iron produced/hr. $K_s = .4 \times 10^{14} \text{ Sec}^{-1}$. $K_s = .8 \times 10^{13} \text{ Sec}^{-1}$

(iv) The production rate can also be increased by increasing the ratio of carbon to iron oxide in the charge till the ratio reaches a critical value when further increase of the ratio does not affect the production rate appreciably. This critical ratio is dependent on the reactivity of fuel and particle size of ore but is practically independent of fraction of solid in the charge.

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Nomenclature

a = Surface area of the charge exposed to the oxidising atmosphere of the kiln (Cm^2)	r_i = Rate of formation of i th. component per unit bed volume ($\text{gm moles/Cm}^2/\text{hr}$)
D_i = Diffusivity of i th. component (Cm^2/Sec)	Re = Reynolds number
f_s = Fraction of reactor volume occupied by the charge	R_k = Radius of the kiln (Cm)
f_i = Fraction of i th. component present in the bed	Sc = Schimolt number
k = Specific reaction rate constant for the equation (25 Cm/Sec)	t = time (Sec).
k_i = Mass transfer coefficient of i th. species through the gas film around the iron ore particles (Cm/Sec)	v = Volume of charge bed (Cm^3)
K_{ig} = Mass transfer coefficient of i th. species through the gas film present over charge bed (Cm/Sec)	W_i = Weight of i th. component per unit volume of charge (gm atoms/Cm^3)
K_e = Equilibrium constant for the reaction 1(a)	P_c = Density of oxygen in iron ore ($\text{gm atoms}/(\text{gm moles/Cm}^3)$)
K_v = Reaction rate constant for carbon gasification equation 1(b) Sec^{-1})	P_c = Density of carbon in solid fuel ($\text{gm moles}/\text{Cm}^3$)
N_i = Flux of i th. component (gm moles/Cm^2)	P_g = Density of gas ($\text{gm moles}/\text{Cm}^3$)
P_i = Partial pressure of i th. component	ϵ = Porosity
PT = Total pressure in the reactor (atm)	λ = Tortuosity factor
	d = Void fraction in the charge bed
	θ = Angle subtended by the charge at the centre of kiln

Subscript

C = Carbon and O = Oxygen in iron oxide