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 carbon monoxide, carbon dioxide and nitrogen inside the charge bed as a function of time.

The numerical solution of equations shows that up to 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 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 carbon monoxide has been built up by the reaction (1), further reduction takes place by the reaction 1(a) followed by the generation of carbon dioxide 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 $5 \times 10^4$ torr, Yen 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 Baldwin and Kohl.

Remembering that at a total pressure of $5 \times 10^4$ Torr the rate of reaction 1(b) which is proportional to the concentration of carbondioxide 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:

$$\frac{dN_{CO}}{dt} = v \cdot \bar{N}_{CO} - a \cdot \bar{N}_{CO} \quad \ldots (2)$$

$$\frac{dN_{CO_2}}{dt} = v \cdot \bar{N}_{CO_2} + a \cdot \bar{N}_{CO_2} \quad \ldots (3)$$

where,

$$\bar{N}_{CO} = \frac{\text{d}r}{\text{d}t} \quad \bar{N}_{CO_2} = \frac{\text{d}r}{\text{d}t} \quad \ldots (4)$$

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

$$N_{CO} = -(1-x)N_{CO_2} \quad \ldots (6)$$

where $x$ is an unknown quantity.

From the definition,

$$\frac{dN_{CO}}{dt} = k_{g} \bar{N}_{CO}^{b} (p_{CO} - p_{CO}^{b}) + p_{CO} (\bar{N}_{CO} + \bar{N}_{CO_2} + \bar{N}_{CO_2}) \quad \ldots (7)$$

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),

$$\frac{dN_{CO}}{dt} = \frac{k_{g} \bar{N}_{CO}^{b} (p_{CO} - p_{CO}^{b})}{1 - x} \cdot \bar{N}_{CO} \quad \ldots (8)$$

Again, the flux of nitrogen being zero,

$$x = \frac{p_{CO} (1-x)}{k_{g} \bar{N}_{CO}^{b} (p_{CO} - p_{CO}^{b})} \quad \ldots (9)$$

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

$$P_{N_2} = p_{N_2} - p_{CO} - P_{CO_2} \quad \ldots (10)$$

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

Substituting the values of $r_{CO}$, $r_{CO_2}$, $N_{CO}$ and $N_{CO_2}$ in equation (2) & (3) and simplifying

$$\frac{dS_{CO}}{dV} = -2\bar{N}_{CO} \frac{\text{d}r}{\text{d}t} + \frac{\text{d}r}{\text{d}t} + \frac{\text{d}r}{\text{d}t} = \frac{k_{g} \bar{N}_{CO}^{b}}{1-x} \left( \frac{p_{CO} - p_{CO}^{b}}{p_{CO}^{b}} \right) \frac{1}{P_{N_2}} \quad \ldots (11)$$

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

$$S_{CO} = \frac{2 \pi \text{diam} \cdot V}{\bar{N}_{CO}} \quad \ldots (12)$$
\[ \frac{dG}{dt} = \frac{2nR}{8} \] 

**Rate of oxygen removal**

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

\[ -\frac{dG}{dt} = 4n \frac{P_{CO}}{\gamma} \frac{D_{CO2}}{K} \] 

where,

\[ D_{CO} = \alpha \frac{P_{CO}}{\gamma} \]

\[ D_{CO2} = \alpha \frac{P_{CO2}}{\gamma} \]

and \( K \) 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 total oxygen removed from the charge bed. Hence,

\[ -\frac{df}{dt} = 2 \frac{P_{CO}}{P_{CO2}} \frac{P_{CO} - P_{CO2}/X}{X_0} \]

**Rate of carbon gasification**

For temperature up to 1100°C, the rate of carbon gasification from a single particle of any solid fuel can be written as:

\[ -\frac{dG}{dt} = 4n \frac{P_{CO}}{\gamma} \frac{D_{CO2}}{K} \] 

where,

\[ \gamma = \left( \frac{\lambda \coth \lambda - 1/3}{\lambda \coth \lambda - 1} \right) \]

\[ \lambda^2 = \frac{\gamma K_{CO2}}{P_{CO2}} \]

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

\[ -\frac{dG}{dt} = \frac{P_{CO}}{\gamma} \left( \frac{P_{CO2}}{P_{CO2}} \right) \]

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

\[ -\frac{df}{dt} = 2 \frac{P_{CO}}{P_{CO2}} \left( \frac{P_{CO} - P_{CO2}/X}{X_0} \right) \]

**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

\[ \text{at } t = 0, \quad f_0 = f_a = 1 \]

\[ P_{CO} = 0 \]

\[ P_{CO2} = 0.21 \]

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 \( CO \) and carbon gasification reactions vary over a wide range. For the present calculation the value reported by Taniguchi is

\[ k = \exp \left( 6.3568 - \frac{6787.8}{RT} \right) \text{ Cm/Sec} \]

\[ K = 0.2, \quad K_c = 0.02 \text{ Sec}^{-1} \]

**Fig. 1** Effect of particle size and \( W_c/W_0 \) on the rate of oxygen removal \( f_a = 0.2 \), \( K_c = 0.4 \times 10^{14} \text{ Sec}^{-1} \)
for the reduction of iron ore and that by Hedden
\[ k_v = k_0 \exp \left( -\frac{86000}{RT} \right) \text{Sec}^{-1} \]  
... (23)
for the gasification were used. The pre-exponential factor, \( K_v \), in equation (23) were found to vary 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 \( k_{CO_2} \), 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 \( k_{CO} \) and \( k_{CO_2} \) were calculated by Gilliland Sherwood equation.

\[ K_D = 0.023 \left( \frac{Re}{Sc} \right)^{0.81} \]  
... (24)

To solve equation (17) the equilibrium constant \( K_e \) for the reaction
\[ \text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2 \]  
... (25)
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. 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 up to 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. 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. 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 that 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 $W_o/W_0$, 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 $W_o/W_0$. 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 $W_{oD}/100p$, where $t_o$ is the time required for 'p' percent reduction. Obviously, the factors which influence $t_o$ or $W_o$ will influence the production rate. It can be noted from figure 5 that with the increase of $W_o/W_0$ which affects both $t_o$ 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 $W_o/W_0$ 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 up to 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.

(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.

**References**

Nomenclature

\( a = \) Surface area of the charge exposed to the oxidising atmosphere of the kiln (\( \text{Cm}^2 \))

\( D_i = \) Diffusity of \( i \)th component (\( \text{Cm}^2/\text{Sec} \))

\( f_s = \) Fraction of reactor volume occupied by the charge

\( f_i = \) Fraction of \( i \)th component present in the bed

\( k = \) Specific reaction rate constant for the equation (25 \( \text{Cm}/\text{Sec} \))

\( k_i = \) Mass transfer coefficient of \( i \)th species through the gas film around the iron ore particles (\( \text{Cm}/\text{Sec} \))

\( K_{ig} = \) Mass transfer coefficient of \( i \)th species through the gas film present over charge bed (\( \text{Cm}/\text{Sec} \))

\( K_e = \) Equilibrium constant for the reaction 1(a)

\( K_\varphi = \) Reaction rate constant for carbon gasification equation 1(b) \( \text{Sec}^{-1} \)

\( N_i = \) Flux of \( i \)th component (\( \text{gm moles}/\text{Cm}^2 \))

\( P_i = \) Partial pressure of \( i \)th component

\( P_T = \) Total pressure in the reactor (atm)

\( r_i = \) Rate of formation of \( i \)th component per unit bed volume (\( \text{gm moles}/\text{Cm}^2/\text{hr} \))

\( Re = \) Reynolds number

\( R_k = \) Radius of the kiln (\( \text{Cm} \))

\( S_c = \) Schimolt number

\( t = \) time (\( \text{Sec} \))

\( v = \) Volume of charge bed (\( \text{Cm}^3 \))

\( W_i = \) Weight of \( i \)th component per unit volume of charge (\( \text{gm atoms}/\text{Cm}^3 \))

\( P_c = \) Density of oxygen in iron ore (\( \text{gm atoms}/(\text{gm moles}/\text{Cm}^3) \))

\( P_c = \) Density of carbon in solid fuel (\( \text{gm moles}/\text{Cm}^3 \))

\( P_g = \) Density of gas (\( \text{gm moles}/\text{Cm}^3 \))

\( \varphi = \) Porosity

\( \lambda = \) Tortuosity factor

\( d = \) Void fraction in the charge bed

\( \theta = \) Angle subtended by the charge at the centre of kiln

Subscript

\( \text{C} = \) Carbon and \( \text{O} = \) Oxygen in iron oxide