Model for Reduction of Iron Oxide Pellet with a C-O-H-N Gas Mixture Considering Water Gas Shift Equilibrium in the Gas While It Diffuses through the Product Layer

Viswanathan N. Nurni[1*] and Bharath N. Ballal[2]

1. Metals and Minerals Research Laboratory, Division of Sustainable Process Engineering, Lulea University of Technology, Lulea 97187, Sweden

2. Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai 4000076, India

Abstract: In metallurgical processes, more and more usage of hydrocarbons is encouraged to bring down the carbon emissions. In this regard, numerous investigations on reduction of oxides by C-O-H-N gas mixture have been reported. Attempts to simulate these reduction processes using shrinking core model, one of the common models used for such studies, have under predicted the reduction rates. This may be owing to the fact that the homogeneous reaction in the gas phase is not being considered. If the reaction temperatures are above 1,000 K, generally so for many reduction processes, the homogeneous gas reaction rates are expected to be high enough that local equilibrium in the gas phase can be assumed. In the present study, reduction of wustite in a C-O-H-N gas mixture has been modeled using shrinking core model considering the water gas shift equilibrium in the gas while it diffuses through the product layer.

Key words: Reduction, iron ore, CO, H_2, water gas shift reaction, kinetics, model, shrinking core.

1. Introduction

With increasing environmental awareness there are efforts towards decreasing carbon emissions by more and more usage of hydrocarbons in place of carbon resources. In pyro-metallurgical processes, hydrogen in hydrocarbons can act as a fuel as well as a reducing agent. Blast furnace operators are replacing more and more expensive coke with pulverized coal and other hydrocarbons injected through tuyeres. Thus, understanding of reduction of iron oxide with gases containing CO, CO_2, H_2 and H_2O along with N_2 is important. Last 4-5 decades, numerous experiments have been conducted to understand the reduction phenomena of iron oxide using these gas mixtures [1-3]. A comprehensive review of reduction of iron oxide is available elsewhere [4].

These experiments have indicated that an even small addition of hydrogen to $CO-CO_2-N_2$ mixture enhances the reduction of iron oxide. One of the reasons for this enhancement has been argued as faster diffusivity of hydrogen through the pores of the pellet. Models based on shrinking model have been reported in the literature based on this argument [3]. However, these models did not take into account the homogenous water gas shift reaction, namely:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (1)$$
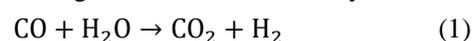
At high temperatures, beyond 1,000 K, it is reasonable to assume that this homogeneous reaction can proceed so fast that the equilibrium is attained. In this paper, along with the multi component diffusion of gaseous species through the pores of the pellet, local equilibrium of the water gas shift reaction has

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*Corresponding author: Viswanathan N. Nurni, Professor, research fields: process modeling of iron and steel making processes. E-mail: nurvis@ltu.se; vichuiitb@gmail.com.

been imposed. Further, the effect of considering the water gas shift reaction on the reduction rate has been compared with that without considering it. Please note that this paper explores the effect of water gas shift reaction at the conceptual level and in our future publications the present model will be substantiated with experimental data.

2. The Model Description

As mentioned earlier, in the present work the shrinking core model has been used to describe the overall reaction kinetics. In the shrinking core model, the following kinetics steps are involved, (1) mass transfer of gaseous reactants and products through the boundary layer gas film around the particle; (2) diffusion of gaseous species (both reactants and products) through the porous product layer; (3) the chemical reaction at the solid product-reactant interface. A schematic showing these steps are illustrated in Fig. 1.

The multi component diffusivities for CO, CO_2, H_2, H_2O and N_2 in the gas mixture are calculated using equations derived from Stefan-Maxwell Eq. (1).

$$\frac{1}{D_{im}} = \frac{\sum_{j=1}^{n} (1/D_{ij})(x_j N_i - x_i N_j)}{N_i - x_i \sum_{j=1}^{n} N_j} \qquad (1)$$

where, D_{ij} is the binary diffusion coefficient estimated using Lennard-Jones parameters, N_i is the molar flux and x is the mole fraction. Please note that the last term in the denominator is zero being an equimolar diffusion. The diffusivities need to be adjusted for particle porosity as well as tortuosity.

In order to make sure that the water gas shift equilibrium is maintained locally, a generation term for the water gas shift reaction (R1) was introduced. Let us denote the rate of the water gas shift reaction per unit volume by $\dot{G}(r)$. Please note that this rate will be function of radial location, since depending on the composition of species at any location the rate of this reaction would change so as to reach the equilibrium.
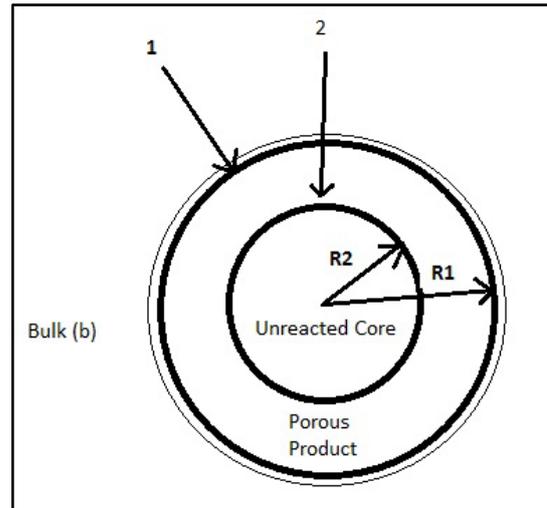

Fig. 1 Schematic of the shrinking core.

$$\frac{D_{CO2m}}{r^2}\frac{d}{dr}\left(r^2 \frac{dC_{CO2}}{dr}\right) - \dot{G}(r) = 0 \qquad (2)$$

$$\frac{D_{COm}}{r^2}\frac{d}{dr}\left(r^2 \frac{dC_{CO}}{dr}\right) + \dot{G}(r) = 0 \qquad (3)$$

$$\frac{D_{H2m}}{r^2}\frac{d}{dr}\left(r^2 \frac{dC_{H2}}{dr}\right) - \dot{G}(r) = 0 \qquad (4)$$

$$\frac{D_{H2Om}}{r^2}\frac{d}{dr}\left(r^2 \frac{dC_{H2O}}{dr}\right) + \dot{G}(r) = 0 \qquad (5)$$

$\dot{G}(r)$ needs to be calculated such that the local equilibrium prevails for the water gas shift reaction (R1). If the authors denote this equilibrium constant as K_{R1}, then:

$$K_{R1} = \frac{C_{CO2}C_{H2}}{C_{CO}C_{H2O}} \qquad (6)$$

The symbol C is used to describe the concentration of species.

Eqs. (2)-(6), form algebraic-differential equations and need to be solved using appropriate boundary conditions.

The boundary conditions for the differential equations are derived from: (a) the mass transfer through the gas boundary layer at the surface of the pellet; (b) the intrinsic reaction kinetics of the oxide with CO and H_2 at the unreacted core surface.

Let the authors look at the boundary conditions at the pellet surface due to gas boundary layer. In

principle, the boundary layer equations need to reformulated, similar to the diffusion through the product layer discussed above. However, boundary layer being very small the rate of water gas shift reaction in the boundary layer can be neglected. It is to be noted that, the bulk gas also should be in equilibrium as far as water gas shift reaction is concerned.

$$k_{m,CO2}\left(C_{CO2}^1 - C_{CO2}^b\right) = -D_{CO2m}\frac{dC_{CO2}}{dr}\bigg|_1 \qquad (7)$$

$$k_{m,CO}\left(C_{CO}^1 - C_{CO}^b\right) = -D_{COm}\frac{dC_{CO}}{dr}\bigg|_1 \qquad (8)$$

$$k_{m,H2}\left(C_{H2}^1 - C_{H2}^b\right) = -D_{H2m}\frac{dC_{H2}}{dr}\bigg|_1 \qquad (9)$$

$$k_{m,H2O}\left(C_{H2O}^1 - C_{H2O}^b\right) = -D_{H2Om}\frac{dC_{H2O}}{dr}\bigg|_1 \qquad (10)$$

The superscripts b, 1 and 2, stands for bulk, outer surface of the pellet and the unreacted core surface respectively, as illustrated in Fig. 1. Similarly, the authors can also apply the boundary conditions on the product-reactant interface (location 2).

$$k_{r,R2}(C_{CO2}^2/K_{R2} - C_{CO}^2) = -D_{COm}\frac{dC_{CO}}{dr}\bigg|_2 \qquad (11)$$

$$-k_{r,R2}(C_{CO2}^2/K_{R2} - C_{CO}^2) = -D_{CO2m}\frac{dC_{CO2}}{dr}\bigg|_2 \qquad (12)$$

$$k_{r,R3}(C_{H2O}^2/K_{R3} - C_{H2}^2) = -D_{H2m}\frac{dC_{H2}}{dr}\bigg|_2 \qquad (13)$$

$$-k_{r,R3}(C_{H2O}^2/K_{R3} - C_{H2}^2) = -D_{H2Om}\frac{dC_{H2O}}{dr}\bigg|_2 \qquad (14)$$

Here $k_{r,R2}$ and $kr_{,R3}$ refers to reactions rate constants for:

$$FeO + CO \longrightarrow Fe + CO_2 \qquad (R2)$$
$$FeO + H_2 \longrightarrow Fe + H_2O \qquad (R3)$$

respectively. K_{R2} and K_{R3} refer to the equilibrium constants for the above two reactions respectively. Mass transfer coefficient, $k_{m,i}$, is evaluated using the Ranz-Marshall equation [6], as given below:

$$Sh_i = 2 + 0.6\,\mathrm{Re}_p^{1/2}\,Sc_i^{1/3} \qquad (15)$$

$Sh_i = \frac{d_p k_{m,i}}{D_{im}^g}$, Sherwood number;

$Re_p = \frac{\rho^g v^g d_p}{\mu^g}$, Reynolds number;

$Sc_i = \frac{\mu^g}{D_{im}^g \rho^g}$, Schmidt number;

$k_{m,i}$, Mass Transfer Coefficient of Species, i (m/s);
d_p, Diameter of the solid particle, m;

D_{im}^g, Multicomponent Mixture Diffusivity of species, i (m²/s).

Please note that the present model determines the overall reaction rate at any particular instant of time where the radius of the unreacted core is known. One can use the overall unsteady mass balance to compute the progression of the shrinking of the unreacted core. In the current paper, results of the overall reaction rate only at a particular instant of time have been presented.

The algebraic-differential equations were solved by discretizing the equation using control volume method which resulted in simultaneous non-linear algebraic equations. A computer program was written to solve these equations using appropriate iterative solution methodology.

3. Results and Discussion

As the reduction of FeO is one of the most important reactions in iron making processes, this has been considered in the present case study. For the sake of comparison simulation were also carried out without considering the water gas shift reaction and those results were compared with those with water gas shift reaction being considered.

Figs. 2 and 3 show the variation of mole fraction of CO and CO_2 as well as that of H_2 and H_2O inside the product shell for the case where water gas shift reaction has been considered as well as that being not considered. The simulation was carried out for a temperature of 1,200 K.

It is interesting to note that the CO and CO_2 profiles become steeper when water gas shift reaction is considered and the reverse for the H_2 and H_2O. This is due to the fact that the reaction *R1* proceeds in the forward direction which generates H_2 concentration while consuming CO. The net flux of CO_2 and H_2O going out from the pellet is more for the case where the water gas shift reaction was considered at this temperature of 1,200 K. This clearly demonstrates that the water gas shift reaction has significant impact on the overall reaction kinetics of the pellet.

Table 1   Inputs used for generating the results.

| Oxide for reduction	FeO
Temperature (K)	1,000-1,200
Pressure (atms)	1
Molefractions x_{CO}, x_{CO2}, x_{H2}, x_{H2O}, x_{N2}	0.4, 0.1, 0.1, 0.021, 0.379
Velocity of the gas stream (m/s)	1
Radius of the pellet, $R1$ (m)	0.005
Radius of the unreacted core, $R2$ (m)	0.002
Porosity in the product layer	0.4
Tortuosity	4
Equilibrium constants	
K_{R1}	Exp (-2.526 + 2068/T) [7]
K_{R2}	Exp (1.0103 – 1972.6/T) [7]
Intrinsic reaction rate constants (cm/s)	
k_{R2}	Exp (3.39-8560/1.987/T) [8]
k_{R3}	Exp (10.4-19000/1.987/T) [8]
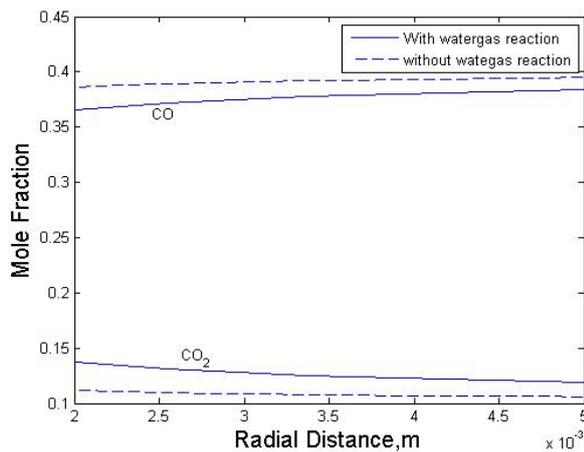
Fig. 2   Variation of mole fraction of CO and CO_2 inside the product shell.
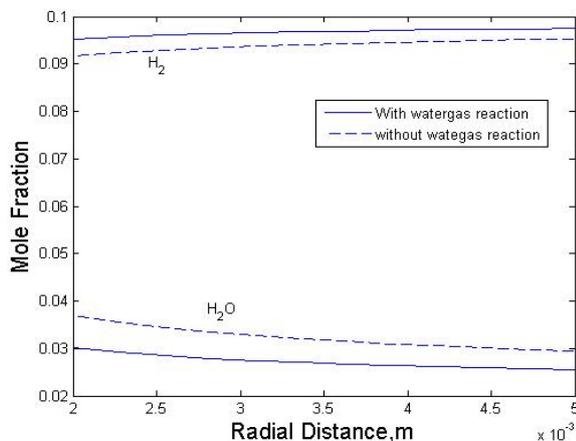

Fig. 3   Variation of mole fraction of H_2 and H_2O inside the product shell.
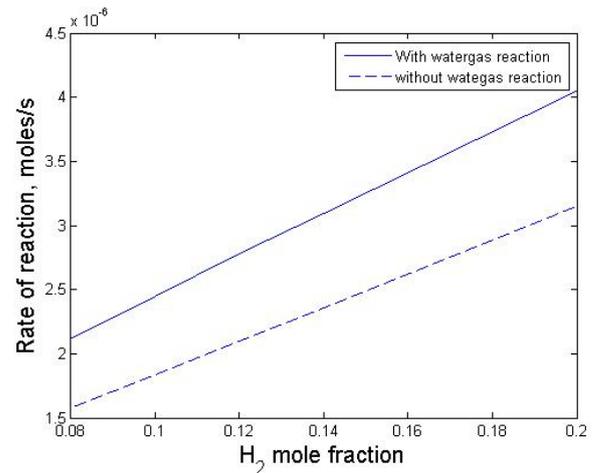

Fig. 4   Variation overall reaction rate with hydrogen content.

Subsequently, simulations were carried out to find the effect of hydrogen composition on the reaction rates at 1,200 K. The mole fractions of CO and CO_2 were kept at 0.4 and 0.1 respectively. The mole fraction of H_2O was changed so that the bulk gas composition is at equilibrium. Accordingly, the mole fraction of N_2 was also changed so that sum of the mole fraction is one. The net reaction rates in terms of mole of "O" removed from the pellet per second is plotted as a function of temperature for cases where water gas shift reaction has been considered as well as that being not considered. As earlier, the reaction rate is always more for the case where the water gas shift reaction is considered as shown in Fig. 4. It is also interesting note that the increase in reaction rate with increasing is hydrogen concentration is slightly more for the case when water gas shift reaction is considered compared that not being considered.

4. Conclusions

In this paper, an investigation at the conceptual level on the effect of water gas shift reaction on the overall reaction kinetics of wustite pellet in C-O-H-N atmosphere has been presented. These results show that water gas shift reaction can affect the overall kinetics significantly especially at higher temperatures.

The results from the model need to be substantiated

by experimental data.

Acknowledgments

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