Effect of Water Gas Shift Reaction on the Non-Isothermal Reduction of Wustite Porous Pellet Using Syngas

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Abstract

Effect of water gas shift reaction ($CO+H_2O=CO_2+H_2$) on wustite reduction has been investigated by a transient, non-isothermal mathematical model based on grain model. In this model, wustite porous pellet is reduced using Syngas, namely a mixture of hydrogen, carbon monoxide, carbon dioxide and water vapor. For this purpose, governing equations containing continuity equation of species and energy equation have numerically been solved by finite volume fully implicit method. The model has been validated by comparing it with experimental data from literature. It was found a good agreement between model results and experimental data. Model results have been presented for the pellet reduction including with and without Water Gas Shift Reaction (WGSR). It was found that in pellet scale model, the effect of WGSR is not considerable on the rate of wustite reduction and temperature distribution inside the pellet. However it affects the distribution of mole fraction of gaseous species considerably.

Keywords: Water Gas Shift Reaction (WGSR), Direct reduction, Wustite pellet, Syngas, Reduction rate, Finite volume method.

1. Introduction

Reduction of hematite iron oxide is usually proceeded at three stages, i.e. Reduction of hematite to magnetite, magnetite to wustite and wustite to iron. Among these stages, the reduction of wustite to iron is the slowest stage[1]. Therefore, it can be considered as the rate controlling step in hematite reduction. Many mathematical models have been reported to understanding the reduction behavior of iron oxides in direct reduction processes. Most of these models deal with hematite reduction[2-11] and according to the best our knowledge, only two models about wustite reduction has been reported. At the first one, Usui *et al.*[12] have developed a mathematical model for isothermal reduction of wustite pellet using hydrogen and at the another one, Valipour and Khoshandam[13] have developed a model to investigate non-isothermal reduction of wustite porous pellet using Syngas, namely a mixture of hydrogen, carbon monoxide, carbon dioxide and water vapor. A significant shortcoming of these models is neglecting the effect of WGSR. For typical operating conditions in an industrial reducing shaft furnace using a mixture of H_2 and CO, water

gas shift reaction (WGSR) is catalyzed by iron and its oxides. Therefore, it is the most important side reaction[14] in direct iron reduction processes. In this study, the effect of water gas shift reaction on wustite reduction has been investigated in pellet scale by a transient, non-isothermal mathematical model based on grain model.

2. Concept of phenomena and assumptions

In order to investigate the behavior of a single pellet in reducing gas flow, the pellet is assumed as a control volume. It is assumed that the spherical porous pellet has been made of small dense grains with almost constant radius. The reducing gas, including mainly of hydrogen and carbon monoxide, diffuses through pores of the pellet to react at the interface and after the reaction with wustite, products of the reaction diffuses back to the outside of the pellet and bulk flow respectively. Figure 1 shows a schematic configuration of a porous pellet under the grain model in reduction process.

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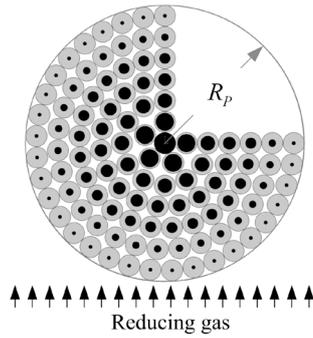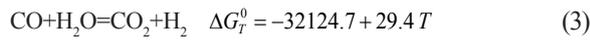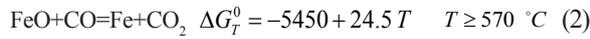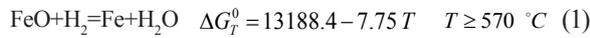*1. Assistant Professor*
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Fig. 1. Schematic configuration of a porous pellet under the grain model in reduction process.

Main reactions considered in this study are the wustite reduction reactions with hydrogen and carbon monoxide and water gas shift reaction as follows:

$$FeO + H_2 = Fe + H_2O \quad \Delta G_T^0 = 13188.4 - 7.75\,T \quad T \geq 570\ ^\circ C \quad (1)$$

$$FeO + CO = Fe + CO_2 \quad \Delta G_T^0 = -5450 + 24.5\,T \quad T \geq 570\ ^\circ C \quad (2)$$

$$CO + H_2O = CO_2 + H_2 \quad \Delta G_T^0 = -32124.7 + 29.4\,T \quad (3)$$

According to the concept of phenomena, the following assumptions have been made to obtain governing equations:
• The pellet has a spherical shape with a constant radius, R_P. It has uniform and constant porosity, ε. It is made of small dense grains with constant radius, r_g.
• The reduction of each grain is reversible, first order and proceeds topochemically.
• The Effect of water gas shift reaction is considered.
• The Heat of reaction for WGSR is given to gas phase.
• Total pressure is the same inside and outside of the pellet.
• There is no change in pellet diameter during the reduction process and no crack is formed.

3. Governing equations
3.1. Reaction rate equations

According to the assumptions, the rate of reduction reaction of a grain using reducing gas is given as follows:

$$\dot{n}_{r,i} = \frac{3(1-\varepsilon)k_{r,i}}{r_g}\left(1 + \frac{1}{Ke_{r,i}}\right)(1-f)^{2/3}(C_i - C_i^e) \quad (4)$$

The local fractional reduction of grains, defined as $f = 1 - (r_l/r_g)^3$, is calculated by equation (5),

$$\frac{\partial f}{\partial t} = \sum_{i=H_2,CO}\left(\frac{3k_{r,i}}{\rho_O r_g}\right)\left(1 + \frac{1}{Ke_{r,i}}\right)(1-f)^{2/3}(C_i - C_i^e) \quad (5)$$

And overall fractional reduction of the pellet may be estimated as an integration of f over the entire pellet.

$$F = \frac{3}{R_P^3}\int_0^{R_P} r^2 f\,dr \quad (6)$$

Also, the rate of forward water gas shift reaction is given by the following equation[15]:

$$\dot{n}_{w,CO_2} = \varepsilon\,k_w P_t^2\,(y_{CO}y_{H_2O} - y_{H_2}y_{CO_2}/Ke_w) \quad (7)$$

3.2. Continuity equation of species

Continuity equation for each component of the reducing gas is written as a combination of diffusion and chemical reactions as follows:

$$\frac{\partial(\varepsilon C_i)}{\partial t} = \nabla\cdot(D_{eff,i}\nabla C_i) - \dot{n}_{r,i} + \nu_{i,w}\dot{n}_{w,i}, \quad i = H_2,CO \quad (8)$$

$$\frac{\partial(\varepsilon C_j)}{\partial t} = \nabla\cdot(D_{eff,j}\nabla C_j) + \dot{n}_{r,j} + \nu_{j,w}\dot{n}_{w,j}, \quad j = H_2O,CO_2 \quad (9)$$

where $\nu_{i,w}$ and $\nu_{j,w}$ are the stoichiometric coefficients of i-th and j-th species appearing in water gas shift reaction. They are positive for the products and negative for the reactants of WGSR.

3.3. Energy equation

Energy equation is written as a combination of conduction heat transfer and heat generation or consumption due to chemical reactions as follows:

$$\frac{\partial((\rho C_P)_{eff}T)}{\partial t} = \nabla\cdot(\lambda_{eff}\nabla T) + \dot{n}_w(-\Delta H)_{T,w} + \sum_{i=H_2,CO}\dot{n}_{r,i}(-\Delta H)_{T,r,i} \quad (10)$$

3.4. Initial and boundary conditions

The governing equations are subjected to the following boundary and initial conditions:
• On pellet surface, $r = R_P$, continuity of heat and mass fluxes yields equations (11) to (13).

$$-\lambda_{eff}\frac{\partial T(R_P,t)}{\partial r} = h(T_s(R_P,t) - T_b) \quad (11)$$

$$-D_{eff,i}\frac{\partial C_i(R_P,t)}{\partial r} = k_{m,i}(C_i(R_P,t) - C_{b,i}) \quad (12)$$

$$-D_{eff,j}\frac{\partial C_j(R_P,t)}{\partial r} = k_{m,j}(C_j(R_P,t) - C_{b,j}) \quad (13)$$

- Symmetry at the centre of pellet, $r=0$, yields following boundary conditions:

$$\frac{\partial T(0,t)}{\partial r} = 0 \tag{14}$$

$$\frac{\partial C_i(0,t)}{\partial r} = 0 \tag{15}$$

$$\frac{\partial C_j(0,t)}{\partial r} = 0 \tag{16}$$

- Initial values of time-dependent variables are defined as follows:

$$T(r,0) = T_0 \tag{17}$$

$$C_i(r,0) = C_{i,0} \tag{18}$$

$$C_j(r,0) = C_{j,0} \tag{19}$$

$$f(r,0) = f_0 \tag{20}$$

4. Parameter estimation

Physicochemical parameters such as heat and mass transfer coefficients, effective diffusivity, effective thermal conductivity and effective heat capacity are estimated by empirical relations. These empirical relations have been introduced by the authors in the previous paper[11].

4.1. Frequency factor and activation energy

Frequency factor and activation energy are required in order to calculate the reaction rate constant with regards to the Arrhenius law. Frequency factor, activation energy and equilibrium constant are listed in Tables 1 and 2 for reduction by hydrogen, equation (1), and water gas shift reaction, equation (3), respectively. Reaction rate constant for reduction by carbon monoxide is assumed 1/5 of the reduction by hydrogen[16]. For water gas shift reaction, when the reduction rate is under 50%, the rate constant is catalyzed by FeO and for the reduction rate above 50%, rate constant is catalyzed by Fe.

5. Numerical solution

Nearly all equations are nonlinear and coupled. Moreover, physicochemical parameters such as rate constants, equilibrium constants and etc. depend on temperature. So, the analytical solution will be complicated and the governing equations are solved by a computational method as finite volume fully implicit method. In this method, the governing equations are discretized using control volume approach[17]. Discretization process has been discussed in detail in previous papers[10, 18]. After discretization, the partial differential governing equations are reduced to a large set of coupled linear algebraic equations. This set of equations is solved by indirect iterative procedure as tri-diagonal matrix algorithm (TDMA) method[17]. The fully implicit method has been applied to ensure numerical stability and to allow the use of a large time step, which is a desirable feature when dealing with reaction problems[13].

6. Model validation

Experimental data reported by Usui et al.[12] for the overall fractional reduction of a reagent wustite pellet has been used for the validation of model estimations. The model is run to simulate the isothermal reduction process in the atmosphere of hydrogen. Figure 2 shows a comparison between the experimental data and predictions of the present model. As shown in this figure, there is a good agreement between model estimations and experimental data.

Table 1. Rate parameters for the reduction of wustite by hydrogen[13]

Reaction	$k_{0,r}$ (m s⁻¹)	E_a (J mol⁻¹)	Ke
$FeO + H_2 \rightarrow Fe + H_2O$	160	92092	exp (-1586.9/T + 0.9317)

Table 2. Rate parameters for water gas shift reaction[15]

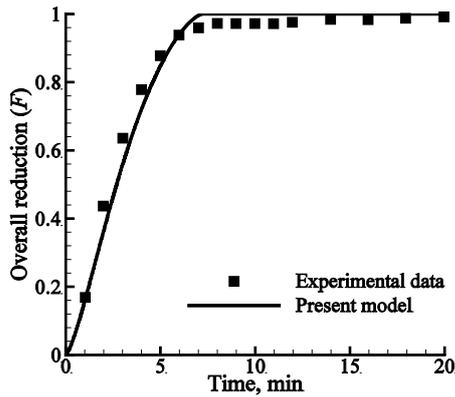| Reaction	Catalyst	$k_{0,w}$ (mol s⁻¹ m⁻³ atm⁻²)	E_a (J mol⁻¹)	Ke
$CO + H_2O = CO_2 + H_2$	Fe	93.32×10^6	-128200	exp (3863.7/T - 3.5414)
	FeO	18.27	137.3	

Fig. 2. Comparison of the overall reduction rate for a reagent wustite pellet by hydrogen among model results and experimental data[12] (R_P=6 mm, ε=0.44, T_b=1173 K).

7. Results and discussion

Results are presented in two ways. At the first one, the simulation is applied for WGSR which is denoted by **WWGSR**. In the Second way, simulation is done without WGSR which is denoted by **NWGSR**. Pellet characteristics and reducing gas parameters which are used in simulations are indicated in Table 3.

Table 3. Pellet characteristics and reducing gas parameters used in model estimations

R_P (mm)	ε	T_b (K)	P_t (bar)	$y_{H2,b}$	$y_{H2O,b}$	$y_{CO,b}$	$y_{CO2,b}$
6.5	0.4	1173	2	0.5258	0.0864	0.2997	0.0881

7.1. Effect of water gas shift reaction

Effect of WGSR on the wustite reduction rate is illustrated in Figure 3. As shown in this figure, effect of WGSR on the rate of wustite reduction is very small. When it is focused in this figure, the reduction rate is lowered due to WGSR.
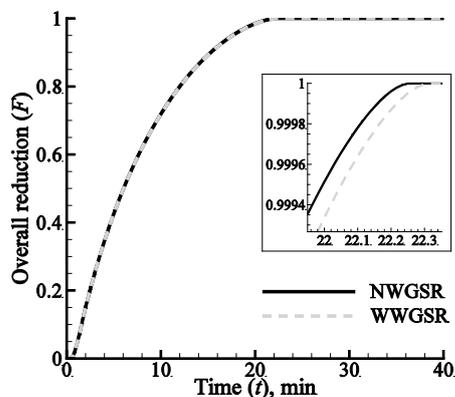

Fig. 3. Influence of WGSR on the wustite overall reduction rate.

Figure 4 shows temperature distribution at three different positions within the pellet in **WWGSR**. As shown in this figure, three temperature distributions are very close to each other. This figure shows that temperature distribution within the pellet depends mostly on time and it is not considerably affected by position inside the pellet. Figure 5 shows the influence of WGSR on temperature distribution at $r=R_P/2$. This figure shows that the effect of WGSR is very small and it is as lowering the temperature. This small effect may be due to the small reaction rate of water gas shift reaction.
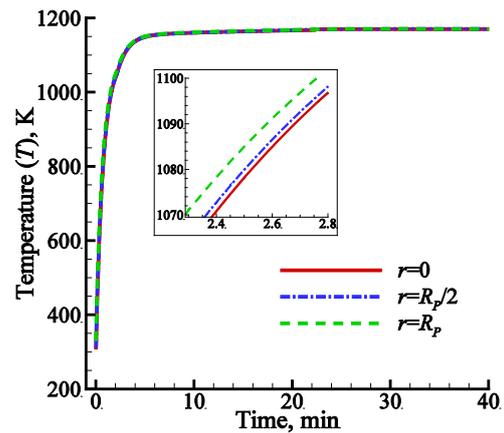

Fig. 4. Temperature distribution versus time at three different positions within the pellet in WWGSR.
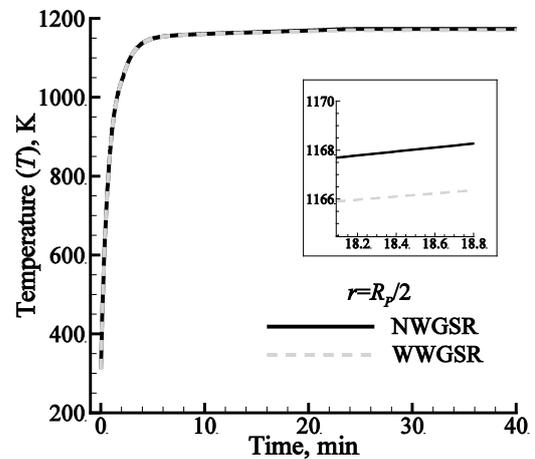

Fig. 5. Influence of WGSR on temperature distribution at $r=R_P/2$.

Effect of WGSR on the mole fraction of gaseous species within the pellet is shown in Figure 6. It is indicated in this figure that:
• In **NWGSR**, mole fraction of each component of the reducing gas at all three different positions within the pellet tends to be the same value. However, in

WWGSR model, these mole fractions tend to be different values. This effect may be explained as follows. In **NWGSR**, when the pellet is completely reduced, there is no more change in gaseous mole fractions by reduction reactions. But in **WWGSR**, after completion of the reduction, WGSR is still proceeded and catalyzed by Fe. Therefore it can change the gaseous species mole fractions.

• With regards to Figure 4, increasing temperature and over time, the equilibrium constant (Ke) of WGSR decreases (see Table 2). Thus, according to mole fractions in Table 3 and equation (7), WGSR proceeds in reverse direction. Consequently, hydrogen and carbon dioxide are consumed and carbon monoxide and water vapour are produced.

• The effect of WGSR on mole fractions is maximum at $r=0$, minimum at $r=R_P$ and intermediate at $r=R_P/2$.

7.2. Effect of gas ratio and gas utility

In industrial reduction processes, gas ratio ($\beta=H_2/CO$) commonly varies in the range of $0<\beta<4.0$ and gas utility ($\gamma=(H_2+CO)/(H_2O+CO_2)$) may be changed in the range of $5<\gamma<49$ depending on the gas reforming system[16]. Figure 7 shows the time required for 85% reduction of the wustite pellet using gas mixtures with a constant gas utility and variable gas ratio in **WWGSR** and **NWGSR**. As shown in this figure, in both **WWGSR** and **NWGSR**, the time required for 85% reduction is decreased as gas ratio is raised. The effect of WGSR on this figure is very small and it is as lowering the reduction rate.

The time required for 85% reduction of the wustite pellet vs. gas utility is illustrated in Figure 8. As shown in this figure, the rate of reduction is increased as the gas utility is raised, in both **WWGSR** and **NWGSR**. Similar to gas ratio, the effect of WGSR on Figure 8 is very little and it is as lowering the reduction rate.
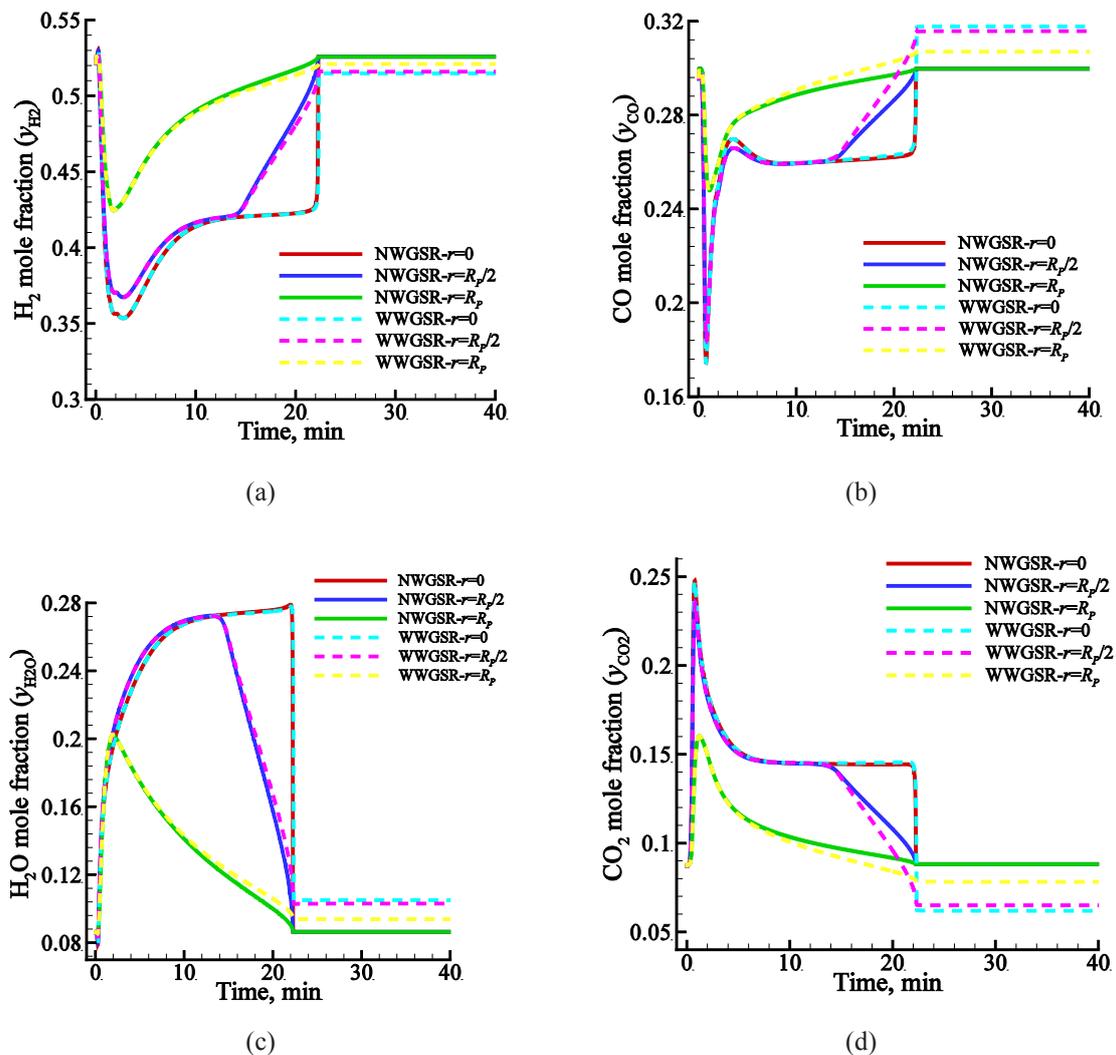

(a)

(b)

(c)

(d)

Fig. 6. Effect of WGSR on the gaseous species mole fractions within the pellet: (a) Hydrogen mole fraction, (b) Carbon monoxide mole fraction, (c) Water vapour mole fraction and (d) Carbon dioxide mole fraction.
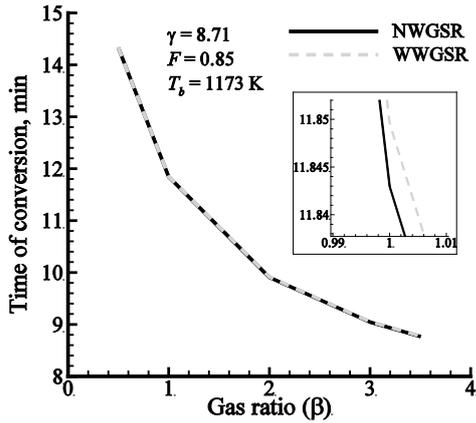
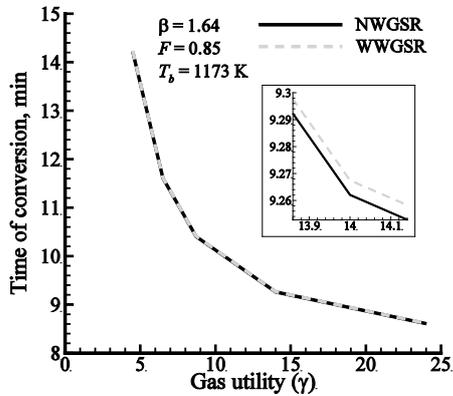*Fig. 7. Time required for 85% reduction of the wustite pellet vs. gas ratio.*

Fig. 8. Time required for 85% reduction of the wustite pellet vs. gas utility.

8. Conclusion

A transient and non-isothermal mathematical model based on grain model is developed to investigate the effect of WGSR on the rate of wustite reduction with and without WGSR. Model results were presented with and without WGSR. The following results have been obtained:

1. Effect of WGSR on the wustite reduction rate is very little and it is lowered due to WGSR.

2. Temperature distribution within the pellet is mostly a function of time and it is not affected by the position inside the pellet.

3. Effect of WGSR on temperature is very small and the temperature is lowered due to WGSR.

4. With considering WGSR, the mole fractions of carbon monoxide and water vapour are increased and the mole fractions of hydrogen and carbon dioxide are decreased.

5. The rate of reduction is increased as gas ratio and gas utility are raised. However, the rate of reduction decreases due to WGSR.

List of symbols

C	concentration of the gaseous species, (mol m^{-3})
C_P	specific heat at constant pressure, (J Kg^{-1} K^{-1})
D	diffusivity of the gaseous species, (m^2 s^{-1})
E_a	activation energy, (J mol^{-1})
f, F	local fractional reduction of grains and overall fractional reduction, respectively, (-)
h	convective heat transfer coefficient, (W m^{-2} K^{-1})
$(-\Delta H)_T$	heat of reaction at temperature T, (J mol^{-1})
k_m	mass transfer coefficient of the gaseous species through gaseous film, (m s^{-1})
k_r	rate constant of reduction reactions, (m s^{-1})
k_w	rate constant of the water gas shift reaction, (mol s^{-1} m^{-3} atm^{-2})
$k_{0,r}$	frequency factor of reduction reactions, (m s^{-1})
$k_{0,w}$	frequency factor of the water gas shift reaction, (mol s^{-1} m^{-3} atm^{-2})
Ke	equilibrium constant, (-)
$\dot{n}$	rate of chemical reactions, (mol m^{-3} s^{-1})
P	pressure, (atm)
r	radial coordinate in the pellet, (m)
r_g, r_l	radii of a grain and reaction interface within a grain, respectively, (m)
R_P	pellet radius, (m)
t	time, (s)
T	temperature, (K)
y	mole fraction of components of the reducing gas, (-)
$\beta = H_2/CO$	reducing gas ratio, (-)
ε	porosity of the pellet, (-)
$\gamma = (H_2+CO)/(H_2O+CO_2)$	reducing gas utility, (-)
λ	thermal conductivity, (W m^{-1} K^{-1})
ρ	mass density, (Kg m^{-3})
ρ_O	molar density of reducible oxygen within the grains, (g-atom O m^{-3})

Subscripts

b   related to bulk flow of Syngas

eff   effective parameters

i   related to gaseous reactants in reduction reactions (H_2 and CO)

j   related to gaseous products in reduction reactions (H_2O and CO_2)

r, w   related to reduction reactions and the water gas shift reaction, respectively

s   related to solid phase (wustite)

t   related to total value of parameters

0   related to initial value of parameters

Superscripts

e   related to equilibrium condition

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