Kinetics of the Carbothermal Reduction of Ilmenite: Grain Pellet Model

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Abstract: A novel mechanism for the carbothermal reduction of Ilmenite is proposed and validated with the help of a comprehensive mathematical model. A time-dependent isothermal pellet-grain model is used to simulate the kinetic behaviour of a spherical pellet of ilmenite ($FeTiO_3$) in CO/CO_2 atmosphere. The proposed mechanism involves diffusion of CO gas through the pores of the pellet and through the product layer of iron in TiO_2 matrix. Shrinking unreacted core model is applied to the grains. Numerical solution based on Finite Element Method is carried out with the help of COMSOL Multiphysics® version 3.3a. The results show considerable agreement with the experimental data reported by Nicholson (1995) for reduction of ilmenite in commercial rotary kiln reactors.

Keywords: Carbothermal Reduction, Pellet-grain Model, Ilmenite, Rotary Kiln.

1. Introduction

High temperature carbothermal reduction of Ilmenite in a rotary kiln reactor is a process of remarkable commercial importance. The process gives rise to the value added product - synthetic rutile - which is the most important source of Titanium metal . Many studies have been carried out so far by researchers from all over the world to elucidate the kinetics and mechanism of Ilmenite reduction in CO/CO_2 atmosphere in the rotary kiln reactor. Because of the complex processes taking place in the rotary kiln reactor and the lack of feasibility of experimental techniques, most of the researchers adopted mathematical modeling to investigate the reduction kinetics. Although many researchers identified the diffusion of reactant gas through the product layer and intrinsic chemical reaction as rate controlling factors during reduction, the mechanisms suggested by them lack theoretical support. There have been a lot of published works on the simulation of non-catalytic gas-solid reactions in general. The pellet-grain model has been found suitable for porous solid (pellet) consisting of an agglomeration of smaller particles (grains).

The present investigation is aimed at suggesting a theoretically sensible mechanism for the reduction of Ilmenite in CO/CO_2 atmosphere and evaluating the mechanism with the help of a comprehensive mathematical model. A pellet-grain model is used with the assumption that each pellet of Ilmenite consists of a number grains.. Shrinking unreacted core model is applied to the grains. Numerical solution based on Finite Element Method is carried out with the help of COMSOL Multiphysics® version 3.3a. Validation of the simulated results is carried out with the reported experimental results

2. Mathematical Model

2.1 Model Description

Consider a spherical pellet of Ilmenite of total radius R_0 and porosity ε and is made up of a number of non-porous grains. Each grain has an initial radius r_0 and undergoes reduction with a shrinking unreacted core at a radius of r_c at time t. Each grain undergoes reduction according to the following overall reaction:

$$FeO.TiO_2\,(s) + CO\,(g) \rightarrow Fe.TiO_2(s) + CO_2(g) \quad (1)$$

Figure 1 shows the schematic representation of reduction of an Ilmenite pellet.

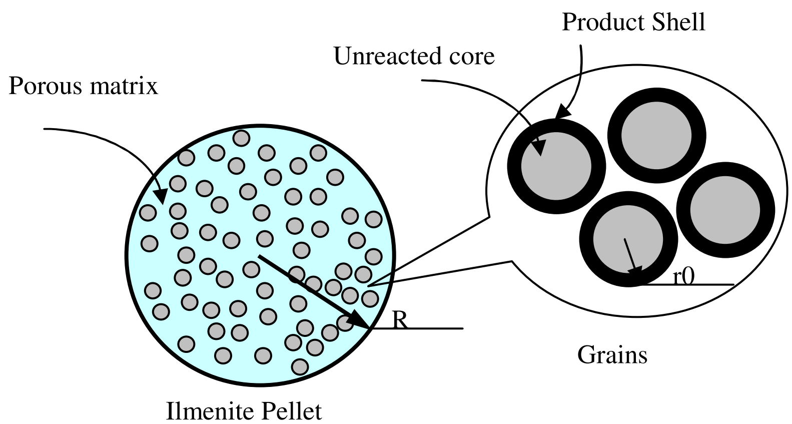

Figure 1. Schematic Representation of Ilmenite Reduction

The following simplifying assumptions are used for this model:
(a) The solid pellet and the grains are spherical in shape and their diameter remains constant during the reaction.
(b) Both the pellets and the grains are sufficiently small so that internal temperature gradients may be neglected.
(c) CO concentration in the bulk gas remains unchanged with time.

2.2 Model Formulation

By applying the shrinking unreacted core model to the grains, we get the rate of reaction in a single grain in terms of CO gas as

$$-\frac{dn_{CO}}{dt} = \frac{4\pi r_c^2 k C_0}{1+\frac{r_c k}{D}(1-\frac{r_c}{r_0})} \qquad (2)$$

Hence the rate of consumption of CO per unit volume of the pellet becomes

$$r_{CO} = \frac{3(1-\varepsilon)\rho_p . y(r_c / r_0)^2 k C_0}{\rho_g . r_0 \left(1+\frac{r_c k}{D}(1-\frac{r_c}{r_0})\right)} \qquad (3)$$

Transient mass balance for CO gas in the pellet can be written as

$$De\left[\frac{\partial^2 C_0}{\partial r^2}+\frac{2}{r}\frac{\partial C_0}{\partial r}\right]-r_{CO}=\varepsilon\frac{\partial C_0}{\partial t} \qquad (3)$$

The rate of disappearance of ilmenite can be expressed in terms of the rate of change of the reaction radius in the grain (r_c) with time or as a stoichiometric proportion of the rate of consumption of carbon monoxide, r_A. Thus,

$$r_{il} = -\left[\frac{3(1-\varepsilon)\rho_p y}{\rho_g 4\pi r_0^3}\right]\frac{\partial}{\partial t}\left(\frac{4}{3}\pi r_c^3\frac{\rho_g}{M_g}\right)$$
$$= \frac{3(1-\varepsilon)\rho_p . y(r_c / r_0)^2 k C_0}{\rho_g . r_0\left(1+\frac{r_c k}{D}(1-\frac{r_c}{r_0})\right)} \qquad (4)$$

3. Numerical Solution using COMSOL Multiphysics

Numerical solution is carried out with the help of Comsol Multiphysics® version 3.3a. Like other models of industrial-transport problems, Ilmenite reduction also allows the assumption that the problem is spherically symmetric. With this assumption it would be appropriate to eliminates two space coordinates and formulate the problem as a 1D problem which is computationally fast and has reasonably small memory requirements.

3.1 Governing Equations

The mass balance equations (equations 3 and 4) derived in the previous section can be rewritten in terms of nondimensional variables as

$$\frac{\partial}{\partial\zeta}\left(\zeta^2\frac{\partial C}{\partial\zeta}\right)-\zeta^2\phi^2\rho^2 FC=\zeta^2 N\frac{\partial C}{\partial\theta} \qquad (5)$$

$$\frac{\partial \rho}{\partial \theta} = \frac{M_g}{M_p}\frac{\rho_p}{\rho_g} FC \qquad (6)$$

Where $N = \dfrac{\varepsilon R_0^2 M_p C_{CO} k}{\rho_p D_{eff} r_0}$

$\phi = R_0 \left(\dfrac{3\rho_p yk(1-\varepsilon)}{\rho_g r_0 D_{eff}} \right)^{1/2}$ and

$$F = \frac{1}{1 + \dfrac{r_0 k\rho}{D_g}(1-\rho)}$$

C, ρ, ζ and θ are the dimensionless parameters defined as:

$$C = \frac{C_0}{C_{CO}} \quad \rho = \frac{r_c}{r_0}, \quad \zeta = \frac{R}{R_0} \quad \text{and} \quad \theta = \frac{tM_p C_{CO} k}{\rho_p r_0}$$

3.2 Boundary and Initial Conditions

The boundary and initial conditions for equations 6 and 7 are deduced from the principles of flux continuity on the pellet surface and spherical symmetry at the centre of the pellet. The boundary condition are given as

$$At\ \zeta = 0, \frac{\partial C}{\partial \zeta} = 0 \quad \text{for } \theta > 0$$

$$At\ \zeta = 1, \frac{\partial C}{\partial \zeta} = N_{sh}\ (1\text{-}C) \quad \text{for } \theta > 0$$

Where N_{sh} is the modified Sherwood number.
Initial condition is given as
ρ = 1 at θ =0 for 0 < ζ <1

The overall fractional conversion can be obtained as

$$F = \int_0^1 3\zeta^2 \left(1 - \rho^3\right) d\zeta \qquad (8)$$

4. Results and Discussion

The model validation is carried out against experimental results. Effect of various parameters such as pellet size, pellet/grain ratio, temperature etc on the overall fractional conversion versus time plots is discussed. The values of the physical and chemical parameters used in this study are selected according to the available experimental and literature values. Figure 2 shows the comparison of simulated overall fractional conversion with experimental and literature results. Figure 3 shows the effect of pellet radius on overall fractional conversion n. The simulated reduction data shows considerable agreement with the experimental as well as reported data. The lowering of overall conversion with increase in pellet radius is realistic and agreeable with the reported values. Figure 4 shows the variation of fractional conversion depending on the FeO content of the sample. As the reported data used for comparison are based on natural ilmenite samples of varying origin having variable compositions, it is significant to study the effect of FeO content on the conversion data. The simulated results show very good agreement with the reported data in this regard. The assumption that conversion is solely based on the oxygen removal from FeO in ilmenite justifies the lower conversion values for samples with higher FeO content.

Figure 5 shows the influence of the pellet/ grain ratio on the fractional conversion data. As would be expected, conversion increases as the ratio increases i.e., the grains become smaller. It is clear that the size of the grains as well as the size of the pellets has a significant role in determining the rate of conversion. This explains the variation of reduction rate with the type of Ilmenite used as reported by various authors.

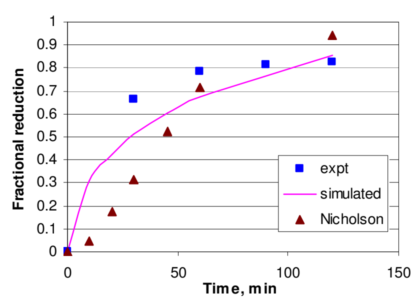

Figure 2. Comparison of simulated, experimental and reported (Nicholson(1995)) fractional conversion vs time data

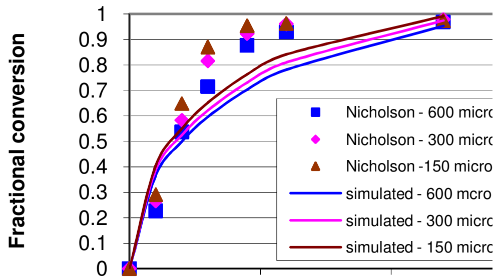

Figure 3. Comparison of effect of pellet radius on reported (Nicholson(1995)) and simulated fractional conversion (x) vs time data

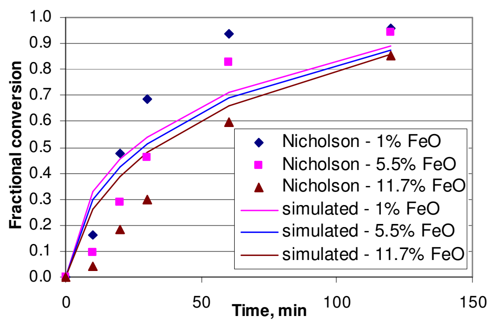

Figure 4. Comparison of effect of FeO content on reported (Nicholson(1995)) and simulated fractional conversion (x) vs time data

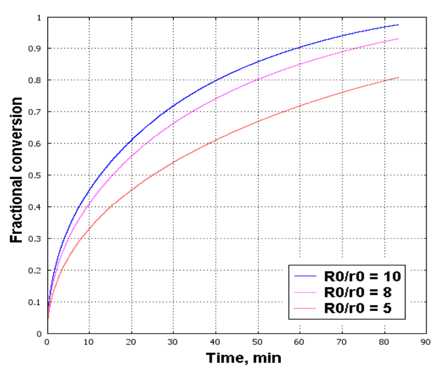

Figure 5 Effect of pellet/grain ratio on fractional conversion for 200 micron pellet

5. Conclusions

A mathematical model for the reduction of Ilmenite in CO/CO_2 atmosphere is developed. The suggested mechanism for Ilmenite reduction is based on the assumption that Ilmenite pellets are made up of FeO grains supported by porous TiO_2 matrix. The mechanism involves gaseous diffusion of CO gas through the pores of the pellet and solid state diffusion of Carbon through the metallic iron layer. The shrinking unreacted core model is used for the reduction of FeO grains.

The simulated reduction data show very good agreement with the experimental results and also with the results reported by Nicholson(1995) for static atmosphere test. Hence the model not only supports the suggested mechanism but also successfully represents the reduction of Ilmenite in CO/CO_2 atmosphere.

6. References

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Nomenclature:

C_{CO}	concentration of CO in the bulk gas.
D	diffusivity in the grain
D_{eff}	effective diffusivity
k	interphase reaction rate constant
M_g	molecular weight of grain
M_p	molecular weight of pellet
r_0	radius of grain
R_0	radius of pellet
y	FeO weight fraction

Greek:

ε	pellet porosity
ρ_g	density of the grain
ρ_p	density of the pellet