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Regenerable MgO-based sorbent for high temperature CO_2 removal from syngas: 2. Two-zone variable diffusivity shrinking core model with expanding product layer

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HIGHLIGHTS

- ▸ A new model is introduced to describe the gas/solid carbonation reaction.
- ▸ The model can describe the expanding product layer and two distinct reactive zones.
- ▸ The model predictions are very similar to those provided by expanding grain model.
- ▸ The model provides an explicit reaction rate expression suitable for CFD applications.

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ABSTRACT

The variable diffusivity model was extended to include physically expanding product layer and two reacting zones, consisting of a high-reactivity outer shell and a low-reactivity inner core, to describe the gas/solid carbonation reaction involving carbon dioxide and a potassium-promoted half-calcined dolomite sorbent. The model provides an excellent fit to the TGA experimental data on sorbent carbonation at various operating conditions. The parameters in the model which include an initial product layer diffusivity and diffusivity decay rate can correctly capture the trends on the effects of operating conditions on the physical properties of the sorbent observed in the experiments.

1. Introduction

Global warming, which has been associated with the increasing concentration of greenhouse gases, mainly carbon dioxide (CO_2), is regarded as one of the key environmental issues in the 21st century. One of the major sources of carbon dioxide emissions is the fossil fuel-based (especially coal-based) power plants. Advanced power generation technologies such as Integrated Gasification-Combined Cycle (IGCC) is among the leading contenders for power generation conversion in the 21st century, because such processes, offer significantly higher efficiencies and superior environmental performance, compared to coal combustion processes. Carbon dioxide can be removed from pre-combustion coal gases by various methods which have been summarized in several review articles [1–5].

In part 1 of this study [6], a highly reactive and mechanically strong low-cost regenerable MgO-based sorbents were prepared using dolomite as the base material. The reversible chemical reaction for CO_2 capture involving magnesium oxide is:

$$MgO + CO_2 \leftrightarrow MgCO_3 \ (\Delta H \sim -96\ \text{kJ/mole}) \qquad (A)$$

The dolomite-based sorbents were prepared by modifying a dolomite that contains about 44% w/w magnesium carbonate and 54% w/w calcium carbonate. The dolomite was partially calcined (half-calcined) at a temperature sufficiently above the decomposition temperature of magnesium carbonate (i.e. 350 °C) and below the decomposition temperature of calcium carbonate (i.e. 650 °C). The partially calcined sorbents were wet-impregnated using a potassium carbonate solution and re-calcined after the impregnation step.

The ranges of the physical and chemical properties of the sorbents are presented in Table 1, indicating that the attrition index (AI) of the sorbents is lower than that of the FCC catalyst (AI ≈ 4%) which makes them suitable for various reactor configurations, including fluidized bed, moving-bed, or fixed-bed applications. The sorbents were also analyzed using a Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDS)

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Nomenclature

C_b	CO_2 concentration in gas, mol/m^3
C_b^o	initial CO_2 concentration in gas, mol/m^3
C_e	equilibrium CO_2 concentration, mol/m^3
C_i	CO_2 concentration at reaction interface, mol/m^3
CMgO	MgO concentration in the particle, mol/m^3
C_R	CO_2 concentration in the pores, mol/m^3
D_e	effective diffusivity in the pores, m^2/s
D_g	product layer diffusivity, m^2/s
D_{g0}	initial product layer diffusivity, m^2/s
D_g^0	initial product layer diffusivity in grain, m^2/s
D_k	Knudsen diffusivity, m^2/s
D_m	molecular diffusivity, m^2/s
E_a	activation energy, J/mol
H	enthalpy, J
k_1	outer layer reaction rate constant, m/s
k_2	inner layer reaction rate constant, m/s
k_s	reaction rate constant, m/s
MW	molecular weight, kg/kmol
N_{MgO}^o	initial number of moles of MgO, mol/m^3
R	radial coordinate of the particle, m
r_c	inner layer radius, m
r_i	reaction front radius, m
r_g	initial grain radius, m

r'_g	expanded grain radius, m
r_{MgO}	reaction rate, mol/m^2 s
r_p	outer layer radius, m
r'_p	product layer radius, m
T	temperature, K
t	time, s
X	conversion, –
X_l	local conversion in the particle, –
X_o	overall particle conversion, –
Z	expansion factor, –

Greek symbols

α	diffusivity decay rate, –
β	variable diffusivity model parameter, –
ε	local porosity within the particle, –
ε_s	product layer porosity, –
δ	highly reactive zone thickness, m
ρ	particle density of the sorbent, kg/m^3
ρ_{product}	density of the $MgCO_3$, kg/m^3
ρ_{reactant}	density of the MgO, kg/m^3
δ	highly reactive zone thickness, m
τ	tortuosity factor, –

Table 1
General characteristics of the sorbent [1].

Sorbent characteristics	Range
Magnesium content (%w/w)	16–17
Specific surface area (m^2/g)	5–6
Average pore diameter (nm)	20–60
Mercury porosity (%)	19–22
Potassium content (%w/w)	4–5
Attrition index (%)	1–2.5

capability. Fig. 1 shows the distribution of calcium, magnesium, and potassium elements across the sectioned particle, indicating that calcium and magnesium are uniformly distributed throughout the cross-section area of the sorbent, but potassium was only detected on the outer shell of the particle. The sorbents were evaluated for their reactivities towards CO_2 and their absorption capacities in a high-pressure thermogravimetric analyzer (HP-TGA). The results clearly indicated that the half-calcined dolomite has very low reactivity and absorption capacity, while the sorbents with the potassium additive have significant reactivity and absorption capacity for CO_2 capture. Following the evaluation of different sorbents formulations in the HP-TGA and sorbent characterization tests, the "best" sorbent formulation was selected and a large batch of the sorbent was prepared for further evaluation in the HP-TGA as well as the high-pressure packed-/fluidized-bed reactor to obtain the necessary data for scale-up.

To describe the experimentally determined carbonation reaction rate obtained in the HP-TGA, the expanding grain model, which was first proposed by Szekely and Evans [7] was extended to include two reacting zones, consisting of a high-reactivity outer shell and a low-reactivity inner core. The two-zone expanding grain model was shown to provide an excellent fit to the TGA experimental data on sorbent carbonation at various operating conditions. However, the implicit formulation of the overall conversion versus time is problematic for incorporation of the reaction rate expression into the computational fluid dynamics (CFD) models to describe the sorbent performance in the fluidized-bed reactor. Therefore, for ease of implementation of the reaction model into a CFD model [8] and to reduce the CFD computational time, it is necessary to provide the overall reaction rate (i.e. dX/dt) as an explicit function of conversion and time.

2. Two-zone variable diffusivity shrinking core model with expanding product layer

In the two-zone expanding grain model described in part 1, the solid particle is treated as an assemblage of numerous smaller grains [6]. Surrounding these grains are macro-pores through which the gas has to diffuse to reach the grains. The reaction occurs at the surface of each grain, according to the unreacted shrinking core model. As the reaction proceeds, the difference in the molar volumes of the solid product and the molar volume of the reactant results in an increase in the grain size, which decreases the pore volume between the grains, and in turn, decreases the diffusion rate of the gaseous reactant through the sorbent particle. The intrinsic surface reaction rate (moles of carbon dioxide captured per unit time and particle volume) was shown to be first order with respect to the CO_2 concentration in excess of equilibrium:

$$r_{\mathrm{MgO}} = k_s \cdot (C_i - C_e) \tag{1}$$

$$K_s = k_{s0} \cdot e^{-Ea/RT} \tag{2}$$

The following equations were solved to obtain the overall sorbent conversion as a function of time:

$$\frac{1}{R^2}\frac{\partial}{\partial R}\left(D_e R^2 \frac{\partial C_R}{\partial R}\right) - \frac{3(1-\varepsilon)k_s r_i^2}{r_g^3}\left[\frac{(C_R - C_e)}{1+\frac{k_s}{D_g} r_i\left(1-\frac{r_i}{r'_g}\right)}\right] = 0 \tag{3}$$

$$\frac{dr_i}{dt} = -\frac{k_s}{C_{\mathrm{MgO}_0}}\left[\frac{(C_R - C_e)}{1+\frac{k_s}{D_g} r_i\left(1-\frac{r_i}{r'_g}\right)}\right] \tag{4}$$

The effective diffusivity, D_e, is generally considered as a function of tortuosity, which represent the twistedness or crookedness of pores and two other diffusivities (i.e., the molecular and Knudsen) [9,10].