Regenerable MgO-Based Sorbent for High Temperature CO₂ Removal from Syngas:

3. CO₂ Capture and Sorbent Enhanced Water Gas Shift Reaction

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ABSTRACT

Regenerable MgO-based sorbent, which was prepared and evaluated in the thermogravimetric analyzer (TGA) in part 1, was also evaluated in high-pressure packed-bed unit in CO₂/N₂/H₂O mixture and simulated pre-combustion syngas environment. In CO₂/N₂/H₂O environment, The CO₂ absorption capacity of the sorbent increases with increasing temperatures from 6.7% at 350°C to 9.5% 450°C. The sorbent is capable of achieving over 95% CO₂ capture and 40% conversion in the WGS reaction, which should be attributed to positive effect of WGS reaction in producing CO₂ during the process. The sorbent reactivity and absorption capacity toward CO₂, as well as its WGS catalytic activity decreases with increasing temperature. The maximum pre-breakthrough WGS conversion occurs at 350°C, which diminishes as the sorbent is carbonated. The variable diffusivity shrinking core reaction model coupled with the two-fluid CFD model was shown to accurately predict the break-through gas compositions at different operating conditions.

KEYWORDS: SEWGS, MgO-based Sorbent, CO₂ Capture, IGCC, Water gas Shift, Gasification, Packed Bed, CFD

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Introduction

In part 1 of this series of papers [1], highly reactive and mechanically strong low-cost regenerable MgO-based sorbents were developed by modification of dolomite. It was shown that the MgO-based sorbents are good candidates for CO₂ removal from Syngas at moderately high temperature. The “best” sorbent formulation was identified and the effect of operating conditions on sorbent performance was presented. A two-zone expanding grain model was introduced which provided an excellent fit to the experimental data obtained in a thermogravimetric analyzer (TGA) unit. In the second part [2], a variable diffusivity two-zone variable diffusivity shrinking core model with expanding product layer was presented, which provides the overall reaction rate (i.e. dX/dt) as an explicit function of conversion and time, to reduce the computational time for CFD modeling of sorbent performance in the reactor.

Sorption-enhanced water-gas-shift (SEWGS) is a promising approach that combines CO₂ capture and the water-gas-shift reaction in a single unit, simultaneously improving carbon capture, while producing hydrogen through the WGS reaction in pre-combustion syngas. Various sorbents, including MgO-Based sorbents have been proposed as potential candidates for SEWGS [3-7].

This paper presents the experimental results of the MgO-based sorbent performance for CO₂ capture in a high-pressure packed-bed reactor. The effectiveness of the sorbent for the sorbent-enhanced water-gas shift reaction is also presented. Furthermore, a computational fluid dynamics (CFD) model based on the two-fluid model coupled with the variable diffusivity shrinking core model [2] was used for the simulation of CO₂ capture and SEWGS experiments using the MgO-based sorbent in the packed-bed reactor.

1. MgO-Based Sorbent Enhanced Water Gas Shift Reaction

In IGCC processes equipped the water-gas-shift reactor(s), the high temperature shift (HTS) reactor is generally operated in the temperature range of 300°-450°C, while the low temperature shift (LTS) is operated in the temperature range of 180°-300°C to further shift Reaction (A) toward hydrogen production [20].

Utilization of a regenerative magnesium oxide-based process can potentially eliminate the need for the LTS, and potentially (both HTS & LTS), while removing CO₂ in the temperature range 350°-450°C and avoiding penalty losses associate with lower temperature application. The cyclic chemical reactions for CO₂ removal involving magnesium oxide are:

In general, oxygen-blown gasification processes are more suitable for H₂ production, mainly because of low nitrogen content. Table 1 shows the typical ranges of concentration of Syngas components from different oxygen-blown gasification processes (i.e., Texaco, shell, .etc.) using different types of coal [8]. Figure 1(a) shows the equilibrium composition of a typical Syngas as a function of temperature without MgO-based sorbent.. The equilibrium composition of the Syngas in the presence of a MgO-based sorbent (i.e., Reactions 1 & 2) is presented in Figure 1(b). These calculations were performed with AspenTech[®] process simulator using the typical Syngas composition (shown in Table 1) at 20 bar. Comparison of the results shown in these figures indicates that up to 95% of the CO₂ in the syngas can be removed by MgO-based sorbents at 350°C, if the MgO sorbents has sufficiently high catalytic activity toward WGS reaction, or can be combined with an effective WGS catalyst to achieve thermodynamic equilibrium.

2. Experimental

1.1. Experimental Set up

The packed-bed unit used in this study consists of three main subsections, which include the gas feeding section, the reactor section, and the gas effluent section. The schematic diagram of the packed-bed unit is shown in Figure 2. Various pure gases are supplied from pressurized cylinders and flow through pre-calibrated mass flow controllers (MFCs) and mixed to achieve the desired gas composition. The mixture is introduced into the top section of the reactor, through a heated section of 1/8”(0.318 cm OD, 0.0686 cm ID) stainless steel tubing. To achieve the desired mole fraction of water vapor in the feed gas, a high-pressure micro-metering pump is used to inject distilled water at the desired flow rate into the heated feed line. The 1/8” tubing is generally

heated to about 250°C to generate steam at the operating pressure of the system. The temperature of tubing is monitored by and controlled using two thermocouples (i.e., T_3 and T_4 in Figure 1) to eliminate potential cold zones or hot spots along the entire tubing line.

The reactor, is a custom made 316 stainless steel tubular reactor with 1" (2.54 cm) OD $\times$ 0.75" (1.905 cm) ID and 75 cm long. The sorbent bed is supported on a porous frit with two-micron openings made of Hastelloy[®]-276 alloys welded 30 cm above the bottom of the reactor. Approximately 45 cm of the reactor is externally heated with a single-zone electric tubular furnace. Two thermocouples are placed inside the bed of sorbents and below the frit, respectively (i.e., T_1 and T_2 in Figure 2). The thermocouple inside the bed, with 0.04" (0.102 cm) OD, is placed inside a 1/8" (0.318 cm) thermo-well and is moved along the bed during each run to measure the temperature of the bed at different axial positions.

Given the relatively high concentration of CO₂ (25-50%) in the inlet gas mixture and the limited capacity of the sorbent, to achieve a reasonable CO₂ breakthrough curve, a total gas flow rate of 200 sccm was used in all of the packed-bed tests. Because of significantly high volume of the empty reactor (about 220 cm³) and the relatively low flow rate coupled with high pressure (20 atm), the residence time of the gas through the system is very large, significant fractions of which are the large gas spaces in the reactor, above and below the sorbent bed. To minimize these gas spaces in the reactor, cylindrical stainless steel "plugs" are inserted into the reactor above and below of the sorbent bed, as shown in Figure 3.

Downstream of the reactor, a highly-sensitive backpressure regulator is used to maintain the desired pressure in the reactor.. A high-pressure filter housing (knockout pot) is used upstream of the regulator to capture most of the condensed water before entering the backpressure regulator. A Shimadzu gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) is used to determine the composition of the product gas downstream of the unit. A manual bubble flow meter is placed at the very end of the unit to measure changes in the flow rate of the outlet gases resulting from CO₂ absorption.

1.2. Experimental Procedure

Table 2 presents the ranges for the operating conditions used in this study. In a typical packed-bed test, about 30 g of the sorbent is placed in the reactor on the top of the frit. To enhance a uniform radial distribution of the gas composition and to minimize back-mixing, a bed of inert quartz beads is placed on the top of the sorbent bed (Figure 3). The test is started by setting the reactor pressure (back-pressure regulator), the reactor temperature, and the temperature of the heated section of the feed line. A predetermined flow of nitrogen is fed into the reactor until the desired reactor pressure and temperature are reached and a steady flow of nitrogen through the bed is established. When needed, water vapor is fed into the system. The reactant gas (i.e., CO₂, and when needed H₂ and CO) replace a portion of nitrogen and are fed into the system after the reactor reaches steady state. During a run, composition of the reactor exit is measured by the gas chromatograph in three minutes intervals and recorded in the data acquisition system.

1.3. Data Analysis

The packed-bed unit consists of three major sections (shown in Figure 4) that significantly affect the residence time distribution (RTD) of the gas mixture reaching the gas analyzer; the packed-bed reactor, the water knockout pot, and the backpressure regulator. To determine the composition of the high pressure gas mixture leaving the bottom of the reactor (point 3), the composition of the low pressure gas mixture determined by the gas chromatograph (point 5) must be coupled with the residence time distributions imposed by the knockout pot and the back-pressure regulator sections. The inlet concentration to any section is related to the outlet concentration and the RTD through the following equation [9]:

$$C_{out}(t) = \int_0^t C_{in}(t')E(t-t')dt' \quad (1)$$

where E , represents the residence time distribution function. The RTD for each of the two sections was experimentally determined by isolating the section and feeding an equimolar gas mixture of CO₂/N₂ (in the form of a step function) into the section and measuring the composition of the gas downstream of the section by the gas chromatograph. Figure 5 shows the residence time distribution of the backpressure regulator in two independent tests, indicating that, after about 20 minutes, the outlet concentrations of CO₂ reached its inlet concentration (i.e. ~50%mol) and steady state was achieved. To validate the experimental procedure, the volume of

the back-pressure regulator was estimated (from Figure 5) to be about 32 cm³, which is very close to 31 cm³ reported by the manufacturer. Similar experiments were conducted to determine the RTD imposed by the knockout pot and backpressure regulator in series and estimate the volume of the knockout pot. The RTD imposed by the reactor was determined by feeding the gas through the reactor containing an inert (quartz) bed that was identical to the sorbent bed (same particle size and volume). The results showed that the reactor exhibit a plug flow pattern with essentially no back mixing in the packed-bed reactor. Because the total volume of the tubing in the unit is at least two orders of magnitude smaller than any of the three major components of the unit, the effect of tubing was not included in the RTD calculations.

The tanks-in-series model was used to describe the experimentally determined residence time distribution (RTD) of the gas mixture in each of the major sections of the packed-bed unit. This model has been widely used to represent non-ideal flow in reactors by envisioning the gas mixture flowing through a series of equal-sized ideal stirred tanks (CSTRs). The only parameter in this model is the number of tanks that exist in the series. The entire packed-bed unit was modeled as a combination of multi-PFRs and -CSTRs connected in series as shown in Figure 3. According to the tank-in-series model, the age distribution function that represents N number of CSTRs connected in series is given by the following equation [9]:

$$E(t^*) = \frac{(\theta_i)^{N-1}}{\tau_i (N-1)!} \exp(-\theta_i) \quad (2)$$

$$\tau_i = \frac{V_{CSTR}}{N \cdot Q_{out}} \quad (3)$$

where,

τ_i : mean residence time of a single CSTR

$$\theta_i = t^* / \tau_i \quad (4)$$

The only parameter in Equation 2 is the number of tanks in series, N , was determined by fitting the model with the packed-bed unit experimental data minimizing the sum of the square of the

errors. The volume of each section of the unit was considered to be determined as an adjustable parameter of the model, with the initial estimates obtained from the experimental results. Figure 5 shows an excellent fit between the experimental data and the RTD model by considering $N=1$ for the backpressure regulator. Similar results were also obtained for the RTD associated with the knockout pot. Therefore, the following equation can be applied to obtain the inlet concentration of CO_2 in each section.

$$C_{\text{CO}_2, \text{in}} = C_{\text{CO}_2, \text{out}} + \frac{V_{\text{CSTR}}}{Q_{\text{out}}} \cdot \frac{dC_{\text{CO}_2, \text{out}}}{dt} \quad (5)$$

where,

V_{CSTR} : Actual volume of the CSTR, cm^3

Q_{in} : total volumetric flow rate of inlet gas mixture, cm^3/min

Q_{out} : total volumetric flow rate of inlet gas mixture, cm^3/min

$C_{\text{CO}_2, \text{in}}$: CO_2 concentration at the inlet of CSTR, mol/cm^3

$C_{\text{CO}_2, \text{out}}$: CO_2 concentration at the outlet of CSTR, mol/cm^3

Because of the high CO_2 concentration in the inlet gas mixture, the gas total flow rate significantly decreases as CO_2 is removed through the absorption reaction in the bed, the outlet gas flow rate (Q_{out}) is continuously measured by a bubble flow meter placed at the downstream of the unit. Because of the transient nature of the packed bed, the total flow rates go to a minimum, representing maximum absorption of CO_2 . The minimum flow rate was 130 sccm, which corresponds to a CO_2 mole fraction of 23% ($P_{\text{CO}_2} = 4.6 \text{ atm}$), which is in close agreement with the equilibrium partial pressure of CO_2 in reaction with MgO at 425°C reported in the literature [1]. Since the data obtained from the bubble flow meter is at atmospheric pressure, the Sour Peng-Robinson Equation of State (Sour PR-EOS) was used to calculate the flow at high operating pressure of the unit. A typical measured flow rate of CO_2 at the outlet of the unit (point 5) is presented in Figure 6 along with the calculated flow rates at the outlet of the sorbent bed (point 3).

3. Mathematical Modeling

There are two Eulerian approaches to model the packed bed reactors: Porous media concept and the two-fluid model. In the porous media concept, the reactor is modeled as a single phase fluid region with a sink term in the momentum equation to allow for additional resistance to flow due to the porous structure. The sink term is calculated based on the relative permeability concept using the Darcy's law [10, 11]. The model is computationally faster compare to the two-fluid model approach; however the default solution of energy equation for the porous media is based on one-temperature model, giving only an effective thermal conductivity for the porous region. It suggests that the temperature of solid phase equals that of gas phase due to the local thermal equilibrium between the gas–solid two phases. The two-fluid model is based on Eulerian-Eulerian approach and the interaction between phases is defined by inter-phase drag forces. In this approach, the solid phase (i.e. packing) is forced to be stationary, thus the initial volume fraction distribution of the solid phase is retained, and the porosity distribution of the packed bed is fixed. In addition, the local thermal equilibrium assumption is removed and the energy equation is solved for each phase. Most of the literature available [12, 13, 14, 15] dealing with packed bed flow simulations used the two-fluid Eulerian model. The latter was adopted here for the simulations of the packed bed reactor and the details of the governing equations can be found elsewhere [16, 17, 18].

The two-fluid-model including species balance equations was coupled with the two reaction rates for the carbonation reaction and the water gas shift reaction that provide an overall source term to the species balance equations. Rate of carbonation reaction can be calculated from the rate of sorbent conversion, obtained from the two zone variable diffusivity shrinking core model [2] which gives the dX/dt in the following correlation:

$$r_{cbn} = \frac{y_{MgO}}{MW_{sorbent}} \frac{dX}{dt} \quad (6)$$

where

$$\frac{dX}{dt} = - \frac{\frac{3}{r_p} \frac{k_s}{N_{MgO}^o} (C_b - C_e)(1-X)^{\frac{2}{3}}}{1 + \frac{k_s}{D_g} r_p (1-X)^{\frac{1}{3}} (1 - \sqrt[3]{\frac{1-X}{1-X+XZ}})} \quad (7)$$

where, C_b is the CO_2 concentration in the bulk gas, C_e is the equilibrium CO_2 concentration, D_g is the product layer diffusivity of CO_2 , r_p is the radius of the particle, k_s is the surface reaction constant rate at each zone, and N_{MgO}^o is the initial number of moles of MgO per unit volume. In the above model, the dependence of the gas diffusion coefficient D_g , through the porous product layer with respect to conversion was assumed to follow an exponential decay function [2]. For the water gas shift reaction

$$r_{WGS} = k_{WGS} \left(y_{CO} \cdot y_{H_2O} - \frac{y_{CO_2} \cdot y_{H_2}}{K_{e,WGS}} \right) \quad (8)$$

where, y_i is the mole fraction of species i in the gas mixture, $K_{e,WGS}$ is the WGS reaction equilibrium constant, k_{WGS} is the forward reaction rate constant. In the temperature range of 315° to 480°C, the following expression provides a good estimate for the WGS equilibrium [19].

$$K_{e,WGS} = \exp \left(\frac{4577.8}{T} - 4.33 \right) \quad (9)$$

where T is WGS reaction operating temperature in K .

The following expression was used to describe the dependence of k_{WGS} on the MgO conversion.

$$k_{WGS} = k_{WGS}^0 \exp(-\beta \cdot X_l) \quad (10)$$

k_{WGS}^0 and β are two parameters for the model that was determined by fitting the model to the experimental data. In the above expression, the k_{WGS}^0 is an Arrhenius function of temperature, and β is constant for the entire temperature range. The model parameters are reported in Table 3.

It should be mentioned that due to the exothermic nature of the reaction between MgO and CO₂, the temperature of the bed increases by 10 to 30°C temperature in the entire packed-bed as the reaction proceeds, which significantly affects the CO₂ equilibrium partial pressure (especially at higher temperatures), resulting in an increase in CO₂ concentration at the exit of the bed (not a perfect S-shaped breakthrough curve). Therefore, the effect of temperature should be considered in the packed model. Since the reactor is externally heated, relevant experimental data is not available for solving the energy equations, the experimentally measured temperature profiles (Figure7) were imposed to the bed. Figure 8 shows the locations of the temperature measurements and the initial temperature profile along the Bed.

Computational fluid dynamic simulations were performed to predict the sorbent performance for CO₂ capture (without the water-gas-shift reaction) at different CO₂ mole fraction in the feed CO₂/N₂ mixtures (0.25-0.5), temperatures (i.e. 350°C - 450 °C). Furthermore, the CFD model was used to predict the sorbent performance for CO₂ capture and H₂ production in SEWGS at different temperatures.

4. Results and Discussion

Figure 9 shows a comparison of the effect of reaction temperature on the reactivity and absorption capacity of the sorbents in the packed-bed reactor predicted by the model with the experimental data. These tests were conducted at 20 atm using an equimolar mixture of CO₂/N₂. The results indicate that the CO₂ captured of the sorbent bed in 40 minutes were 6.7%, 9.3%, and 9.5% ($W_{CO_2}/W_{sorbent}$) at 350°C, 425°C, and 450°C, respectively. The initial pre-breakthrough CO₂ concentration corresponds to the equilibrium concentration of CO₂ at the operating temperature. The effect of CO₂ concentration on the sorbent performance is shown in Figure 10, indicating excellent agreement between the experimental results and those predicted by the CFD model. The results in Figure 10 indicate higher the breakthrough CO₂ concentration and lower sorbent capacity (from 9.3% to 4.25%) as the mole fraction of CO₂ in the inlet stream decreases from 50% to 25%, which should be attributed to thermodynamic equilibrium limitation at operating condition of the bed and the resulting smaller temperature variations within the bed. At lower CO₂ inlet concentrations (i.e. 25%) the lower driving force, which is the difference between local and equilibrium CO₂ concentrations, leads to a lower CO₂ removal and a higher

pre-breakthrough CO_2 concentration. Because of the high CO_2 concentration in the gas mixture, the total flow rate of the gas mixture significantly changes as the CO_2 is absorbed by the sorbent in the reactor. The CFD model prediction of this transient changes in the flow rate through the bed is shown in Figure 11, for 50% inlet CO_2 concentration.

The effectiveness of the sorbent in removing CO_2 from a simulated pre-combustion Syngas is shown in Figure 12, indicating that more than 95% of the CO_2 can be captured by the MgO sorbent in the packed bed reactor at 350°C over an extended pre-breakthrough period. Figure 12 also shows an excellent agreement between the experimental results and the CFD model predictions.

Figure 13 presents the extent of WGS reaction by monitoring the concentration of hydrogen in the mixture. The results indicate that the pre-breakthrough WGS conversion diminishes as the sorbent is carbonated and CO_2 concentration approaches the inlet concentration. Figure 14 shows the hydrogen concentration in the dry pre-combustion gas, increases from about 37.5% to 60% through the SEWGS process. Furthermore, the results in Figures 13 and 14 clearly indicate that the catalytic activity of MgO is significantly greater than that of MgCO_3 because, during the pre-breakthrough period, as the extent of WGS conversion gradually decreases as the sorbent is carbonated. The results in Figures 9 and 13 also indicate that, the CO_2 absorption capacity of the sorbent in pre-combustion Syngas environment containing 20% CO_2 at 350°C (i.e., 13%) is about twice the capacity obtained with a CO_2/N_2 mixture containing 50% CO_2 (i.e., 6.7%). This significant increase in the sorbent capacity is the result of the positive effect of WGS reaction in producing CO_2 during the process.

A case study using the packed-bed model (Figure 15) shows that, by increasing the activity of the sorbent towards WGS reaction by a factor of 10 at the operating temperature of 350°C (i.e. $k_{\text{WGS}}=0.003 \text{ mol/g.min}$), it is possible to produce a highly concentrated stream of hydrogen (i.e. $>90\%\text{mol}$) through the SEWGS process. This increase in the activity of the sorbent may be achieved either by adding a WGS reaction promoter within the porous media of the particle or by mixing the sorbent bed with a commercial WGS catalyst at various weight ratios. Investigation of this model prediction is a part of the future work of this study.

Conclusion

The results obtained in this study indicate that the MgO-based sorbent (EP68), which is a partially calcined dolomite impregnated with potassium carbonate, is an effective sorbent for the sorbent-enhanced water-gas-shift (SEWGS) process. The CO₂ absorption capacity of the sorbent increases with increasing temperatures from 6.7% at 350°C to 9.5% at 450°C. The sorbent was shown to be capable of achieving 95% CO₂ capture and 40% conversion in the WGS reaction. The sorbent reactivity and absorption capacity toward CO₂, as well as its WGS catalytic activity decreases with increasing temperature. The results indicate that the pre-breakthrough WGS conversion diminishes as the sorbent is carbonated and CO₂ concentration approaches the inlet concentration, leading to the conclusion that the catalytic activity of MgO is significantly greater than that of MgCO₃. The CO₂ absorption capacity of the sorbent in pre-combustion Syngas environment containing 20% CO₂ at 350°C (i.e., 13%) is twice the capacity obtained with a CO₂/N₂ mixture containing 50% CO₂ (i.e., 6.7%). This dramatic increase in the sorbent capacity is the result of the positive effect of WGS reaction in producing CO₂ during the process.

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Table 1. Syngas Compositions

Operating Condition	Range
CO, % v/v	10-40
H ₂ , % v/v	15-50
CO ₂ , % v/v	8-30
H ₂ O, % v/v	7-25
CH ₄ , % v/v	0-15
N ₂ , % v/v	0-2
Pressure, bar	10-70
Temperature, °C	800-1200
HHV of syngas, Btu/SCF	100-500

Table 2. Ranges of High-Pressure Packed-Bed Operating Parameters

Operating Parameter	Range
Temperature, °C	350-450
Pressure, atm	20
Space Velocity, hr ⁻¹	1000
Gas Composition, mol%	
CO ₂	20-50
CO	0-30
H ₂	0-30
H ₂ O	0-20
N ₂	Balance

Table 3. WGS Reaction Model Parameters at Different Operating Temperatures

Model Parameter	350°C	400°C	425°C
k_{WGS0} , <i>mol/g.min</i>	0.0003	0.001	0.002
β	3.5	3.5	3.5

(a)

(b)

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Figure 11. Instantaneous gas velocity (m/s) contours at $t = 10$ min, for 50% CO_2 inlet concentration.

Figure 12. Effect of Temperature on Sorbent Performance in Syngas environment (Model vs. Experiment)

Figure 13. Effect of Temperature on SEWGS in Syngas environment (Model vs. Experiment)

Figure 14. Composition of Syngas after SEWGS at 400°C (Model vs. Experiment)

Figure 15. Case Study with the Model at 350°C