

High temperature CO₂ capture using calcium oxide sorbent in a fixed-bed reactor

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ABSTRACT

The gas–solid reaction and breakthrough curve of CO₂ capture using calcium oxide sorbent at high temperature in a fixed-bed reactor are of great importance, and being influenced by a number of factors makes the characterization and prediction of these a difficult problem. In this study, the operating parameters on reaction between solid sorbent and CO₂ gas at high temperature were investigated. The results of the breakthrough curves showed that calcium oxide sorbent in the fixed-bed reactor was capable of reducing the CO₂ level to near zero level with the steam of 10 vol%, and the sorbent in CaO mixed with MgO of 40 wt% had extremely low capacity for CO₂ capture at 550 °C. Calcium oxide sorbent after reaction can be easily regenerated at 900 °C by pure N₂ flow. The experimental data were analyzed by shrinking core model, and the results showed reaction rates of both fresh and regeneration sorbents with CO₂ were controlled by a combination of the surface chemical reaction and diffusion of product layer.

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1. Introduction

It is now widely acknowledged that CO₂ in the atmosphere contributes to the greenhouse effect, is gradually warming the planet. Global efforts in reducing greenhouse gas emissions have spurred intense research in sustainable production methods of hydrogen and CO₂ capture [1]. Among the renewable energy sources, biomass plays an important role for fuel production or power generation. Steam reforming process is able to convert the chemical energy of biomass into a hydrogen-rich fuel gas. Nowadays, considerable interest is focused on a pure hydrogen energy production, a concept combining hydrogen production and capture of CO₂ is the sorption-enhanced steam reforming process of biomass [2]. The process utilizes a solid CO₂ acceptor to in situ remove CO₂ from steam reforming reactor and thereby changes the normal thermodynamic limitations of reactions. As a consequence, hydrogen production can be run at lower temperature than the traditional steam reforming process, which will reduce energy consumption, coking and sintering of the catalyst, and investment costs [3]. Kinoshita and Turn [4] investigated the simulation of hydrogen production from bio-oil steam reforming by the sorption-enhanced reforming process. The results showed that the use of such process greatly increases bio-oil conversion and decreases the reaction temperature.

The steam reforming of biomass and CO₂ capture steps occur in a single, integrated process, and integrating these reaction steps

involves selecting suitable reaction conditions under which all of the processes can be carried out. This requirement limits the available techniques for CO₂ capture, e.g. membrane and cryogenic separation processes require high pressures or low temperatures for efficient CO₂ capture, adsorption of CO₂ with carbon based adsorbents is limited to low temperatures of 150–250 °C and hydro-talcite compounds have a significantly diminished capacity for CO₂ capture beyond 300 °C [5]. Some studies have demonstrated high reactivity of metal oxides for CO₂ capture under the conditions suitable for sorption-enhanced steam methane reforming (SE-SMR) process [6,7]. Although many metal oxides can react with CO₂ to form carbonates. However, not all metal oxides are suitable for CO₂ capture under conditions suitable for biomass steam reforming. Metal oxides for in situ CO₂ capture during hydrogen production from catalytic steam reforming of biomass must satisfy several criteria [5]: (i) they must exhibit high reactivity at a temperature range of biomass steam reforming; (ii) their decomposition temperatures should be greater than the temperature range for steam reforming, but not too high to avoid imposing severe energy penalties during the sorbent regeneration step; (iii) sorbent particles should be resistant to physical deterioration due to attrition or sintering; (iv) sorbent particles should be resistant to decay in reactivity through multiple CO₂ capture and release reactions, which is not discussed in this paper; (v) rates of reaction and regeneration of sorbent should be high; (vi) sorbents highly vulnerable to chemical poisoning of the active sites from byproducts are unlikely to be suitable for this process [5,8].

Thus, the advantage of a low cost sorbent is most apparent. In this regard, a number of synthetic oxides developed for high temperature CO₂ capture including Ca₂SiO₄ [9], Li₂ZrO₃ [10,11] and

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Table 1
Properties of fresh calcium oxide sorbent.

Sorbent	Particle size (mm)	Specific surface area (m ² /g)	Pore volume (ml/g)	Average pore diameter (Å)
Calcium oxide	0.45–0.10	6.2079	0.02706	223.18

Nomenclature

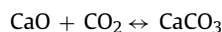
b	stoichiometric coefficients
c, c_0	CO ₂ gas percentage concentration (%)
D_e	effective diffusion coefficient in a porous structure (m ² s ⁻¹)
$g(x)$	conversion function under chemical control
K_a	equilibrium constant
k_s	intrinsic reaction rate constant (s ⁻¹)
$P_{CO_2}^{eq}$	equilibrium partial pressure of CO ₂
$p(x)$	reaction function under diffusion control
q	capability of sorbent (%)
q_0	maximum capability of sorbent (%)
Q	function of sum of the squares of the errors
r, r_0	radius of particle (mm)
S_0	surface area of the solid sample (m ² m ⁻³)
SSE	sum of the squares of the errors
t, t_b, t_g, t_p	time (min)
T	temperature (K)
x	c/c_0

Greek letters

$\Delta G_{rxn}^\circ(T)$	standard state Gibbs free energy change
$\Delta v_i, \Delta v_i^{t=0}$	volumetric shrinkage rate at t and $t=0$, respectively.
α	shrinkage factor
δ^2	ratio of diffusion to chemical reaction resistance
$\phi(x)$	reaction function under the combination of chemical control and product layer diffusion
ρ_s	solid particle density (kg m ⁻³)
τ_g, τ_p	characteristic time for chemical reaction and diffusion control (min), respectively.

Na₂ZrO₃ [12] are likely to be prohibitively expensive. Abanades et al. [13] argued that the performance of Li-based sorbents must be proven for up to ~10,000 reaction cycles to be economically competitive with sorbents derived from naturally occurring limestone.

CO₂ is captured in the form of CaCO₃, a common and stable solid species, according to the following equation:



Up to date, although there have been a few studies on the use of TGA to extensively study CO₂ capture and conversion of sorbent [14–17], little has been found in the literatures on breakthrough curves and reaction of calcium oxide sorbent with CO₂ at high temperature. This forms the main motivation for carrying out this study on the use of a low cost calcium oxide sorbent for CO₂ capture. The paper presents the effects of operating parameters and the detailed kinetic analysis of CO₂ capture with calcium oxide sorbent at high temperature.

2. Experimental

2.1. Preparation of sorbent

Calcium oxide sorbent was prepared by pelletizing the CaO substance from catalyst industry, and it mainly consisted of higher than 96 wt% CaO compound based on the data provided by the manufacturer. Other compounds listed were CaCO₃ (<2.0 wt%), MgO (<1.0 wt%), inorganic salts (<1.0 wt%). The specific surface area of sorbent was determined with the BET method using a Micrometric Acusorb 2100E apparatus. Table 1 gives the specific surface area, pore volume and average pore diameter of fresh calcium oxide sorbent. MgO in the sorbent was prepared by mixing MgO and CaO using wet and dry methods [18], and the mixture was placed in the temperature-controlled oven where the heating rate was controlled so that it increased from room temperature to 100 °C in 1 h, and calcined at 900 °C for 2 h. In all the experiments, sorbent was crushed and sieved to 0.45–0.10 mm.

2.2. Apparatus and procedure

Fig. 1 shows a schematic diagram of the laboratory system used for high temperature capture of CO₂. The experimental system for the fixed-bed reactor consists of a gas manifold, a fixed-bed

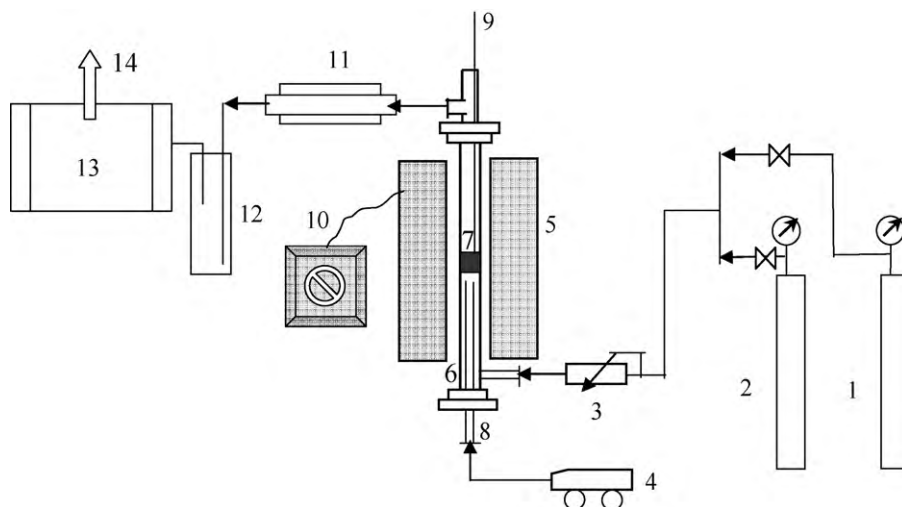


Fig. 1. Schematic diagram of the experimental setup. (1) N₂ cylinder; (2) CO₂ cylinder; (3) flow controller; (4) syringe pump and steam feed injector; (5) oven; (6) reactor; (7) sorbent; (8) injector; (9) thermocouple; (10) temperature controller; (11) condenser; (12) silica gel; (13) CO₂ analyzer; (14) outlet.

Table 2

Typical operation conditions in the experiments.

Parameter	Value
Particle size of sorbent	0.45–1.0 mm
Bed porosity	0.50–0.60
Inlet CO ₂ concentration, <i>c</i> ₀	5–10 vol%
Space velocity	2000–3000 h ⁻¹
Temperature	400–550 °C
Operating pressure	1 atm

reactor with temperature control, and a CO₂ analysis section. In the gas manifold, the gas mixture is prepared by CO₂ and N₂ cylinder. The sorbent is supported by quartz wool in the center of tube in the fixed-bed reactor, and the reactor had an internal diameter (ID) of 0.010 m and was 0.80 m long. The sample temperature is indirectly measured by a thermocouple. A nitrogen flow of $0.5 \times 10^{-3} \text{ m}^3 \text{ min}^{-1}$ (STP) serves as a carrier. Water with a preset ratio is then injected by a micro-syringe pump into the injector. As the injector is housed in the furnace, the water is heated above 300 °C to vaporize it and is subsequently mixed with the diluting N₂ stream at a position of 0.03–0.04 m below the sorbent bed. Before each run, the sorbent is heated with a continuous N₂ flow of $0.5 \times 10^{-3} \text{ m}^3 \text{ min}^{-1}$ at 550 °C for 1 h. During the start-up stage, the gas flow is directed away from the sample to prevent any reaction. To start the capture process, the gas flow switches to the sample section of the reactor. The CO₂ concentration at the inlet and outlet from the sorbent bed is determined by an online portable GXH-3010E CO₂ analyzer. During CO₂ capture process, the CO₂ concentration in the effluent gas rises rapidly when the sorbent has reached certain capacity. This rapid change is termed breakthrough [18]. The breakthrough curve of CO₂ capture is characterized by a variation of dimensionless concentration value (*c/c*₀) with time, and the dimensionless concentration is a ratio of outlet CO₂ concentration (*c*) to inlet CO₂ concentration (*c*₀). In this study, the typical experimental conditions are summarized in Table 2.

3. Results and discussion

3.1. Thermodynamic equilibrium for CO₂ capture using CaO as a solid sorbent

The driving force for CO₂ capture is the difference between the partial pressure of CO₂ in the reactor and the equilibrium partial pressure of CO₂ [19]. The extent of the gas–solid reaction between CaO sorbent and CO₂ to form CaCO₃ can be first predicted from thermodynamic equilibrium theory. CaCO₃ decomposes to form CaO and CO₂:



This decomposition reaction is favored when the CO₂ partial pressure in the product gas is lower than the equilibrium partial pressure of CO₂ resulting from the decomposition of CaCO₃. Conversely, CaO will react with CO₂ when the CO₂ partial pressure in the product gas is greater than the equilibrium partial pressure, assuming there is sufficient CaO to capture CO₂ and sufficient time to account for mass transfer resistances. Determination of the equilibrium partial pressure of CO₂ resulting from the decomposition of CaCO₃ has been attempted by several investigators for many years [5]. Calculation of the equilibrium partial pressure is equivalent to the calculation of the equilibrium constant (*K*_a) [5]:

$$K_a = P_{\text{CO}_2, \text{eq}} = \exp\left(\frac{-\Delta G_{\text{rxn}}^\circ(T)}{RT}\right) \quad (1)$$

In Eq. (1), *P*_{CO₂,eq} is the equilibrium partial pressure of CO₂ from the decomposition of CaCO₃. $\Delta G_{\text{rxn}}^\circ(T)$ is the standard state Gibbs free energy change for the reaction, calculated from tabulated ther-

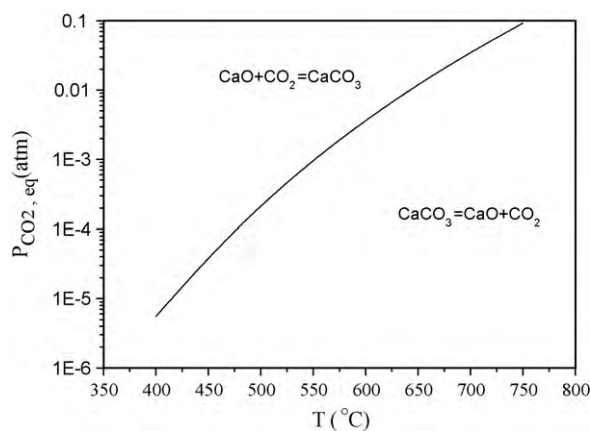


Fig. 2. Equilibrium partial pressure of CO₂ resulting from the decomposition of CaCO₃.

mochemical data. The thermochemical data are obtained from the NIST-JANAF Thermochemical Tables [5,20].

Fig. 2 shows the equilibrium partial pressure of CO₂ from the decomposition of CaCO₃ at temperatures between 400 and 750 °C. The experimental data from some studies in the literatures are in close agreement with the predicted equilibrium partial pressure according to Eq. (1) [5]. A temperature of 550 °C is suitable for the steam reforming of biomass, and the CO₂ equilibrium pressure of 0.001 atm at this temperature is shown in Fig. 2. This equates to the removal of 90% of CO₂ from a typical product gas containing 1.0 vol% CO₂ at atmospheric pressure. The trend in Fig. 2 suggests that decreasing the temperature at a constant total pressure or increasing the total pressure at a constant temperature will promote further capture of CO₂ by CaO. Hence, there is a compromise for choosing conditions, which should be suitable for CO₂ capture and also most suitable for low temperature H₂ generation from biomass.

3.2. Effect of temperature

The CO₂ capture at different temperatures is shown in Fig. 3. As can be seen from Fig. 3, in the temperature range of 400–500 °C, the CO₂ concentration at outlet rapidly increases, which indicates the CO₂ capture capability by calcium oxide sorbent is fairly low at these temperatures. It is observed that CO₂ of more than 70% is captured at 550 °C within the first 13.0 min. This high CO₂ capture offers a great opportunity for calcium oxide sorbent in industrial application at this temperature. Generally, we also hope hydro-

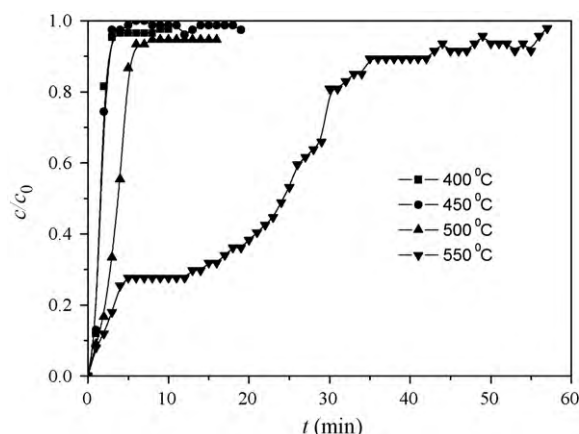


Fig. 3. CO₂ breakthrough curves at different temperatures from 400 to 550 °C.

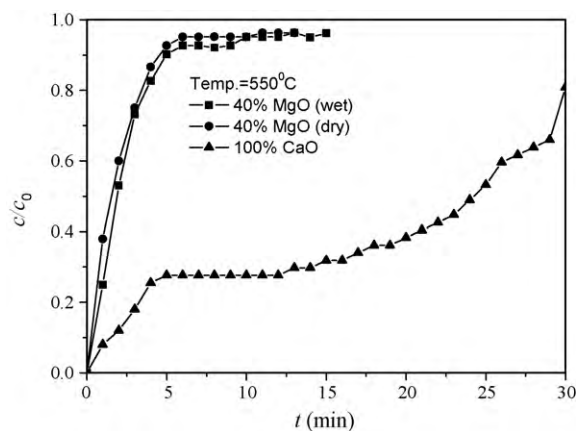
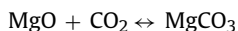


Fig. 4. Effect of MgO content in sorbent on CO₂ capture at 550 °C.

gen production from steam reforming of biomass can be operated below 600 °C [2].

3.3. Effect of MgO content in sorbent

The effect of MgO content in sorbent on the capture of CO₂ is shown in Fig. 4. The results clearly indicate that the sorbent in CaO mixed with MgO of 40 wt% has extremely low reactivity and capture capacity at 550 °C. In fact, the ideal temperature for CO₂ removal with magnesium-based sorbents may be 300–500 °C. The reversible chemical reaction for CO₂ removal involving magnesium oxide is:



The equilibrium CO₂ partial pressure for MgO–CO₂ carbonation/decomposition has been presented in literature [21]. Given that the CO₂ partial pressure in the gas is in the range of 0.05–0.50 atm, MgO cannot be used to remove CO₂ at the temperatures of higher than 500 °C.

3.4. Effect of inlet CO₂ concentration

Fig. 5 shows the influence of inlet CO₂ concentration on the capture characteristics at 550 °C. With the increase of the CO₂ concentration from 5.0 to 10.0 vol%, the dimensionless concentration value (c/c_0) is increased within initial 5 min. It is mentioned earlier that the CO₂ capture can be affected by its partial pressure in the system. The results indicated that inlet CO₂ concentration as

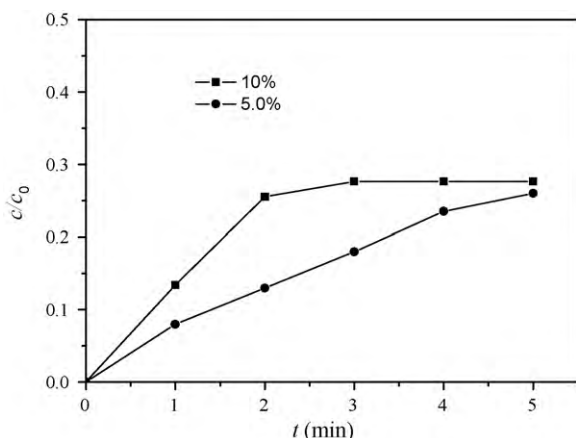


Fig. 5. Effect of inlet CO₂ concentration on CO₂ capture.

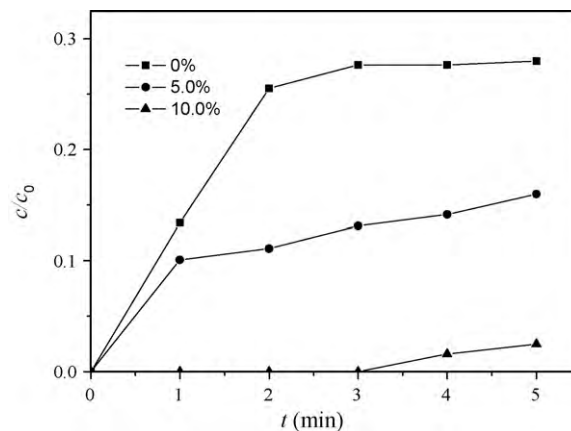
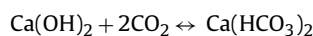
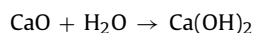


Fig. 6. Effect of steam in the feeding on CO₂ capture.

a kinetic factor may affect the diffusion of gas–solid reaction of calcium oxide sorbent with CO₂.

3.5. Effect of steam

Fig. 6 shows the effect of steam in the feeding on CO₂ capture at 550 °C. Dry CO₂ capture without the steam has a maximum c/c_0 of 0.26 at 5 min, whereas the values of c/c_0 in wet CO₂ capture with the steam of 5.0 and 10.0 vol% decrease to 0.16 and 0.025, respectively, clearly showing presence of steam in the feeding has a positive impact on the CO₂ capture using calcium oxide sorbent. Especially, the CO₂ concentration can be decreased to 0 within at least 3 min by calcium oxide sorbent under the conditions of 550 °C with the steam of 10 vol%. Similar results were also observed in our previous studies on glycerol steam reforming with in situ CO₂ removal [2]. Literatures indicated some plausible mechanisms for the reason of the enhancement of CO₂ capture by steam [16], and for example, a possible mechanism was pointed out that the steam first reacts with CaO to form Ca(OH)₂ and then Ca(OH)₂ undergoes carbonation [16]. The reaction formula is as follows:



In fact, in previous study, crude glycerol experiments with in situ CO₂ sorption yielded longer breakthrough times than the pure glycerol in the same conditions because of significantly higher steam partial pressure in the reactor, and Ca(OH)₂ in spent dolomite sorbent was also detected by SEM-EDX during the steam reforming of glycerol using in situ CO₂ removal [2,22]. A study by Pimenidou et al. on the kinetics of dolomite carbonation in conditions simulating those of steam reforming had shown that the presence of steam had a great effect on the kinetics of the carbonation, with the result that CO₂ capacities in dry conditions may double in the presence of steam, bringing them to the theoretical maximum [23].

3.6. Regeneration

CO₂-capture system is necessarily large-scale system. Therefore, very fast sorption and regeneration rates of sorbent for CO₂ capture are required to allow for compact capture and regeneration reactors. These properties are tested by continuous reaction with CO₂–N₂ mixture flow at 550 °C and high temperature regeneration with pure N₂ flow at 900 °C, and the results are shown in Fig. 7. It is observed that regeneration time of sorbent is less than 20 min, and the maximum concentration of CO₂ is observed at approximately 10 min regeneration and, then, the outlet concentration of

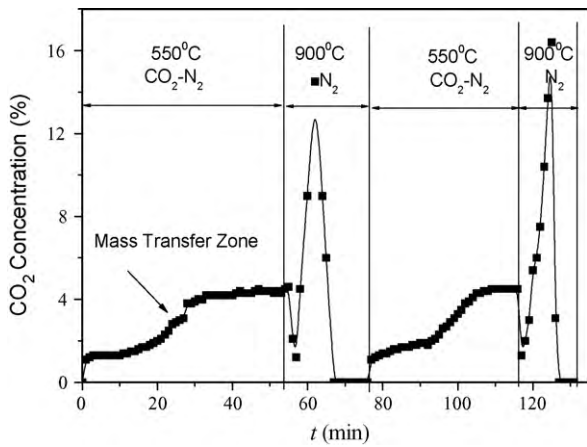


Fig. 7. Continuous reaction and regeneration of sorbent.

CO₂ rapidly decreased. As shown in Fig. 7, the regeneration rate of the fresh sorbent is a little more than that of regeneration sorbent. It is clear that the spent sorbent could be completely regenerated at 900 °C. Of cause, issues related to the regenerability of the sorbent, its stability as it undergoes many cycles of carbonation-decomposition, need to be addressed in the future.

3.7. Kinetics

The CO₂ capture process at high temperature in a fixed-bed reaction system is considered to be a very complex phenomenon involving a large number of sub-processes. The CO₂ breakthrough curve of a fixed-bed reactor roughly followed an S shape, which shows the active part of the fixed-bed where reaction actually takes place, resulting in a gradient in CO₂ concentration in the product gas to equilibrium. The modeling of the mass transfer zone of fixed-bed reactor is based on the conservation equation derived from the mass balance on the fluid and solid phase. When concentration of CO₂ in gas product is very small, and assuring the breakthrough pattern to be constant through the bed, a simple correlation of the gas and the solid can be obtained [18,24,25]:

$$\frac{c}{c_0} = \frac{q}{q_0} = x \quad (2)$$

where q is capacity of sorbent, q_0 is the maximum capability of sorbent and x is the conversion of sorbent.

The process is modeled here with the following assumptions [17]: (i) the fixed-bed is isothermal; (ii) gas velocity is constant; (iii) plug flow conditions for the gas phase is without axial dispersion, implying the use of a one-dimensional model along the reactor axis, z ; (iv) the gas phase is ideal. The reaction is unlikely to be controlled by the gas-film mass transfer; therefore, the rate controlling steps should be the chemical reaction or the product layer diffusion, or both. For the surface chemical reaction, the rate of the CO₂ capture is defined as [18,26,27]:

$$\frac{dx}{dt} = -bk_s c \quad (3)$$

where k_s is the rate constant of surface chemical reaction, b is the stoichiometric coefficient.

The rate of gas diffusion through the solid product layer is given by [18,26,27]:

$$\frac{dx}{dt} = -D_e \frac{S_0 dc}{dr} \quad (4)$$

where D_e is the effective diffusion coefficient, S_0 is the surface area of the particle, and r is the radius of the particle. A model of the

reaction core allows for a change in the radius of the particle to be given by [26]:

$$\frac{r^3}{r_0^3} = 1 - \alpha x \quad (5)$$

where r_0 is the initial particle radius, and the shrinkage factor α is defined as [26]:

$$\alpha = \frac{\Delta v_i}{\Delta v_i^{t=0}} \quad (6)$$

where i refers to single volume element, and Δv_i , $\Delta v_i^{t=0}$ represent the volumetric shrinkage rate at time t and $t=0$, respectively.

If the process is controlled by the surface chemical reaction, then the data can be modeled through the use of the shrinking core model expression. The reaction time is given by [27]:

$$t_g = \frac{\rho_s r_0 (1 - (r/r_0))}{bk_s c_0} \quad (7)$$

where ρ_s represents the density of the particle.

The characteristic time τ_g required for the maximum efficiency of CO₂ capture can be obtained using the following equation [27]:

$$\tau_g = \frac{\rho_s r_0}{bk_s c_0} \quad (8)$$

Thus, Eq. (7) can be obtained [26]:

$$\frac{t_g}{\tau_g} = g(x) = 1 - (1 - \alpha x)^{1/3} \quad (9)$$

If the reaction is controlled by the gas diffusion through the solid product layer, it may follow the expression given by [27]:

$$t_p = \frac{\rho_s r_0^2}{6bD_e c_0} \left[1 - 3 \frac{r^2}{r_0^2} + 2 \frac{r^3}{r_0^3} \right] \quad (10)$$

At last, we can obtain [26]:

$$\frac{t_p}{\tau_p} = p(x) = 1 - 3(1 - \alpha x)^{2/3} + 2(1 - \alpha x) \quad (11)$$

where

$$\tau_p = \frac{\rho_s r_0^2}{6bD_e c_0} \quad (12)$$

If the process is assumed to be a combination of rate limiting mechanisms such as chemical reactions and gas diffusion, the time required for a certain reaction is the sum of two parcels and corresponds as follows:

$$t - t_b = t_g + t_p \quad (13)$$

or

$$\frac{t - t_b}{\tau_g} = \phi(x) = g(x) + \delta^2 p(x) \quad (14)$$

where t_b is the breakthrough time, and

$$\delta^2 = \frac{\tau_p}{\tau_g} = \frac{k_s r_0}{6D_e} \quad (15)$$

The value of δ^2 represents the ratio of diffusion resistance to chemical reaction resistance. When $\delta^2 \ll 1$, the process can be assumed to be controlled by the rate of the chemical reaction. When $\delta^2 > 10$, it is safely assumed that it is under the control of product layer diffusion. An intermediate value of δ^2 suggests that the CO₂ capture at high temperature is controlled by the chemical reaction and the product layer diffusion [18,24,26–28].

Eqs. (9), (11) and (14) are used to model the $x-t$ data and τ_g , τ_p and δ^2 can be estimated by minimizing the equation for the sum of

Table 3
Kinetic parameters, $\alpha = 1$.

Reaction	Model	SSE	τ_g (min)	τ_p (min)	δ^2
Fresh sorbent	(9)	0.331	27.2	–	–
	(11)	0.515	–	31.4	–
	(14)	0.108	13.8	14.5	1.05
Regeneration sorbent	(9)	0.299	23.3	–	–
	(11)	0.187	–	25.5	–
	(14)	0.099	13.4	9.5	0.71

the squares of the errors (SSE):

$$\sum_{i=1}^N [\tau_g g(x_i) + \tau_p p(x_i) - (t - t_b)_i]^2 = Q(\tau_g, \tau_p) \quad (16)$$

From the data from Fig. 7, we defined the breakthrough time, t_b at CO₂ capture efficiency was 0.40. Thus, the models data using x vs. t from the CO₂ capture curves is within the efficiency of CO₂ capture, x of 0.40–0.90 for fresh and regeneration sorbents. The rate expressions of $g(x)$ and $p(x)$ (refer to Eqs. (9) and (11)) are applied to Eq. (14) by minimizing (16) first with respect to one of the τ_g and τ_p by setting the other to zero and then with respect to both τ_g and τ_p simultaneously. The computed parameters are shown in Table 3. The model curves are shown in Fig. 8. We tested the effect of different values of α on kinetics, and results showed that the value of α was not sensitive to the models. Thus, $\alpha = 1.0$ has been used in the model in order to simplify the computations [26].

The kinetic results show that the estimated SSE for the combined model (14) is less than those for the chemical reaction control model (9) and the diffusion control model (11) for fresh and regen-

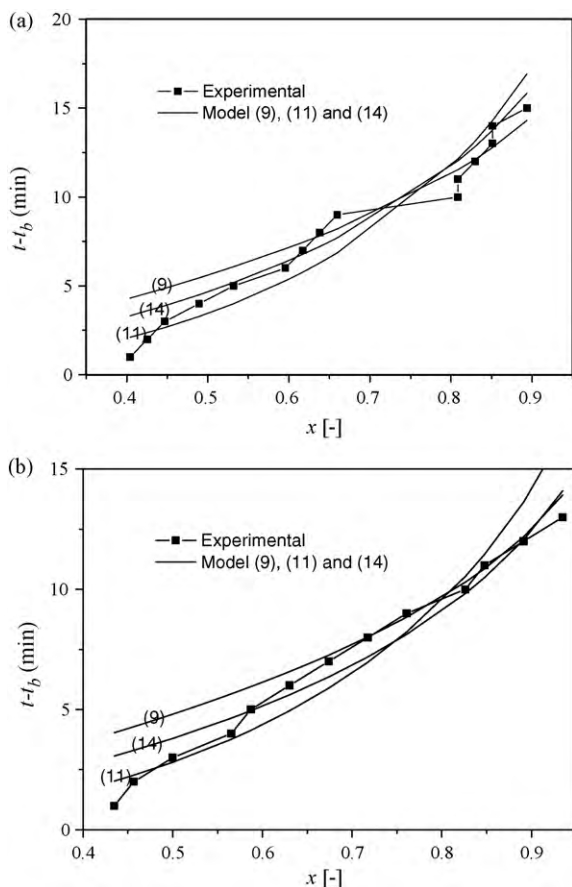


Fig. 8. x vs. $(t - t_b)$ for both (a) fresh and (b) regeneration sorbents.

eration sorbents. The results also show that the value of δ^2 is 1.05 and 0.71 for fresh and regeneration sorbents, respectively. Therefore, the fitting based on a model derived from the shrinking core models suggests that the CO₂ capture by calcium oxide sorbent is governed by a combination of the chemical reaction and product layer diffusion. In combination rate controlling steps, the experimental results and model predictions are in agreement. In addition, the overall reaction rate may be affected due to the great difference existing between the molar volumes of the solid reagent and the product. The molar volume of the solid product in comparison with that of the solid reagent is high. This similarity behavior has been widely studied for CaO sulfation.

4. Conclusions

The reaction between calcium oxide sorbent and CO₂ gas at high temperatures was investigated in a fixed-bed reactor. The effects of temperature, MgO content in sorbent, steam feeding, inlet CO₂ concentration on reaction between sorbent and CO₂ gas were investigated. The results showed the enhancement of CO₂ capture by steam. Sorbent in CaO mixed with MgO of 40 wt% is very poor for CO₂ capture at 550 °C. Calcium oxide sorbent can be easily regenerated at 900 °C by pure N₂ flow. Under the considered operating conditions, the reaction rates of both fresh and regeneration sorbents with CO₂ gas were controlled by a combination of the surface chemical reaction and diffusion of product layer based on the shrinking core model.

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