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Continuous CO₂ Capture from Flue Gases Using a Dual Fluidized Bed Reactor with Calcium-Based Sorbent

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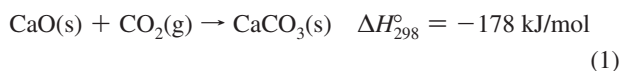
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CO₂ capture using multiple carbonation and calcination reaction looping is an emerging postcombustion capture technology. Dual fluidized bed reactors are the key technology to fulfill the carbonation/calcination looping process. Dual bubbling fluidized bed reactors were constructed to demonstrate the process feasibility of continuous CO₂ capture from flue gases. First, a cold model of the dual bubbling fluidized bed reactor was built and tested on the foundation of analyzing different types of dual fluidized bed reactors. Long-term stable operation and continuous solids circulation between the two reactors was achieved in the cold model. The solids circulation rate increased with increasing bed material height, solid injection nozzle diameter, and hole diameter on the solid injection nozzle. Second, a hot model of the dual bubbling fluidized bed reactor was constructed. The sorbent particles successfully circulated between the carbonator and the regenerator at high temperatures and the CO₂ in the flue gases was continuously captured by the Ca-based sorbent, dolomite. Experimental results indicate that ~95.0% CO₂ capture efficiency could be achieved. In the carbonator, about 70.4% CaO in the sorbent was converted to CaCO₃. In the regenerator, the CaCO₃ did not decompose completely with more than 13.9 wt % CaCO₃ still in the sorbent leaving the regenerator. The carbonation temperature and the sorbent attrition were found to significantly influence the carbonation/calcination looping process.

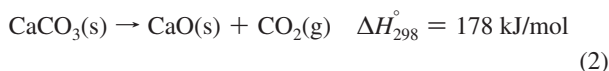
1. Introduction

Anthropogenic carbon dioxide (CO₂) emission is a major contributor to the greenhouse effect that causes global warming, which is now recognized to be a major risk to mankind.¹ Power generation combustion systems are responsible for one-third of the anthropogenic CO₂ emissions, and coal is known to release larger amounts of CO₂ per unit power generation than oil or natural gas. One approach to reduce CO₂ emissions into the atmosphere is the separation of CO₂ from the flue gases and storage in geological formations.²

There are various approaches to separate CO₂ from flue gas streams. One promising method for CO₂ capture from flue gases is to use the multiple carbonation/calcination reaction looping with Ca-based sorbents illustrated in Figure 1.^{3,4} The overall system for the carbonation/calcination looping process consists of a carbonation reactor and a calcination reactor. In the carbonator, CaO is carbonated to CaCO₃ at a relatively low temperature in the flue gases (about 600–700 °C) at atmospheric pressure.



For continuous processes, the CO₂ sorbents must be regenerated after the carbonation reaction to be used repeatedly. The CaCO₃ is then removed from the carbonator and delivered to the regenerator. The calcination of CaCO₃ regenerates the sorbent to CaO and produces a concentrated stream of CO₂ at higher temperatures (>900 °C).



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Naturally occurring Ca-based sorbents, such as limestone and dolomite, which are plentiful, cheap, and widely available, are suitable for the CO₂ separation process. Many previous studies^{5–15} have investigated the different aspects of the carbonation/calcination looping process, such as multicycle performance of carbonation/calcination reactions of Ca-based sorbents, sorbent reactivation studies, modeling, and process simulations. However, despite the increasing number of published works that deal with these systems, most of these studies have focused on analyses using thermogravimetric analyzers (TGA), or single fixed/fluidized bed reactors. In the carbonation/calcination looping, the CO₂ sorbent circulates between the carbonator and the regenerator, and the dual fluidized bed reactors being connected by solids transport lines are considered to be a suitable system. Therefore, the dual fluidized bed reactors are the key technology to fulfill a continuous cyclic carbonation/calcination process for CO₂ capture. The carbonation/calcination looping process in dual fluidized bed systems was studied by Lu et al.,¹⁶ Abanades et al.,¹⁷ and Charitos et al.,¹⁸ who achieved high CO₂ capture efficiencies. However, there is still a lack of sufficient information about the CO₂ capture using carbonation/calcination reaction looping with dual fluidized bed reactors.

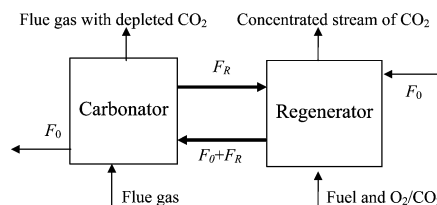


Figure 1. Schematic of carbonation/calcination reaction looping using Ca-based sorbents. (F_0 (kmol/s) is the molar flow rate of fresh sorbent. To maintain a fixed amount of materials in the system, the same amount of spent sorbent (F_0 (kmol/s)) must be discharged. F_R (kmol/s) is the sorbent molar flow rate from the carbonator to the regenerator. $F_R + F_0$ is the solids molar flow rate from the regenerator to the carbonator.)

This paper describes continuous CO₂ capture from flue gases in dual fluidized bed reactors using Ca-based sorbent to study the carbonation and calcination characteristics of Ca-based sorbent and the particle attrition in the continuous carbonation/calcination looping process. First, a dual bubbling fluidized bed reactor was selected on the basis of analyses of different forms of the dual fluidized bed reactors, with a cold model of the dual bubbling fluidized bed reactor then being built. Second, the cold model of the dual bubbling fluidized bed reactor was used to investigate the effects of the structure and operating conditions on the solids circulation rate to give useful information for the design of a hot dual fluidized bed CO₂ capture system. Finally, the hot dual bubbling fluidized bed reactor system was constructed to study the continuous CO₂ capture from flue gases at high temperatures.

2. Experimental Section

2.1. Selection of the Dual Fluidized Bed Reactors. The carbonation/calcination looping process consists of two fluidized bed reactors, acting as the carbonator and the regenerator, both operating at atmospheric pressure and connected by solids transport lines. The four most likely types of dual fluidized bed reactors are (1) the dual bubbling fluidized bed reactor, (2) the dual high-velocity fluidized bed reactor, (3) a bubbling fluidized bed reactor as the regenerator and a high-velocity fluidized bed reactor as the carbonator, and (4) a bubbling fluidized bed reactor as the carbonator and a high-velocity fluidized bed reactor as the regenerator. The advantage of using a high-velocity fluidized bed reactor is to allow the processing of a large amount of gases in a continuous basis, but attrition will increase because of the high gas velocity. For the application of the carbonation/calcination looping process to capture CO₂ from flue gases at large-scale industrial processes (i.e., power plants), the use of high-velocity fluidized bed reactors for both the carbonator and regenerator seems to be the best option. However, the CO₂ in the flue gases may not be absorbed efficiently, if the carbonator is not tall enough.

Use of a bubbling fluidized bed reactor will improve the gas–solid contact to increase reaction efficiency. For the carbonator, the CO₂ in the flue gases is expected to be absorbed efficiently. Using a bubbling fluidized bed reactor as the regenerator, the CaCO₃ can be more completely calcined because of the high heat capacity. Therefore, the bubbling fluidized bed reactor can be also used for the carbonation/calcination looping process under some conditions, for example, in small industrial processes or in laboratory scale.

2.2. Cold Model of the Dual Bubbling Fluidized Bed Reactor. A dual bubbling fluidized bed reactor was then selected for the laboratory-scale system to study the CO₂ capture. A schematic of the dual bubbling fluidized bed reactor is given in Figure 2. This type of dual bubbling fluidized bed reactor is similar to that developed by Ryu et al.¹⁹ with two bubbling fluidized bed reactors, solid injection nozzles (pipes with small diameter), risers, cyclones, and downcomers, and the carbonator and the regenerator are connected by cyclones and downcomers. However, the connection of the downcomer to the reactor is changed, with the downcomer located on the wall side of the reactor to improve flow of the sorbent particles into the reactor. Both reactors made of plexiglass had heights above the perforated distributor plate of 1.0 m with internal diameters of 0.149 m. The solid particles could be sampled from an outlet about 50 mm above the distributor plate, with this solid sampling outlet controlled by a ball valve. Solid particles could be added into the reactor from the sorbent loading inlet. The fluidizing

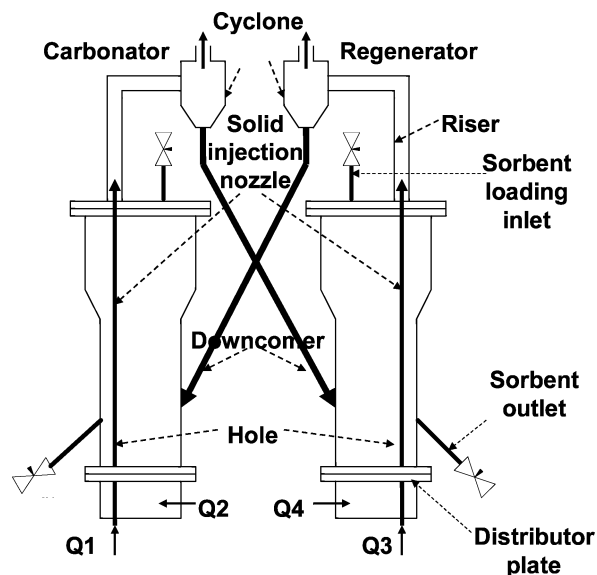


Figure 2. Schematic of the dual fluidized bed reactor facility. (Q1, Q2, Q3, and Q4 are the gas inlets.)

gases were introduced at the bottom of the bubbling fluidized bed reactors through Q2 and Q4. The solid injection nozzles had holes through which the solids in the reactors could flow into the solid injection nozzles and be carried to the risers by the gases from Q1 and Q3. Then, the sorbent went to the other reactor through the risers, the cyclones, and the downcomers, and the fluidizing gas (from Q2 or Q4) and the gas for carrying the sorbent in the solid injection nozzle (from Q1 or Q3) mixed in the riser and exited from the cyclones.

2.3. Hot Model of Dual Bubbling Fluidized Bed Reactor. The design of the dual bubbling fluidized bed reactor shown in Figure 2 was then used to build the hot dual fluidized bed system shown in Figure 3. The sizes of each section of the hot dual fluidized bed reactor were the same as in the cold model of the dual fluidized bed reactor, except that the internal diameter of the regenerator was 0.117 m and the wind caps were used on the distributor plate to evenly distribute the fluidizing gas in the bed. Each reactor was wrapped with four electric furnaces (2.5 kW each) which provided supplemental heating during warm-up and provided supplemental heating for the heat losses when the carbonator and the regenerator temperatures were appropriate for the carbonation and calcination reactions.

There were a number of ports for installing differential pressure transducers and thermocouples. For example, a differential pressure transducer installed between a location above the distributor plate and the reactor outlet measured the bed differential pressure, and a thermocouple placed about 0.1 m above the distributor plate in the reactors measured the temperature inside the reactor. A self-developed program was used to control the facility and for data acquisition. The exit streams from the fluidized bed reactors were directly sampled at the reactor outlets by online gas analyzers to estimate the CO₂ capture efficiency.

The flue gas stream for the CO₂ removal at the carbonator consisted of synthesized mixtures of air and pure CO₂. The gases for carrying the sorbent in the solid injection nozzles in both the carbonator and regenerator were air. The application of the carbonation/calcination looping process for CO₂ capture implies that sorbent regeneration needs to be carried out in a relatively highly CO₂ concentrated environment to produce an almost pure CO₂ stream suitable for later purification and storage. In this way, the calcination environment in the regenerator will lead

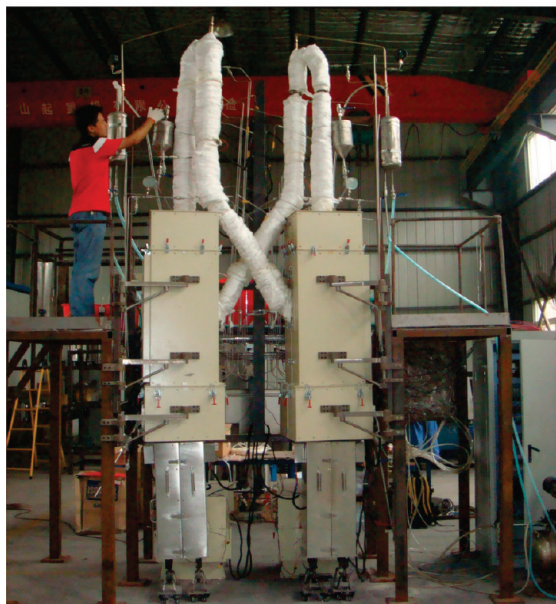


Figure 3. Schematic of the hot dual fluidized bed reactor facility.

to calcination temperatures well over 900 °C to achieve enough fast calcination of the sorbent. The alternative is to use steam in the regenerator to lower the partial pressure of CO₂, thus permitting lower regeneration temperatures. However, to simplify the experimental work, the air was used as the fluidizing gas for the regenerator, and since the reaction of CaO and CO₂ is exothermic, the reaction heat of calcination was driven by electrical furnaces in this work. All the air was from an air compressor, with CO₂ from high-purity cylinders. The gas flow rates were controlled by mass flow controllers. Before the gases entered plenums, they were preheated by preheaters. The flue gases exiting the cyclone passed through heat exchangers and then entered a deposition tank for fine particle removal before emission to the atmosphere.

3. Results and Discussion

3.1. Results for the Cold Model of the Dual Bubbling Fluidized Bed Reactor. This study focused on testing the technology used in the cold model of the dual bubbling fluidized bed reactor, for example the capacity for long-term stable operation and how to control the solids circulation rate between the carbonator and the regenerator. Air was used as the fluidizing gas and the gas for carrying the sorbent in the solid injection nozzle. The bed materials were glass microspheres with a bulk density of 1526 kg/m³, which was similar to the bulk density of CaCO₃ particles, and the superficial gas velocity at minimum fluidizing conditions, U_{mf} , 0.034 m/s. All the particles were between 0.2 and 0.4 mm in size with a $d(0.5) = 0.28$ mm. The solids circulation rate was measured by weighting the particles when the dual bubbling fluidized bed reactor were operating steadily with the solids flow from the downcomer collected to measure the solids circulation rate over a specified period of time.

The long-term stable operation and the continuous solids circulation between the two reactors was successfully achieved. Ryu et al.¹⁹ found that the structure of the injection nozzle and the operating conditions affected the circulation rate between the two reactors. Therefore, the operating conditions and solid

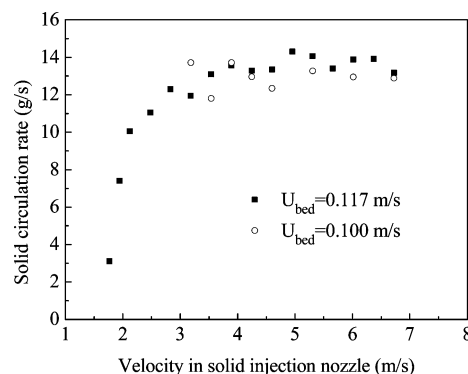
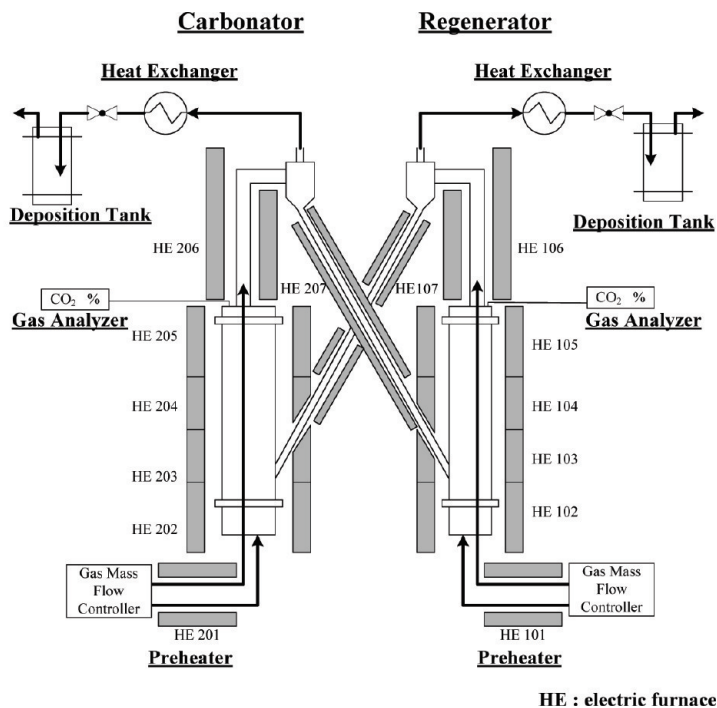


Figure 4. Solids circulation rates for various fluidizing gas velocities.

injection nozzle structures were changed to test the solids circulation rate between the two fluidized bed reactors.

Figure 4 shows the solids circulation rates for various fluidizing gas velocities in the cold bubbling fluidized bed reactor. The solids height above the distributor plate, H_{bed} , was 0.3 m. The solid injection nozzle internal diameter, $D_{injection}$, was 10 mm, and the hole diameter on the injection nozzle, D_{hole} , was 4 mm. The solids circulation rate first increased with increasing gas velocity in the solid injection nozzle and then became stable when the gas velocity was high enough. The solids circulation rates were basically the same when the fluidizing gas velocity, U_{bed} , was increased from 0.100 to 0.117 m/s, which means that fluidizing gas velocity had negligible effect on the solids circulation rate between the carbonator and the regenerator.

Figure 5 shows the solids circulation rates for various solid masses/bed heights in the fluidized bed reactors ($U_{bed} = 0.108$ m/s, $D_{injection} = 10$ mm, and $D_{hole} = 6$ mm). The solids circulation rate increased as the amount of sorbent in the reactor increased, and the solid flows between the two reactors referred to the cross-sectional area of the solid injection nozzle is 190–370 kg/m² s. Figure 6 shows the solids circulation rates for various solid injection nozzle sizes ($U_{bed} = 0.108$ m/s; $H_{bed} = 0.3$ m),

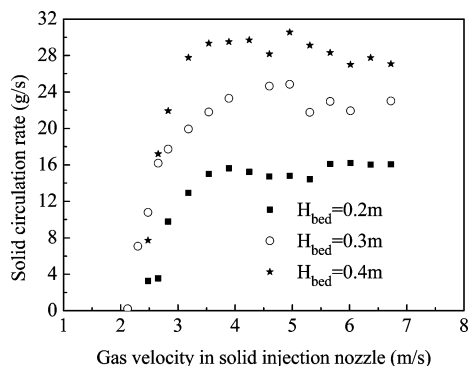


Figure 5. Solids circulation rates for various solid masses/bed heights in the fluidized bed reactor.

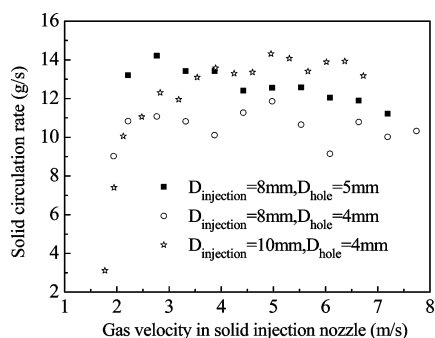


Figure 6. Solids circulation rates for various solid injection nozzle sizes.

Table 1. Composition of the Ca-Based Sorbent

sorbent	wt %	sorbent	wt %	sorbent	wt %
CaO	51.0	SiO ₂	7.9	Fe ₂ O ₃	1.1
MgO	37.9	Al ₂ O ₃	1.1	others	1.0

where the solids circulation rate increased as the injection nozzle diameters and the injection nozzle hole diameters increased. Therefore, the solids circulation rate between the carbonator and the regenerator can be controlled by changing the gas velocity in the solid injection nozzles, the amount of sorbent in the reactors, and the structure of the solid injection nozzles.

3.2. Results for the Hot Model of the Dual Bubbling Fluidized Bed Reactor. The design and operating experience from the experimental results of the cold model of the dual bubbling fluidized bed reactor was used to construct the hot dual bubbling fluidized bed system shown in Figure 3. The natural Ca-based sorbent, dolomite, with particle diameters of 0.2–1.0 mm with $d(0.5) = 0.5$ mm was used, and its composition after being completely calcined is shown in Table 1. The circulation rate between the carbonator and regenerator measured using the same method as that for the cold model of the dual fluidized bed reactor was 500–600 g/min at room temperature when the sorbent heights in the carbonator and the regenerator were both about 30 cm.

3.2.1. Operation of the Dual Bubbling Fluidized Bed Reactor at High Temperatures. Continuous and stable solids circulation between the two reactors is critical to the dual fluidized bed reactor operation. Thus, this investigation focused on testing continuous operation of the hot model of the dual bubbling fluidized bed reactor at high temperatures. Screened dolomite with particle sizes in the range of 0.2–1.0 mm with $d(0.5) = 0.5$ mm was used with this Ca-based sorbent already slightly calcined (15% decomposition conversion). About 4.5 kg of dolomite was added into the carbonator with 2.9 kg in the regenerator with both bed inventory heights being about

0.17 m. External electric heaters were used to provide the heat for the gas preheating, the carbonator, the regenerator, the risers, the cyclones, and the downcomers. When the carbonator and the regenerator inside temperatures approached about 500 °C, the flow controllers were turned on to provide gas flows to the two solid injection nozzles and the two reactors with the gas volumetric flow rates listed in Table 2. The carbonator was fluidized by a gaseous mixture of compressed air and CO₂. The regenerator and the two solid injection nozzles were fluidized by air. Since the gas volumetric flow rates increase with temperature, the gas volumetric flow rates were adjusted to maintain constant gas velocities in both reactors and in the solid injection nozzles during heating period. Several access ports were added to the dual bubbling fluidized bed reactor for measuring temperatures, pressure drops, and gas concentrations. Gas analysis samples were taken from the top of the carbonator and the regenerator for continuous monitoring of the CO₂ concentrations.

Figure 7 shows an operating record for about 6 h including the pressure drops in the two reactors, the temperatures in both the reactors, and the CO₂ volume fractions at the reactor outlets versus operating time. At the beginning (0–20 min), a gas mixture with 12.1% CO₂ was introduced into the carbonator with the CO₂ fraction at the carbonator outlet of about 9.1%, meaning only 27.3% CO₂ in the gas mixture was captured by the sorbent. During this initial period (0–20 min), the carbonator temperature was about 500 °C and the reaction rate between CaO and CO₂ was quite slow, resulting in the low CO₂ capture efficiency. As the temperature increases (second period, 20–75 min), the CO₂ capture efficiency increased but was still very low (only ~49.5%). When both reactor temperatures approached about 600 °C, a gas mixture with a new CO₂ fraction (air/CO₂, 85.5/14.5) was introduced into the carbonator. The CO₂ fraction at the carbonator outlet increased to above 10.5% and the CO₂ capture efficiency decreased to 32.3%, because a large amount of CaO in the sorbent was converted to CaCO₃. At the same time, the pressure drops in both reactors did not change much, meaning that the amount of sorbent in the two reactors remained relatively constant. In the third period (75–130 min), the regenerator temperature was increased to 850 °C while the carbonator temperature was maintained at 630 °C. The results in Figure 7 show that the CaCO₃ calcination reaction began at a temperature of ~710 °C and the CO₂ fraction at the regenerator outlet increased with increasing temperature. From 130 to 160 min, the CO₂ fraction at the carbonator outlet decreased continuously, indicating that the sorbent calcined in the regenerator was already transported into the carbonator. The solids transport system for the carbonation and calcination reaction cycles is critical in the dual fluidized bed reactor system.²⁰ These results indicated that the sorbent particles were successfully circulated between the carbonator and the regenerator at high temperatures. From 160 to 250 min, the temperatures in both the carbonator and the regenerator remained constant with the CO₂ fraction at the carbonator outlet being 1.2% and stable, giving a CO₂ capture efficiency of 89.2%. At about 250 min, 1 kg of fresh sorbent was added into the regenerator, resulting in a temperature drop in the regenerator, because the added sorbent was cold and more heat was required to heat the cold sorbent. At the same time, the pressure drop in the regenerator and the CO₂ fraction from the carbonator increased, as shown in Figure 7.

3.2.2. Effect of Carbonation Temperature on the CO₂ Capture. Figure 7 also illustrates the effect of carbonation temperature on the sorbent CO₂ capture for the regenerator

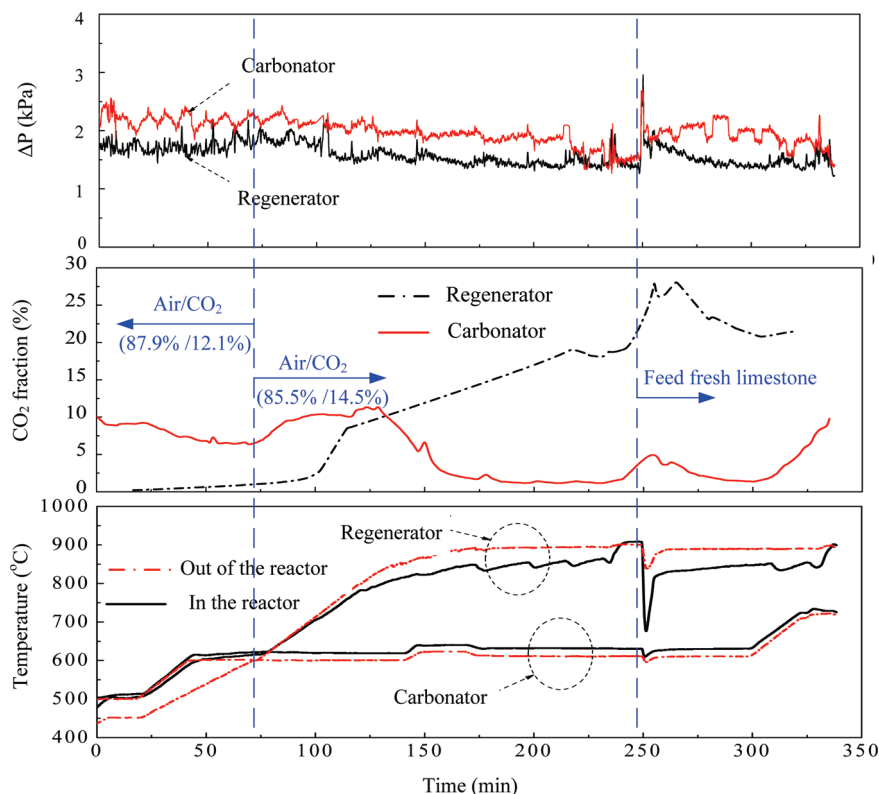


Figure 7. Pressure differences, outlet CO₂ volume fractions, and temperatures versus time during CO₂ capture.

Table 2. Experimental Conditions at the Beginning of the Experiment

	gas for solid injection	fluidizing gas
carbonator	11.0 L/min air (25 °C)	53.0 L/min air, 7.3 L/min CO ₂ (25 °C)
regenerator	9.8 L/min air (25 °C)	40.3 L/min air (25 °C)

Table 3. Experimental Conditions

	gas for solid injection	fluidizing gas
carbonator	9.8 L/min air (25 °C)	42 L/min air, 6.5 L/min CO ₂ (25 °C)
regenerator	6.8 L/min air (25 °C)	32 L/min air (25 °C)

temperature of about 850 °C (300–340 min). The carbonator temperature was first set at ~630 °C, with about 89.0% CO₂ capture efficiency at this temperature. The effect of carbonation temperature on the CO₂ capture was first investigated by increasing the carbonator temperature to about 680 °C from 630 °C after 300 min, resulting in little change in the CO₂ capture efficiency. When the temperature was then set higher than ~680 °C, the CO₂ capture efficiency decreased because of the thermodynamic limit of the carbonation reaction. Thus, the best CO₂ removal efficiencies are achieved in the temperature window of 600–680 °C.

3.2.3. Continuous CO₂ Capture from Flue Gases Using the Dual Bubbling Fluidized Bed Reactor with Calcium-Based Sorbent. The previous experiments investigated the operation of the dual bubbling fluidized bed reactor at high temperatures and the effect of carbonation temperature on the CO₂ capture. This section discusses continuous CO₂ capture from flue gases in the dual bubbling fluidized bed reactor with Ca-based sorbent. About 5.3 kg of fresh Ca-based sorbent was added to the carbonator with 3.4 kg added to the regenerator, with the system temperature then being increased. When the carbonator and regenerator temperatures were above 600 °C, air was introduced for the solid injection nozzles and for fluidizing the beds to make the sorbent circulate between the carbonator and the regenerator. Table 3 shows the gas volumetric

flow rates, but there is no CO₂ flow in the carbonator fluidizing gas in this period. Then, the regenerator temperature was increased to 810 °C while keeping the carbonator temperature unchanged. When the regenerator temperature was higher than 710 °C, CO₂ appeared at the regenerator outlet, indicating that the CaCO₃ began to be calcined. As the regenerator temperature further increased, the CO₂ fraction increased at the regenerator outlet and the maximum CO₂ fraction approached about 22.5% at a calcination temperature of 810 °C. After ~100 min, the CO₂ fraction at the regenerator outlet remained constant at about 22.0%. Then, a gas mixture with an air/CO₂ volume ratio of 86.6/13.4 was introduced into the carbonator. The evolution of the CO₂ volume fractions at the carbonator outlet and the regenerator outlet with time when the carbonator and regenerator temperatures were stable are shown in Figure 8. The CO₂ fraction at the carbonator outlet was not higher than 0.7% after introducing the gas mixture (air/CO₂, 86.6/13.4) into the carbonator, indicating that about 95.0% CO₂ in the gas mixture was absorbed by the sorbent. Figure 8 also shows that the CO₂ fraction at the regenerator outlet remained at about 20.5% for the carbonator temperature of ~640 °C and the regenerator temperature of ~810 °C. These results indicate that the CO₂ in the flue gases can be efficiently captured continuously using this type of dual fluidized bed reactor, and it was feasible to capture CO₂ from flue gases based on the carbonation/calcination

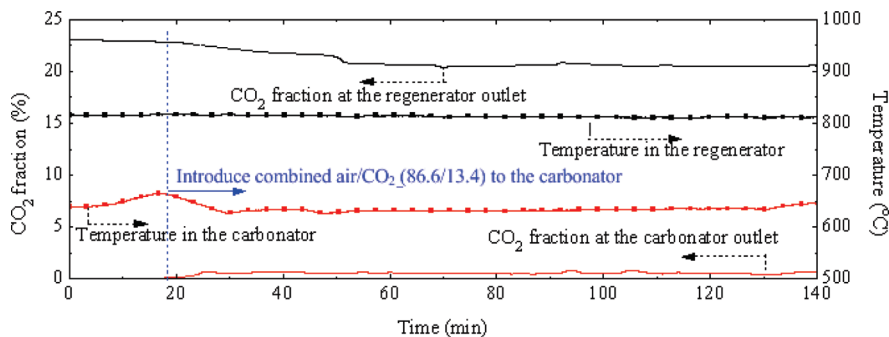


Figure 8. Outlet CO₂ volume fractions and temperatures during the continuous CO₂ capture test.

looping process. It should be noticed that the CO₂ capture efficiency in Figure 8 was higher than that in Figure 7, because there was more sorbent loaded in the carbonator (5.3 kg sorbent in the carbonator in Figure 8, with 4.5 kg of sorbent in the carbonator in Figure 7) which increased the contact time of the CO₂ in the flue gases with the CaO.

For practical application, a relatively pure stream of CO₂ should be achieved for regeneration, and then the temperature should be over 900 °C for the regeneration step to be fast. The alternative is to use steam to lower the partial pressure of CO₂, thus permitting lower regeneration temperatures. The use of a stream of high concentrated CO₂ or steam to regenerate the sorbent in the regenerator is our further investigation.

3.2.4. Sorbent Conversion. For the process shown in Figure 1, a solids material balance for the carbonator yields the following:¹⁵

$$(F_R + F_0)\Delta X = F_{CO_2}/(\text{kmol/s}) \quad (3)$$

F_{CO_2} in eq 3 represents the amount of absorbed CO₂:

$$F_{CO_2}/(\text{kmol/s}) = F'_{CO_2} - F''_{CO_2} \quad (4)$$

The conversion of CaO, X , is the actual mass of CO₂ absorbed divided by the mass of CO₂ that would be absorbed if the sorbent was fully carbonated:

$$X = \frac{M_{\text{actual}} - M_{f,\text{reg}}}{M_{f,\text{abs}} - M_{f,\text{reg}}} \quad (5)$$

where $M_{f,\text{abs}}$ is the molar mass of the fully carbonated sorbent, $M_{f,\text{reg}}$ is the molar mass of the fully calcined sorbent, and M_{actual} is the actual molar mass of the sorbent in its partially carbonated state. The solids in the two reactors were assumed to be well-stirred, so the conversion of the solids is, therefore, equal to the conversion of the solid flows leaving these reactors. Since the CO₂ is transferred from the carbonator to the regenerator, the average conversion, X_{abs} , is higher in the carbonator than in the regenerator, X_{reg} , with the difference in conversion, ΔX , being¹⁵

$$\Delta X = X_{\text{abs}} - X_{\text{reg}} \quad (6)$$

ΔX is an important parameter in the CO₂ capture process using carbonation and calcination reaction cycles. Injection of fresh sorbent is necessary to compensate for the decrease in sorbent activity over several cycles. For a given sorbent, F_0 and F_R vary as a function of ΔX and decrease with increasing ΔX . The value of ΔX requires knowledge of the conversion of CaO in both the carbonator and the regenerator. Solid samples from both the carbonator and the regenerator were analyzed to get this information. A Dupont 951 thermogravimetric analyzer (TA Instrument 1200) was used to study the conversion of CaO to CaCO₃ of the sorbent. The operating conditions for the

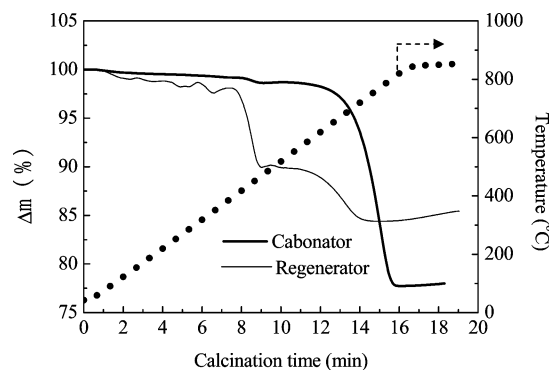


Figure 9. Weight loss of sorbent collected from the two reactors.

calcination tests were as follows: a gas flow rate of 100 mL/min with pure N₂ and temperatures increased to 850 °C with a 50 °C/min heating rate. Figure 9 shows the sorbent weight loss evolution with calcination time during the decomposition period. The sorbent from the regenerator easily reacted with water in the air to produce Ca(OH)₂, because the CaCO₃ in the surface layer of the sorbent was calcined to CaO with more CaO in the sorbent from the regenerator. Therefore, the sorbent collected from the regenerator lost weight when the calcination temperature was ~450 °C, which means that the Ca(OH)₂ was converted to CaO, as shown in Figure 9. Therefore, it can be calculated from Figure 9 that $X_{\text{abs}} = 70.4\%$, and there is still more than 13.9 wt % CaCO₃ in the sorbent leaving the regenerator which equals $X_{\text{reg}} = 16.2\%$, so the difference between the conversion, ΔX , is 54.2%. However, it should be noticed that the real X_{reg} should be larger than 16.5%, because the solid samples were collected near the regenerator wall as shown in Figure 2 when all the gas flows were stopped. At this time, the wall temperature must be higher than 850 °C, which would make the collected solid sample regenerate more.

At low values of X_{abs} , a large amount of sorbent is required to absorb a fixed amount of CO₂ from the flue gases; thus, large values of F_R are needed. At the same time, since the CaO conversion is low, the activity loss of the Ca-based sorbent has a negligible effect on the CO₂ capture process with only a small amount of fresh sorbent, F_0 , needed. As X_{abs} increases, a smaller amount of recycled sorbent, F_R , is required, but because of the higher CaO conversion, the effect of sorbent activity loss becomes more and more important; therefore, a larger amount of fresh sorbent is needed.¹⁵ At the same time, X_{reg} also has an important effect on F_0 and F_R . When X_{reg} is equal to zero, $\Delta X = X_{\text{abs}}$, in this case, F_0 and F_R approach their minimum values. It should be noted that in the system of the dual fluidized bed reactor, since the solid sorbent circulates continuously between the two reactors, the calcination cannot proceed completely and X_{reg} will not approach zero, as shown in Figure 9. Li et al.¹⁵



Figure 10. Sorbent collected from the regenerator and outside the regenerator cyclone.

assumed that the CaCO_3 decomposed completely in the regenerator; therefore, X_{reg} was equal to zero and $\Delta X = X_{\text{abs}}$, but this is not possible in the real process. At high values of X_{reg} indicating the sorbent average residence time in the regenerator is low, a larger amount of recycled sorbent, F_R , is required with more operation cost. As X_{reg} decreases, the sorbent is regenerated more completely with more residence time in the regenerator, so a small amount of sorbent transferred from the regenerator is required to absorb a fixed amount of CO_2 from the flue gases. However, at the same time, since the sorbent stays in the regenerator longer with X_{abs} lower, the sinter increases, resulting in the sorbent CO_2 capture capacity decrease. Therefore, the sorbent residence time in the regenerator should be further investigated.

Besides the important effect of X_{reg} on F_0 and F_R , X_{reg} may also affect the sorbent activity loss characteristics. Many previous studies^{5–10} have investigated the multicycle performance of carbonation/calcination reactions of Ca-based sorbent using TGA or single fixed/fluidized bed reactors. In TGA or single fixed/fluidized bed reactors, the reactions in both the carbonation and the calcination steps continued for a long time, so the sorbent was carbonated and regenerated completely. However, in the dual fluidized bed system, since the sorbent circulates between two the reactors and the sorbent residence time in the regenerator is limited, the sorbent is not regenerated completely, as shown in Figure 9. In this case, the sorbent activity loss characteristics may be different from previous results. The cyclic carbonation/calcination characteristics of sorbent undergoing incomplete regeneration should be studied more in the future.

3.2.5. Attrition. The sorbent fragmentation and attrition is an important issue for the carbonation and calcination reaction cycles. As shown in Figure 7, the pressure differences in the two reactors slowly decreased, indicating that the amount of sorbent in both reactors decreased because of attrition and fragmentation of the sorbent. Solid samples were collected outside the cyclone of the regenerator and from the regenerator, with Figure 10 showing their typical appearances. The sorbent collected outside the cyclone was very fine with particle sizes much smaller than the particles collected from the regenerator, indicating the sorbent suffered fragmentation and attrition. The amount of sorbent in the dual fluidized bed system was maintained constant by adding about 1 kg of fresh sorbent to each reactor after ~ 250 min continuous operation. With the introduction of fresh sorbent into the two reactors, the carbonator and the regenerator temperatures decreased abruptly, as shown

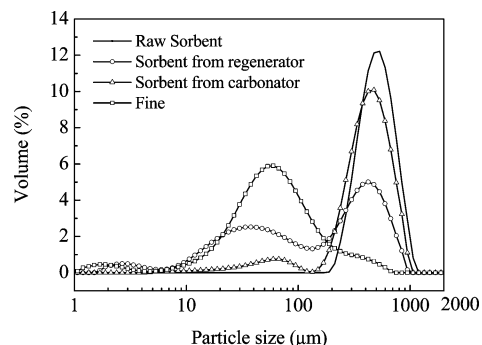


Figure 11. Particle size distribution of the raw CaCO_3 , the bed material in the regenerator and carbonator after 7 h operation, and the fines collected outside the regenerator cyclone.

in Figure 7, because the fresh sorbent was cool (room temperature).

Experimental work by Jia et al.²¹ in a small pilot-scale CFBC suggested that multiple carbonation/calcination looping resulted in severe fragmentation during the first one or two calcination periods. The particle size distributions (PSD) of the raw Ca-based sorbent, the bed material in the regenerator and carbonator after 7 h operation, and the fines collected outside the cyclone of the regenerator were tested using a laser particle size analyzer (Mastersizer 2000), with the results shown in Figure 11. The PSD of the raw Ca-based sorbent was between 0.2 and 1.0 mm with a $d(0.5) = 0.50$ mm. However, after 7 h of operation, significant attrition was observed and the $d(0.5)$ of the bed materials in the regenerator and in the carbonator were further reduced to 0.16 and 0.42 mm. The PSD of the bed material in the regenerator and carbonator indicated that there was a shift in the mass distribution from the larger size range to the 0.01–0.1 mm range. Comparison of the PSD of the bed material from the regenerator with that from the carbonator showed that the sorbent had undergone a great deal more attrition in the regenerator, because CaCO_3 is more difficult to attrite than CaO . The cyclone filtered the particles mainly above 0.1 mm.

The mechanical stability of sorbent may be enhanced by partial sulfation,²¹ albeit with the risk of a reduction of the reaction reversibility. Other solutions may also be employed, such as pelletization, synthesized sorbents with inert support, or heat treatment to improve the mechanical stability of the particles. The cost of the CO_2 capture will be increased by these treatments, so a detailed economic analysis will be required to evaluate such approaches.

4. Conclusions

The dual bubbling fluidized bed reactor was selected in this work to be the laboratory-scale dual fluidized bed system to capture CO_2 from flue gases based on analyzing different forms of dual fluidized bed reactors. First, a cold model of the dual bubbling fluidized bed reactor was built to study the long-term stable operation and the continuous solid circulation between two reactors. The solids circulation rate between the carbonator and the regenerator could be controlled by changing the gas velocity in the solid injection nozzles, the amount of sorbent in the reactors, and the structure of the solid injection nozzles. A hot dual bubbling fluidized bed system was then constructed. The carbonation/calcination looping process has been demonstrated using the dual bubbling fluidized bed reactor. The experimental results indicate that the sorbent particles circulated successfully between the carbonator and the regenerator at high temperatures with a high CO_2 capture efficiency of $\sim 95.0\%$.

Increasing carbonation temperatures induced the CO₂ capture efficiency, and the best CO₂ removals efficiency was achieved in the temperature window of 600–680 °C. In the carbonator, about 70.4% CaO in the sorbent was converted to CaCO₃. In the regenerator, the conversion of CaO to CaCO₃ was more than 16.2%. The sorbent fragmentation and attrition are important issues for the carbonation and calcination reaction cycles. The issues of sorbent loss caused by attritions, the treatment to improve the mechanical stability of the particles, and the economic analysis to evaluate such approaches need further investigation.

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Literature Cited

- (1) Houghton, J. T. *Climate Change 1995, The Science of Climate Change, Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: Cambridge, U.K., 1996.
- (2) Pachauri, R. K.; Reisinger, A. *Climate Change 2007 Synthesis Report*; IPCC: Geneva, Switzerland, 2007.
- (3) Abanades, J. C.; Anthony, E. J.; Wang, J. S.; Oakey, J. E. Fluidized Bed Combustion Systems Integrating CO₂ Capture with CaO. *Environ. Sci. Technol.* **2005**, *39*, 2861.
- (4) Shimizu, T.; Hiramata, T.; Hosoda, H.; Kitano, K.; Inagaki, M.; Teijima, K. A Twin Fluid Bed Reactor for Removal of CO₂ from Combustion Processes. *Trans. Inst. Chem. Eng.* **1999**, *77*, 62.
- (5) Sun, P.; Lim, C. J.; Grace, J. R. Cyclic CO₂ Capture by Limestone-Derived Sorbent During Prolonged Calcination/Carbonation Cycling. *AIChE J.* **2008**, *54*, 1668.
- (6) Fennell, P. S.; Pacciani, R. P.; Dennis, J. S.; Davidson, J. F.; Hayhurst, A. N. The Effects of Repeated Cycles of Calcination and Carbonation on a Variety of Different Limestones, as Measured in a Hot Fluidized Bed of Sand. *Energy Fuels* **2007**, *21*, 2072.
- (7) Abanades, J. C.; Alvarez, D. Conversion Limits in the Reaction of CO₂ with Lime. *Energy Fuels* **2003**, *17*, 308.
- (8) Ryu, H. J.; Grace, J. R.; Lim, C. J. Simultaneous CO₂/SO₂ Capture Characteristics of Three Limestones in a Fluidized-Bed Reactor. *Energy Fuels* **2006**, *20*, 1621.
- (9) Li, Z. S.; Cai, N. S.; Huang, Y. Y.; Han, H. J. Synthesis, Experimental Studies, and Analysis of a New Calcium-Based Carbon Dioxide Absorbent. *Energy Fuels* **2005**, *19*, 1447.
- (10) Li, Z. S.; Cai, N. S.; Huang, Y. Y. Effect of Preparation Temperature on Cyclic CO₂ Capture and Multiple Carbonation–Calcination Cycles for a New Ca-Based CO₂ Sorbent. *Ind. Eng. Chem. Res.* **2006**, *45*, 1911.
- (11) Gupta, H.; Fan, L. S. Carbonation–Calcination Cycle Using High Reactivity Calcium Oxide for Carbon Dioxide Separation from Flue Gas. *Ind. Eng. Chem. Res.* **2002**, *41*, 4035.
- (12) Abanades, J. C.; Anthony, E. J.; Lu, D. Y.; Salvador, C.; Alvarez, D. Capture of CO₂ from Combustion Gases in a Fluidized Bed of CaO. *AIChE J.* **2004**, *50*, 1614.
- (13) Fang, F.; Li, Z. S.; Cai, N. S. Experiment and Modeling of CO₂ Capture from Flue Gases at High Temperature in a Fluidized Bed Reactor with Ca-Based Sorbents. *Energy Fuels* **2009**, *23*, 207.
- (14) Hughes, R. W.; Lu, D. Y.; Anthony, E. J.; Macchi, A. Design, Process Simulation and Construction of an Atmospheric Dual Fluidized Bed Combustion System for in Situ CO₂ Capture Using High-Temperature Sorbents. *Fuel Process. Technol.* **2005**, *82*, 1523.
- (15) Li, Z. S.; Cai, N. S.; Eric, C. Process Analysis of CO₂ Capture from Flue Gas Using Carbonation/Calcination Cycles. *AIChE J.* **2008**, *54*, 1912.
- (16) Lu, D. Y.; Hughes, R. W.; Anthony, E. J. Ca-Based Sorbent Looping Combustion for CO₂ Capture in Pilot-Scale Dual Fluidized Beds. *Fuel Process. Technol.* **2008**, *89*, 1386.
- (17) Abanades, J. C.; Alonso, M.; Rodriguez, N.; González, B.; Grasa, G.; Murillo, R. Capture CO₂ from Combustion Flue Gases with a Carbonation Calcination Loop. Experimental Results and Process Development. *Energy Procedia* **2009**, *1*, 1147.
- (18) Charitos, A.; Hawthorne, C.; Bidwe, A. R.; Holz, H.; Pfeifer, T.; Schulze, A.; Schlegel, D.; Schuster, A.; Scheffknecht, G. Parametric Study on the CO₂ Capture Efficiency of the Carbonate Looping Process in a 10 kW Dual Fluidized Bed. *20th Int. Conf. Fluidized Bed Combust. (Xi'an, China)* **2009**, 583.
- (19) Ryu, H. J.; Park, Y. C.; Jo, S. H.; Park, M. H. Development of Novel Two-Interconnected Fluidized Bed System. *Korean J. Chem. Eng.* **2008**, *25*, 1178.
- (20) Anthony, E. J. Solid Looping Cycles: A New Technology for Coal Conversion. *Ind. Eng. Chem. Res.* **2008**, *47*, 1747.
- (21) Jia, L.; Hughes, R.; Lu, D.; Anthony, E. J.; Lau, I. Attrition of Calcining Limestones in Circulating Fluidized-Bed Systems. *Ind. Eng. Chem. Res.* **2007**, *46*, 5199.

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