Chemical Engineering Journal 146 (2009) 244–248

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

CO_2 capture from atmospheric air via consecutive CaO-carbonation and $CaCO_3$-calcination cycles in a fluidized-bed solar reactor

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ARTICLE INFO

Article history:
Received 13 March 2008
Received in revised form 3 June 2008
Accepted 7 June 2008

Keywords:
CO_2
Capture
Air
Solar
Energy
Fluidized-bed
Carbonation
Calcination
CaO
$CaCO_3$
$Ca(OH)_2$
Thermochemical cycle

ABSTRACT

A thermochemical cyclic process and associated reactor is presented for the continuous removal of CO_2 from ambient air via consecutive CaO-carbonation and $CaCO_3$-calcination steps using concentrated solar energy as the source of high-temperature process heat. A fluidized-bed solar reactor is applied to accomplish the carbonation at 365–400 °C and the calcination at 800–875 °C, with reacting particles directly exposed to high-flux solar irradiation. Water vapor was introduced during the carbonation step to enhance its kinetics. Five consecutive cycles were performed, yielding complete removal of CO_2 from a continuous airflow containing 500 ppm of CO_2 within a residence time of 1.3 s during each carbonation step, and subsequent complete release of CO_2 and regeneration of the CaO reacting particles during the calcination step. The reactor design, set-up, and experimentation using a high-flux solar simulator are described.

1. Introduction

Most CO_2 capture technologies deal with the decarbonization of fossil fuels prior to combustion or with the separation of CO_2 from combustion flue gases [1–3]. CO_2 capture from ambient air could become necessary for achieving stabilization of the global CO_2 concentration in the atmosphere in view of increasing emissions derived from transportation and other distributed sources [4,5]. The capture of CO_2 from air-vis-à-vis capture from a flue gas stream-is thermodynamically unfavorable because of the higher Gibbs free energy change needed to separate a much more diluted gas. However, in this case, the capture plant could be strategically located next to a source of renewable energy and to the final storage site, such as inhabited deserts with high solar irradiation and vast geological storage reservoirs. There are logistical and environmental advantages for capturing CO_2 from the air, taking place far away from populated cities and without generating additional CO_2 for its capture and transportation. Several processes have been proposed previously for accomplishing this separation [6–11]. Of special interest is the carbonation-calcination thermochemical cycle based on CaO, represented by the net reversible reaction:

$$CaO(s) + CO_2(g) = CaCO_3(s) \qquad (1)$$

This reaction has been extensively studied for separating CO_2 from combustion flue gases [12–15], and is presently being considered for separating CO_2 from air using solar energy [16]. Steam is usually added to the carbonation step to enhance its reaction rate by the intermediate formation of $Ca(OH)_2$ [17,18]. The recyclability of the reactants and products is crucial. The carrying capacity of CaO has been reported to drop to 60% after five cycles [19,20]. Partial reactivation of the sorbent has been accomplished with H_2O and pure CO_2, or by doping with Na_2CO_3 and NaCl [17,18,21,22].

A thermodynamic analysis of the CaO–$Ca(OH)_2$–$CaCO_3$ based cycle for capturing CO_2 from air was carried out to calculate the equilibrium compositions and reaction enthalpies as a function of temperature for the pertinent reactions, and theoretical net energy requirements and maximum energy conversion efficiencies when using concentrated solar energy to supply for process heat [16]. The reaction kinetics and associated reaction rates were

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doi:10.1016/j.cej.2008.06.005

determined by thermogravimetry [23]. This paper describes the design of a solar reactor for effecting both steps of the cycle (carbonation and calcination) and presents the experimental set-up and results of the reactor system applied to five consecutive cycles.

2. Solar reactor and experimental set-up

The solar reactor concept is illustrated in Fig. 1. It features a fluidized bed that serves the functions of both the carbonator and calcinator, eliminating the need for transportation of solids. During the carbonation step, ambient air with added steam is the fluidizing gas, particles of CaO are transformed to $CaCO_3$, and CO_2-depleted air leaves the reaction site. During the calcination step, H_2O or CO_2 is (optionally) the fluidizing gas, particles of $CaCO_3$ are transformed to CaO, and pure CO_2 (after H_2O condensation if necessary) leaves the reaction site. The operation of two equivalent reactors of this type side by side further allows the conduction of both carbonation and calcination steps simultaneously by switching the corresponding gaseous reactants between the reactors and adjusting the corresponding temperatures as required by the carbonation and calcination steps.

A laboratory-scale solar reactor prototype was fabricated. It consists of a quartz tube, 25 mm-outer diameter, 22 mm-inner diameter, and 25 cm-height, containing a fluidized bed of reacting particles (CaO or $CaCO_3$). It is positioned at the focal plane of the solar concentrator and subjected to lateral and top irradiation. With this arrangement, the particles are directly exposed to concentrated solar radiation, providing efficient heat transfer to the reaction site. Such a reactor concept is characterized by its uniform irradiation, temperature and gas–solid contacting surface scheme over the reaction domain, to provide efficient heat and mass transport, and also to serve as a suitable tool for measuring interfacial kinetics [24].

The schematic diagram of the experimental set-up is depicted in Fig. 2. Experimentation was carried out at the ETH's High-Flux Solar Simulator. This research facility provides a rapid external source of intense thermal radiation that approaches the heat transfer characteristics of highly concentrating solar systems. The light source is a high-pressure Ar arc close-coupled to a precision elliptical trough reflector, with one of the linear foci coinciding with the arc and the second with the solar reactor. With this arrangement, up to 75 kW of continuous radiative power at peak fluxes exceeding 4250 suns[1] and confined within a 45° rim angle are attained at the focal plane, mostly at visible wavelengths with additional power in the near infrared and ultraviolet regions of the spectrum. Power, power fluxes, and temperatures can be adjusted to meet the specific requirements by simply varying the electrical input power to the arc electrodes.

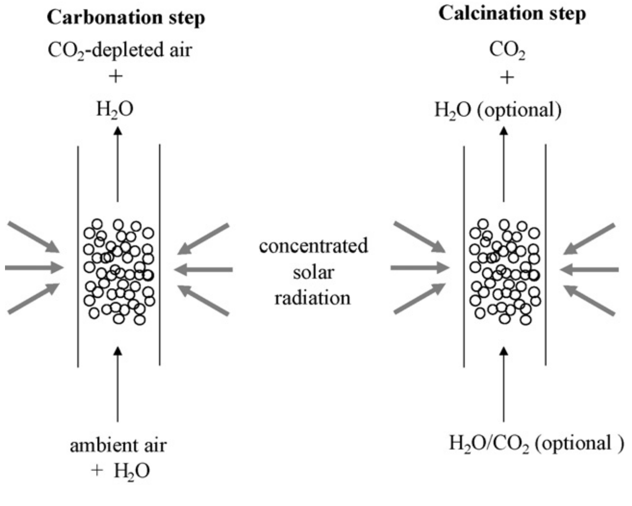

Fig. 1. Schematic of a solar fluidized-bed reactor for the consecutive conduction of the carbonation and calcination steps using solar energy.

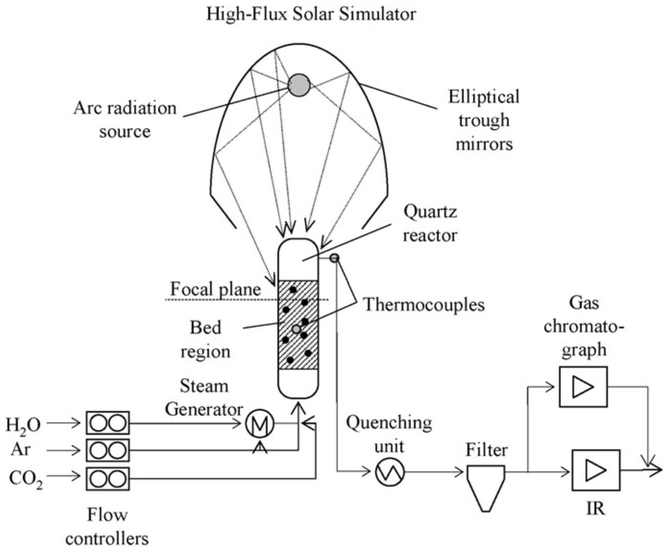

Fig. 2. Experimental set-up at ETH's High-Flux Solar Simulator.

The nominal fluidized-bed and off-gas temperatures are measured by a thermocouple Type S and K, respectively. Quartz wool is introduced into the outlet port to trap elutriated particles. The incoming Ar, CO_2, and H_2O flows are controlled using electronic flowmeters (Bronkhorst HI-TEC). The concentration of CO_2 in the off-gas was continuously analyzed by an IR analyzer (Siemens Ultramat 23) equipped with two detectors for the ranges of 0–1000 ppm and 0–5%, at 1 Hz sampling rate and 0.2% of range detection limit. In addition, the composition of the off-gas was verified every 90 s by gas chromatography (2-channel Varian Micro GC, equipped with a Molsieve-5A and a Poraplot-U columns), at $0.33\ \mathrm{min}^{-1}$ sampling rate and 100 ppm detection limit. Solid samples were characterized by means of their particle size distribution determined by laser scattering (HORIBA LA-950 analyzer), BET specific surface area determined by N_2 adsorption at 77 K (Micromeritics TriStar 3000), and composition determined by X-ray powder diffraction (XRD, Philipps XPert-MPD powder diffractometer FeK_{α}, $\lambda = 1.93740$ Å, $2\theta = 20–80°$, 0.05° step).

3. Experimental procedure

3.1. Sorbent preparation (Cycle "0")

A typical sorbent preparation consisted of using $Ca(OH)_2$ (Fluka #21181) of 96% purity and specific surface area of 17.43 m^2/g. SiO_2 particles (MERK #1.07711.1000) of specific surface area of 1.73 m^2/g were added to help fluidization. The minimum fluidization [25] and terminal velocities [26] for the coarse SiO_2 particles were 0.0345 m/s and 1.56 m/s, respectively, and the terminal velocity of

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[1] 1 sun = 1 kW/m^2.

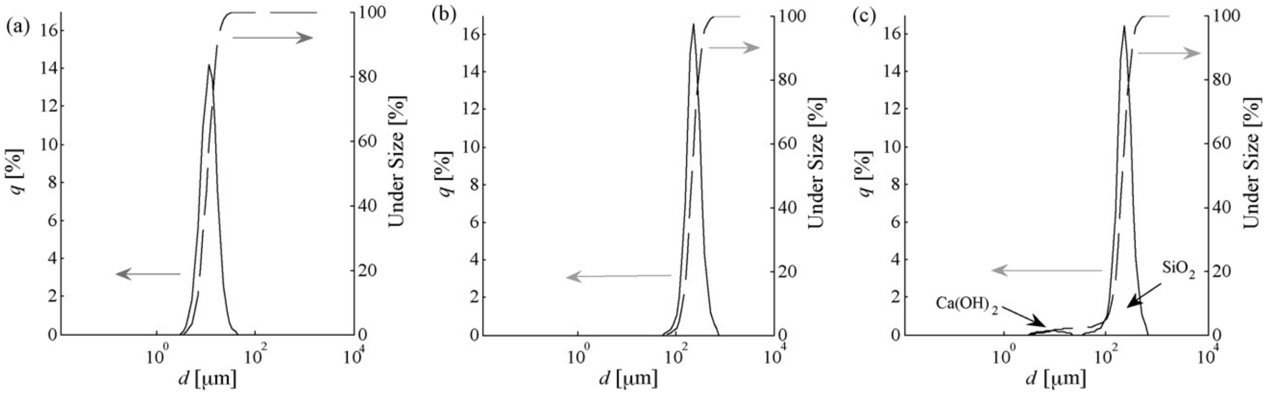

Fig. 3. Particle size distributions of (a) $Ca(OH)_2$, (b) SiO_2, and (c) binary mixture $Ca(OH)_2/SiO_2$ with 1:9 mass ratio.

the fine $Ca(OH)_2$ particles was 6.34×10^{-3} m/s, assuming a sphericity of 0.95 for the coarse particles and 0.70 for the fines. An initial binary mixture $Ca(OH)_2/SiO_2$ with 1:9 mass ratio was prepared, classified as Geldart B-C mixture [25,27]. Particle size distributions of $Ca(OH)_2$, SiO_2, and the binary mixture, are plotted in Fig. 3a, b, and c, respectively. The mean particle sizes of $Ca(OH)_2$ and SiO_2 are 11 μm and 229 μm, respectively. This mixture is subjected to a carbonation–calcination step, yielding 3%wt CaO in SiO_2, with a mean CaO particle size of 9 μm, as determined by the bimodal distribution function shown in Fig. 4. This CaO/SiO_2 mixture is used for the five consecutive carbonation–calcination steps. The tubular reactor is initially charged with 7 g of the CaO/SiO_2 mixture and heated to 375 °C under Ar flow. No particles were added during the cyclic runs. The prepared CaO/SiO_2 mixture preformed better than the initial $Ca(OH)_2/SiO_2$ mixture, as it will be shown in the analysis that follows. The reaction extent of the carbonation is defined as

$$X = \frac{n_{CaCO_3}(t)}{n_{CaCO_3,\max}} \tag{2}$$

where $n_{CaCO_3}(t)$ and $n_{CaCO_3,\max}$ are the $CaCO_3$ molar contents of the sample at time t and after the reaction goes to completion.

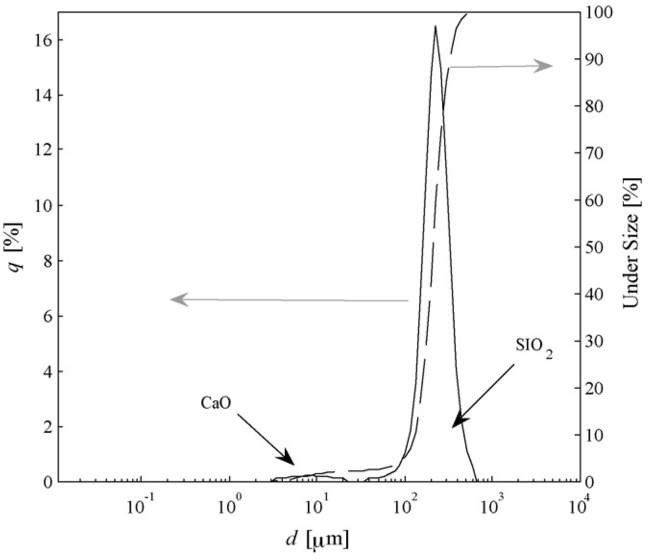

Fig. 4. Particle size distributions of binary mixture CaO/SiO_2 used in the cyclic process.

3.2. Carbonation step

The fluidizing gas was switched to synthetic air containing 500 ppm of CO_2[2] and 17% of water vapor at a mass flow rate of 2 l_n/min.[3] The reactor was maintained in the temperature range 365–400 °C for 600 s. At the end of this step, the fluidized-bed particles were not removed from the reactor and served as the solid reactants for the subsequent calcination step.

3.3. Calcination step

The fluidizing gas was switched to Ar at a mass flow rate of 1.75 l_n/min.[4] The bed was heated to above 800 °C where the calcination reaction is kinetically favored [28], and maintained below 875° to avoid sintering. The calcination completion was determined when CO_2 concentration in the off gas flow went to zero. At the end of this step, the fluidized-bed particles were not removed from the reactor and served as the solid reactants for the subsequent carbonation step.

Note that to achieve calcination in a pure CO_2 stream at a reasonable rate the reactor temperature should be increased to above 900 °C, but sintering may deteriorate the sorbent reactivity [29,30]. Nevertheless, limestone could be reactivated in humid, ambient air [31].

4. Experimental results

Prior to the cycle study and for the purpose of determining the CO_2-uptake capacity of the fluidized bed as a function of time, a long-term isothermal carbonation run at 364 °C was performed using $Ca(OH)_2/SiO_2$ and CaO/SiO_2 (after cycle "0") mixtures, fluidized in synthetic air containing 500 ppm CO_2 and 17% H_2O. The reaction extent and the CO_2 concentration in the off-gas are plotted in Fig. 5 as a function of the reaction time. During the first 1800 s of the experiment, all CO_2 was practically removed from air since the off-gas contained less than 1 ppm CO_2. The reaction proceeded through the formation of an H_2O/OH^- interface controlled by intrinsic chemical reaction taking place over the surface that is not covered by $CaCO_3$ [24,32–33]. Afterwards, the build-up of a thin $CaCO_3$ layer induced a progressive change in the reac-

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[2] Assumption: predicted 500 ppm CO_2 concentration in the air by the time the proposed technology would be commercially available for application.

[3] l_n means liters at normal conditions; mass flow rates are calculated at 273 K and 1 bar.

[4] CO_2 or H_2O may be used as fluidizing gases for avoiding the energy penalty (and costs) associated with the recycling of an inert gas.

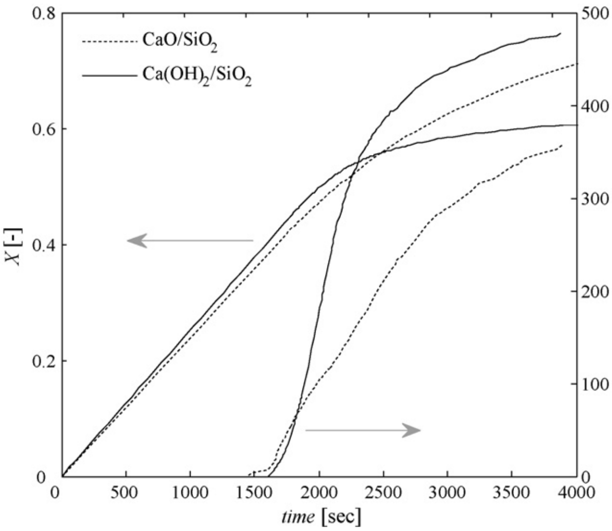

Fig. 5. Variation of the reaction extent of the carbonation and CO_2 concentration in the off-gas as a function of time using $Ca(OH)_2/SiO_2$ and CaO/SiO_2 mixtures fluidized in synthetic air containing 500 ppm CO_2 and 17% H_2O.

tion mechanism towards a CO_2 diffusion-controlled regime [23,33], resulting in a decline of the CO_2 uptake capacity of the fluidized bed and a subsequent increase in the CO_2 concentration of the off-gas, approaching 500 ppm. After 4000 s, the reaction extent reached 61% for the $Ca(OH)_2/SiO_2$ mixture and 71% for the CaO/SiO_2 mixture.

Fig. 6 shows the experimental results for five consecutive carbonation–calcination cycles. Plotted is the measured concentration of CO_2 in the off-gas as a function of the reaction time for five consecutive carbonation–calcination cycles. During all carbonation steps, CO_2 was practically completely removed from air since the off-gas contained less than 1 ppm CO_2. During all calcination steps, CO_2 was released until reaction reached completion after about 500 s. XRD of the products after five cycles revealed pure CaO. The total amount of CO_2 removed from ambient air, calculated by integration over the five carbonation steps, was 21.05×10^{-4} mol. The total amount of CO_2 released, calculated by integration over the five calcinations steps, was 21.08×10^{-4} mol. Thus, the mass balance on CO_2 was closed to 99.9%. The calculated residence time of the reacting airflow through the fluidized bed, was 1.3 s.

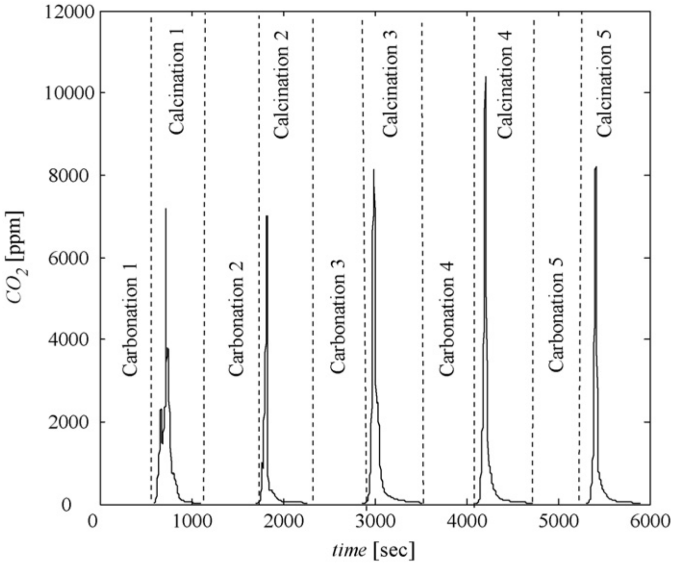

Fig. 6. Measured CO_2 concentration in the off-gas for five consecutive carbonation–calcination cycles. Indicated is the duration of each carbonation/calcination step.

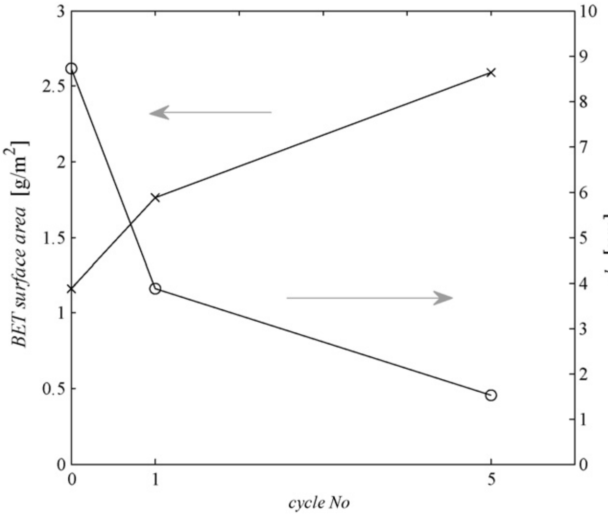

Fig. 7. Mean particle size and BET specific surface area of CaO particles after cycles 0, 1, and 5.

No sorbent deactivation was observed after five cycles. This is partially attributed to the addition of water [15,17,18,34]. During hydration, H_2O penetrates through the $CaCO_3$ layer and reacts with the CaO core to form $Ca(OH)_2$. The larger molar volume of $Ca(OH)_2$ induces cracks in the carbonate shell. Further, as the reaction progresses, $Ca(OH)_2$ dehydrates, exposing fresh and accessible unreacted lime for further carbonation, as it was previously observed in the sulfation process [34,35]. The SiO_2 grains, added to help fluidization, may also help reactivation. As these collide with the reacting particles, breakage, attrition, and/or rounding off of the CaO particles occur [35,36]. This is corroborated by a remarkable decrease in the mean particle size (by a factor of 5 after five cycles) and increase in the BET specific surface area (by a factor of 2.3 after five cycles) of CaO particles with the number of cycles, as shown in Fig. 7. Relatively low calcination temperatures and rates further improve the reversibility of the carbonation/calcination reactions, and consequently, help maintain the sorbent reactivity from cycle to cycle [37–39].

The fluidized-bed system proved to be a suitable reactor concept for effecting both steps of the thermochemical cycle. Switching between carbonation and calcination modes was trouble-free and uniform temperatures throughout the bed were rapidly achieved. Feeding or removal of solids was unnecessary. The direct solar irradiation of the reacting particles provided a very efficient mean of heat transfer directly to the reaction site, where the energy was needed, thereby eliminating the need for indirect transfer of thermal energy by conduction/convection through the reactor walls or via heat exchangers. Although not yet proven, the absorption of solar radiation may stimulate a photochemical enhancement of the reaction kinetics.

For a scaled-up reactor capturing CO_2 from air at a rate of 1 mol/s CO_2, which corresponds to an air mass flow rate of 58 kg/s for a CO_2 concentration of 500 ppm, the inventory of CaO in the absorber would be 286 kg and the total solar thermal energy requirement would be 2.5 MW [16].

5. Summary and conclusions

We designed, fabricated, and tested a laboratory-scale solar reactor system for performing both steps of a carbonation–

calcination thermochemical cycle for the removal of CO_2 from ambient air using solar energy. The solar reactor consisted of a fluidized bed of reacting particles that are directly exposed to concentrated solar radiation, providing effective heat and mass transfer. Five consecutive cycles were experimentally demonstrated in a high-flux solar simulator. The carbonation step was carried out at 365–400 °C with a continuous flow of synthetic air containing 500 ppm of CO_2 and 17% H_2O. The calcination step was carried out at 800–875 °C with a continuous flow of Ar. CO_2 or H_2O may be used as fluidizing gases for avoiding the energy penalty (and costs) associated with the recycling of an inert gas. Complete removal of CO_2 from the ambient airflow was observed within 1.3 s residence time in each carbonation step of 600 s, and complete release of CO_2 and regeneration of the CaO particles was observed in each calcination step of about 500 s. The mass balance on CO_2 after five consecutive cycles was closed to 99.9%. CaO particles decreased in size and increased in BET specific surface with the number of cycles, as a result of attrition with SiO_2 grains added for helping fluidization. The addition of water vapor and the direct solar irradiation were demonstrated to be beneficial for augmenting the reaction and heat transfer rates.

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