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CO_2 capture at ambient temperature in a fixed bed with CaO-based sorbents

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HIGHLIGHTS

- CaO-based pellets can be used for CO_2 capture at ambient temperature.
- Pre-hydration of pellets improves CO_2 capture capacity significantly.
- CO_2 capture capacity of 0.5 g/g is obtained in a CaO-based fixed bed.
- The capture capacity is sensitive to moisture and CO_2 inlet concentration.

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ABSTRACT

This work investigates post-combustion CO_2 capture at ambient temperature in a fixed bed by means of CaO-based sorbents. Two sorbents were used: limestone and pellets prepared from powdered limestone using calcium aluminate cement as a binder. The results showed that pre-hydration had a significant effect on CO_2 capture performance of the two sorbents. For instance, after 8 h pre-hydration, the breakthrough time increased from 21 min to 660 min for lime, and from 19 min to 750 min for pellets. The performance of pellets was more sensitive to hydration conditions than for the lime. At breakthrough, full carbonation conversion over half of the reactor was achieved in a pre-hydrated bed of pellets exposed to a feed with 0.5% CO_2, resulting in an average specific capture of 0.51 g CO_2/g bed material. This was considered a sufficient capture performance, with a distinct mass transfer zone (MTZ) located in the upper half of the reactor. However, increasing CO_2 inlet concentration to 2% shortened the breakthrough time and shifted the MTZ toward the entrance zone of the reactor. It was concluded that capturing CO_2 from low-CO_2 flue gases at ambient temperature using a fixed bed of pre-hydrated CaO-based pellets is a promising approach that has the potential to achieve reasonable capture performance at relatively low cost. The proposed process can be used for CO_2 capture from CO_2-depleted flue gases (residual CO_2) from processes such as amine scrubbing and calcium looping. And it would allow for the possibility that capture could be increased to any given level required by new legislation for plant with carbon capture.

1. Introduction

CO_2 is the primary greenhouse gas emitted by human activities, such as the combustion of fossil fuels for energy and transportation [1]. Coal-fired power plants are one of the major sources for CO_2 emissions and, therefore, mitigation of CO_2 emissions from these plants is urgently required. Carbon capture and storage (CCS) has been receiving increased attention because it is considered as a feasible method for short-term mitigation of post-combustion CO_2 from power plants and other stationary sources [2–4]. A typical CO_2 concentration in flue gas of such coal-fired plants is 12–15%, depending on coal type and the technology used in the combustion system [5]. Generally, the goal of most capture processes is to achieve >90% CO_2 capture from these flue gases. Achieving this capture capacity will still leave a CO_2-depleted flue gas containing low amounts of CO_2 (residual CO_2), i.e. <2% CO_2 that will be released to the atmosphere. Although this residual CO_2 still contributes to the increasing anthropogenic CO_2 emission, processes for its capture have not been studied in order to further reduce the amount of CO_2 released to atmosphere.

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Currently, the commercially applied method for post-combustion CO_2 capture is based on amine-scrubbing processes, which operate at low temperatures, e.g. <50 °C on wide ranges of gas sources with CO_2 concentration of up to 15% [6,7]. Although this technology has been in use for many years, there are a number of issues that limit its application, such as the degradation of the expensive amine solutions due to impurities in flue gas, corrosion in the system, and high energy demand for the amine regeneration [8,9]. Another route for capturing CO_2 is swing adsorption processes (by pressure (PSA), temperature (TSA), or vacuum (VSA)) [10–13]. Typically, such systems use relatively expensive molecular sieve zeolites, activated carbons, and amine-based sorbents. The application of these technologies for capturing CO_2 from low-CO_2 sources raises questions about the economic feasibility of such approaches [14]. Capturing CO_2 from air (or the so-called direct air capture (DAC)) is perhaps the extreme example of CO_2 capture from low-CO_2 sources [15]. Wet procedures for DAC have been proposed, where CO_2 is captured at ambient temperature using sodium-based and potassium-based solutions [16].

Limestone, as a CaO-based sorbent, is an abundant material and can be obtained in large quantities at low cost. Theoretically, 1 g of CaO can capture 786 mg of CO_2, which represents a promising large capacity (e.g. activated carbon typically captures 80 mg of CO_2 per g of adsorbent [17]) via the following reaction:

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} \tag{1}$$

After hydration (Eq. (2), the $Ca(OH)_2$ product upon calcination has a higher pore volume and pore surface area than the parent material and can be used for CO_2 capture [18].

$$CaO_{(s)} + H_2O_{(g)} \leftrightarrow Ca(OH)_{2(s)} \tag{2}$$

Although carbonation and the effect of moisture in concrete constructions have been investigated in detail [19–22], to date we have found no recent literature on using CaO-based sorbents in fixed beds as a means of capturing residual CO_2 from flue gases at ambient or near ambient temperature. The implicit assumption was that this reaction would be too slow at such temperatures for practical systems. In this work, a fixed-bed system with CaO-based sorbents was used for capturing CO_2 from low-CO_2 gas streams (<2% CO_2). CO_2 inlet concentration was varied to investigate its effect on the CO_2 capture performance of the fixed bed. The concentration–time relationship or breakthrough curve of CO_2 in the effluent stream was obtained, and selected systems were modeled to obtain kinetic parameters. The mass transfer zone (MTZ) was also analyzed to obtain a better understanding of the capture system.

2. Experimental

2.1. Sorbents

Two sorbents were used in this work: Cadomin limestone and pellets prepared from calcined Cadomin powder using 10% calcium aluminate cement as a binder. The pelletization was carried out in a mechanical pelletizer (Glatt GmbH) in batch mode, where lime and cement were mixed vigorously for a few seconds followed by addition of water under continuous mixing. The mixing was facilitated by two blades: an agitator at the bottom of the vessel and a chopper on the side. The rotation speed of the blades was controllable, thus the mixing speed was adjusted to obtain the desired product consistency. Both natural and pelletized sorbents were sieved to a particle size of 300–850 μm. This particle size was chosen because in preliminary experiments with smaller-sized particles there were problems related to: (1) expansion of sorbent particles due to the formation of $Ca(OH)_2$ and $CaCO_3$ which have larger molar volumes than CaO (respectively 33.5 and 36.9 versus 16.7 cm^3/mol), and (2) agglomeration inside the column causing the operating pressure for the fixed bed to increase.

2.2. Fixed-bed set-up

The experimental set-up used in this work is shown in Fig. 1. All units were connected using ¼″ Teflon tubes.

A stainless steel fixed-bed reactor of column size (D_c) 10.8 mm i.d. and length (L) 140 mm was used. Thus, the design parameter of D_c/d_p and L/D_c were ~19 and ~13, respectively, where d_p is the mean particle diameter. These design values were used to avoid wall effects [23] and to minimize axial dispersion [24]. To prevent elutriation of small sorbent particles, a mesh disc layered with filter paper (with a pore size of 1.2 μm) was positioned at each end of the column occupying a combined depth of 5 mm (thus bed effective length was 135 mm). The mesh at the bottom of the column also supported the packing material and acted as a distributor.

2.3. Methods

The sides of the loaded column were lightly tapped to settle the packing (loose bulk density is ~10% lower than compacted bulk density). The column was then attached to the capture system. The capture process at ambient temperature (~22 °C) was started by opening the feed tank valve and adjusting the rotameters to a flow rate of 650 mL/min, which was maintained constant throughout the experiment. After passing through the bubbler, the humidified gas was then introduced to the bed. The capture pressure was ~100 kPa gauge pressure, which was maintained constant by adjusting the controlling valves of the rotameters. CO_2 concentration in the bed effluent was measured by a CO_2 analyzer. Two analyzers with different detection ranges were used to ensure high accuracy of measurements: 0–5000 ppm, and 0–3%. The measurement of breakthrough was stopped when CO_2 concentration in the bed effluent was considered to be too low to reach a complete breakthrough curve in a reasonable period of time. After recording the breakthrough data, the system was shut down and the material from the column was removed for analysis. The MTZ was determined by analyzing the hydration and carbonation conversions across the length of the bed, and obtained at the end of the breakthrough measurement (50% of breakthrough). CO_2 inlet concentration was varied from 0.5% to 2% (N_2 balance). The pre-hydration experiment was performed by flowing N_2 through the bubbler to the column at ambient temperature and a flow rate of 650 mL/min.

Samples were taken from the system as required and analyzed for conversion in a Mettler Toledo TGA/SDTA851 thermogravimetric analyzer (TGA). In this analysis, a sample of ~10 mg was heated in the TGA from ambient temperature to 900 °C at a heating rate of 50 °C/min under N_2 flow of 40 mL/min. Carbonation and hydration conversions were then calculated from the calcination profile.

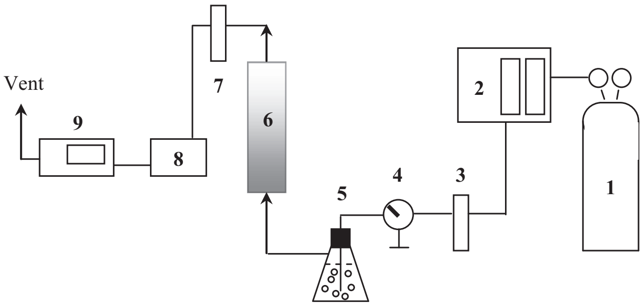

Fig. 1. Schematic of the experimental set-up; (1) gas cylinder, (2) flow control panel, (3) high-pressure rotameter, (4) pressure gauge, (5) bubbling humidifier, (6) fixed bed, (7) rotameter, (8) dehumidifier, and (9) CO_2 analyzer.