

# Capturing CO<sub>2</sub> from ambient air using a polyethyleneimine–silica adsorbent in fluidized beds

Wenbin Zhang, Hao Liu<sup>\*</sup>, Chenggong Sun, Trevor C. Drage, Colin E. Snape

Faculty of Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK

## HIGHLIGHTS

- PEI–silica adsorbent capturing CO<sub>2</sub> from ambient air evaluated in a BFB reactor.
- The equilibrium CO<sub>2</sub> adsorption capacity for air capture as high as 7.3 wt%.
- 40 t-CO<sub>2</sub>/day CFB air capture system using PEI–silica adsorbent proposed.
- The energy penalty for the proposed air capture system estimated to be 6.6 GJ/t-CO<sub>2</sub>.
- The operating cost of the air capture system estimated to be \$152/t-CO<sub>2</sub> avoided.

## ARTICLE INFO

### Article history:

Received 15 January 2014

Received in revised form

9 May 2014

Accepted 11 May 2014

Available online 16 May 2014

### Keywords:

Carbon capture

Air capture

PEI–silica adsorbent

Fluidized bed

## ABSTRACT

Carbon Capture and Storage (CCS) uses a combination of technologies to capture, transport and store carbon dioxide (CO<sub>2</sub>) emissions from large point sources such as coal or natural gas-fired power plants. Capturing CO<sub>2</sub> from ambient air has been considered as a carbon-negative technology to mitigate anthropogenic CO<sub>2</sub> emissions in the air. The performance of a mesoporous silica-supported polyethyleneimine (PEI)–silica adsorbent for CO<sub>2</sub> capture from ambient air has been evaluated in a laboratory-scale Bubbling Fluidized Bed (BFB) reactor. The air capture tests lasted for between 4 and 14 days using 1 kg of the PEI–silica adsorbent in the BFB reactor. Despite the low CO<sub>2</sub> concentration in ambient air, nearly 100% CO<sub>2</sub> capture efficiency has been achieved with a relatively short gas–solid contact time of 7.5 s. The equilibrium CO<sub>2</sub> adsorption capacity for air capture was found to be as high as 7.3 wt%, which is amongst the highest values reported to date. A conceptual design is completed to evaluate the technological and economic feasibility of using PEI–silica adsorbent to capture CO<sub>2</sub> from ambient air at a large scale of capturing 1 Mt-CO<sub>2</sub> per year. The proposed novel “PEI-CFB air capture system” mainly comprises a Circulating Fluidized Bed (CFB) adsorber and a BFB desorber with a CO<sub>2</sub> capture capacity of 40 t-CO<sub>2</sub>/day. Large pressure drop is required to drive the air through the CFB adsorber and also to suspend and circulate the solid adsorbents within the loop, resulting in higher electricity demand than other reported air capture systems. However, the Temperature Swing Adsorption (TSA) technology adopted for the regeneration strategy in the separate BFB desorber has resulted in much smaller thermal energy requirement. The total energy required is 6.6 GJ/t-CO<sub>2</sub> which is comparable to other reference air capture systems.

By projecting a future scenario where decarbonization of large point energy sources has been largely implemented by integration of CCS technologies, the operating cost under this scenario is estimated to be \$108/t-CO<sub>2</sub> captured and \$152/t-CO<sub>2</sub> avoided with an avoided fraction of 0.71. Further research on the proposed 40 t-CO<sub>2</sub>/day ‘PEI-CFB Air Capture System’ is still needed which should include the evaluation of the capital costs and the experimental investigation of air capture using a laboratory-scale CFB system with the PEI–silica adsorbent.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/3.0/>).

## 1. Introduction

The Intergovernmental Panel on Climate Change (IPCC) has concluded that a significant reduction of worldwide greenhouse-gas (GHG) emissions is required in order to stabilize the global average temperature increase at 2.0–2.4 °C above pre-industrial

<sup>\*</sup> Corresponding author. Tel.: +44 115 8467674.

E-mail address: [liu.hao@nottingham.ac.uk](mailto:liu.hao@nottingham.ac.uk) (H. Liu).

levels (Solomon et al., 2007). It is widely accepted that anthropogenic carbon dioxide emission released from the continuously increasing consumption of fossil fuels is the main contributor to the observed rising CO<sub>2</sub> concentration in the atmosphere. The concentration of CO<sub>2</sub> in the Earth's atmosphere is currently 393.52 ppm (NOAA, 2013), approximately 110 ppm higher than the level at the start of the Industrial Revolution.

Fossil fuels currently supply about 80% of the world's primary energy needs and will remain to be the main components of the world primary energy mix in the short to medium terms (IEA WEO, 2013). Before fossil fuels can be largely replaced by low-carbon energy sources such as renewables, Carbon Capture and Storage (CCS), which uses a combination of technologies to capture the CO<sub>2</sub> released from the fossil fuel use, and to transport the captured CO<sub>2</sub> to a safe and permanent storage location, has been regarded as a potential solution for the mitigation of CO<sub>2</sub> emissions from the continued use of fossil fuels. Most CCS technologies currently under development are aiming at CO<sub>2</sub> emissions from large point sources such as power plants and cement industries. Even under the most ideal scenarios proposed by IPCC AR4 (Solomon et al., 2007), current CCS for large point sources can at best slow the rate of increase in the atmospheric CO<sub>2</sub> concentration. Furthermore, roughly one-third of global carbon emissions are associated with distributed sources such as transportation vehicles, under which situation on-board CO<sub>2</sub> capture may not be a cost-effective solution (Lackner et al., 2012).

Air capture can be one of the very few truly negative CO<sub>2</sub> emission technologies which provide the possibilities not only to help maintain the current atmospheric CO<sub>2</sub> levels but to remediate the anthropogenic impact on climate since the Industrial Revolution. It has the potential to enable the continuous consumption of powerful and convenient energy carriers such as gasoline and diesel in a carbon-neutral or carbon-negative manner. Lackner proposed the use of CO<sub>2</sub> capture directly from the atmospheric air as a possible climate mitigation option in 1999 (Lackner et al., 1999). Although it was argued that the cost of air capture may be prohibitively high (Herzog, 2013), a number of researchers (Keith et al., 2006; Keith, 2009; Lackner, 2009; House et al., 2011) have claimed that air capture is physically and economically feasible and can play a key role in managing CO<sub>2</sub> emissions in the long term. More recently, Lackner et al. (2012) emphasized the urgency of developing air capture as a complementary solution to the conventional CCS on the basis that it can act as insurance against CO<sub>2</sub> leaking from storage and it may also provide an option to deal with emissions from mobile dispersed sources.

Capturing CO<sub>2</sub> from air is not technically difficult and has been practiced in the application of air separation or air purification in closed-circuit breathing systems such as in submarines and space-ships (Spector and Dodge, 1946; Carey et al., 1983; DallBauman and Finn, 1999). Physi-sorbents such as activated carbons and zeolites are expected to have low CO<sub>2</sub> adsorption capacities in air capture because the heat of adsorption is relatively low for these materials, leading to shallow adsorption isotherms with low adsorption capacities at ultra-low CO<sub>2</sub> partial pressures (Choi et al., 2009). The hydroxides of Na and Ca have been well known as CO<sub>2</sub> absorbents for air capture (e.g. Nikulshina et al., 2008, 2009). In comparison, for post-combustion CO<sub>2</sub> capture, there are different classes of adsorbents including supported amines (Drage et al., 2008; Hicks et al., 2008), carbon-based adsorbents (Drage et al., 2007; Lu et al., 2008), and zeolites (Lu et al., 2008; Siriwardane et al., 2001) which are under development in recent years. Among these, amine-based solid adsorbents have been regarded as the most promising candidates for post-combustion CO<sub>2</sub> capture due to their lower energy penalty in regeneration comparing to conventional aqueous amines scrubbing technology (Choi et al., 2009). In 2010, the first attempt using amine-functionalized silica for removing

CO<sub>2</sub> directly from air was made by Belmabkhout et al. (2010). The potential of amine-based adsorbents for air capture has been further explored by evaluating their performance in terms of uptake capacity, kinetics and regenerability by a few research groups (Chaikittisilp et al., 2011; Choi et al., 2011a, 2011b; Goepfert et al., 2011; McDonald et al., 2012; Wagner et al., 2013).

Research on air capture using solid adsorbents is very much in its infant stage. Most of the investigations carried out so far are focusing on the material characterization using a very small amount of adsorbents under idealized laboratory conditions (Chaikittisilp et al., 2011; Choi et al., 2011b; McDonald et al., 2012). In addition, the energy requirement that is regarded as an essential process indicator for evaluation of the economic performance of a practical air capture system has not been extensively addressed. To investigate the feasibility of air capture technology technically and economically when scaling up to a practical application, one has to consider a series of challenging issues such as the process design for efficient air/adsorbent contact, the regeneration strategy, material durability and cyclic regenerability. This paper presents the experimental results on the performance of a Polyethyleneimine(PEI)–silica adsorbent in capturing CO<sub>2</sub> from ambient air in a laboratory-scale Bubbling Fluidized Bed (BFB) reactor system. Furthermore, for the first time, a novel air capture system consisting of a Circulating Fluidized Bed (CFB) adsorber and a BFB desorber using PEI–silica adsorbent as the circulating bed materials is proposed. The overall energy requirement, operating cost and net CO<sub>2</sub> emissions for the proposed system are evaluated at the process assessment level and compared with other reported air capture systems.

## 2. Experimental section

Fig. 1 shows the schematic and a photograph of the BFB reactor system designed and built for the evaluation of CO<sub>2</sub> capture and regeneration using solid adsorbents. The total height of the BFB reactor is 1.7 m, consisting of a fluidized bed section which is 1.2 m in height and 67 mm in internal diameter, and a freeboard section which is 0.5 m in height and 108 mm in internal diameter. The BFB reactor is surrounded by four individually controlled electric heating elements for heating the bed materials to the desired temperatures in adsorption and desorption processes. A series of thermocouples and pressure sensors are installed at different heights of the reactor wall for monitoring the fluidization and reaction behaviour. At the exit of the BFB, a cyclone is used to separate the entrained fine particles from the gas effluent before it is released to the atmosphere. At the bottom of the BFB, three gas streams i.e. air, carbon dioxide and nitrogen with individual valves and mass flow controllers are regulated to serve as the feed gas for adsorption or stripping gas for regeneration for different research purposes. An electrically heated moisture saturator with separate temperature controls is used to generate the moisture for the feed gas or the stripping gas. CO<sub>2</sub> concentrations at the inlet and outlet of BFB are continuously monitored by a regularly calibrated gas analyser. Pressure drops, temperatures and the CO<sub>2</sub> concentrations are recorded by a data logger.

The adsorbent used throughout this study was synthesized by impregnating a mass ratio of 40% of polyethyleneimine (PEI) into an inorganic mesoporous silica support which had a BET surface area of approximately 250 m<sup>2</sup>/g, pore volumes of 1.7 cm<sup>3</sup>/g and a mean pore diameter of approximately 20 nm (Drage et al., 2008). The PEI has a molecular mass (MM) of 1800 in hyperbranched forms acquired from Sigma-Aldrich, UK. PEI was incorporated into the silica support by a wet impregnation method. Characterization of the as-received adsorbent by means of TGA, NMR, DRIFT and

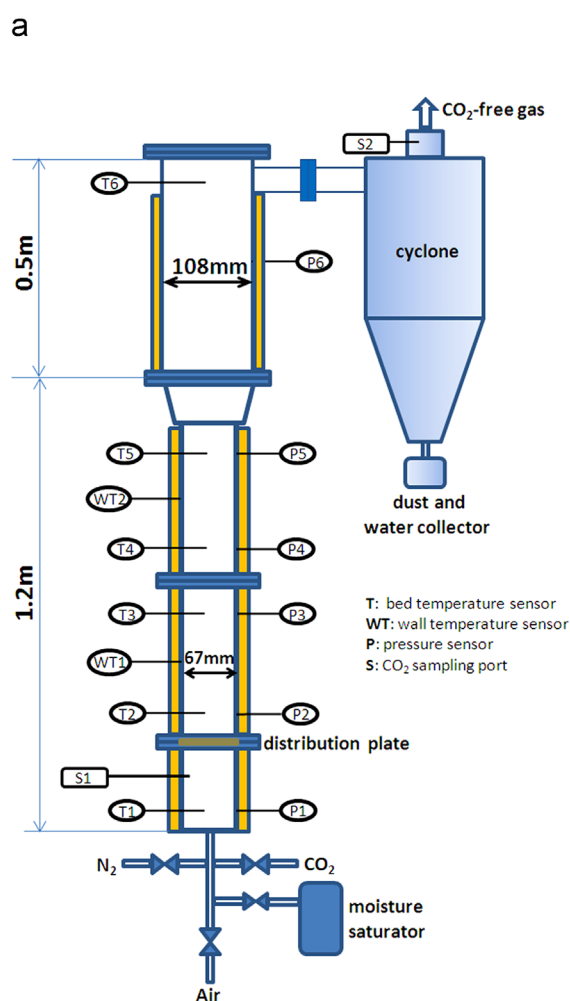


Fig. 1. Schematic and photograph of the bubbling fluidized bed reactor.

XPS can be found in previous publications (Drage et al., 2007, 2008).

The key parameters of the PEI-silica adsorbent and some operational conditions of the BFB reactor system are listed in Table 1. The average particle diameter of 250  $\mu\text{m}$  is deduced through the particle size distribution profiles obtained from standard sieve analysis. Minimum fluidization velocity  $U_{mf}$  is determined by air fluidization tests under room conditions (20  $^{\circ}\text{C}$ , 1 atm). The superficial fluidization velocity (20  $^{\circ}\text{C}$ , 1 atm) for both adsorption and desorption tests is adopted to be about 4 times of  $U_{mf}$ .

Two batches of PEI-silica adsorbent, namely PEI-A and PEI-B were used for the air capture tests in the BFB reactor system. PEI-A denotes the adsorbent that had already undergone about 20 cycles of  $\text{CO}_2$  adsorption/desorption tests under simulated power plant flue gas conditions prior to the air capture tests (Zhang et al., 2014). As no measures (such as the addition of moisture to the stripping gas during the desorption stage) during the prior  $\text{CO}_2$  adsorption/desorption cycles were taken to prevent the degradation of the adsorbent materials, PEI-A had been partially degraded before the commencement of the air capture tests. PEI-B represents the fresh adsorbent especially used for the air capture testing purpose. The specific heat capacity of PEI-B was measured using a DSC III (Differential Scanning Calorimetry) device and the heat of adsorption was measured by a SENSYS Evo TG-DSC provided by SETARAM<sup>®</sup>. The mass of solid adsorbent tested in the BFB reactor for each batch is about 1.0 kg, leading to a static bed height of

Table 1

Key parameters of PEI-silica adsorbent and BFB reactor.

Real density of bed material ( $\text{kg}/\text{m}^3$ )	1400
Bulk density of bed material ( $\text{kg}/\text{m}^3$ )	700
Average particle diameter ( $\mu\text{m}$ )	250
Specific heat capacity $C_p$ ( $\text{kJ}/\text{kg K}$ )	1.7
Heat of adsorption ( $\text{kJ}/\text{kg-CO}_2$ )	2045
Minimum fluidization velocity $U_{mf}$ (m/s)	$9.5 \times 10^{-3}$
Superficial fluidization velocity $U_0$ (m/s)	$3.8 \times 10^{-2}$
Loaded bed mass (kg)	1.0
Static bed height (m)	0.41
Gas-solid contact time (s)	7.5

0.41 m and a gas-solid contact time of around 7.5 s under the room temperature and atmospheric pressure conditions.

The working conditions for the air capture and subsequent adsorbent regeneration by means of Temperature Swing Adsorption (TSA) are listed in Table 2. The ambient air containing 393.5 ppm of  $\text{CO}_2$  was fed into the BFB by an air compressor with a flow rate of 8 l/min. The moisture (ca. 0.9–1.4 vol%) contained in the ambient air is believed to have no detrimental effect on the performance of amine-based solid adsorbents as reviewed by Choi et al. (2009).  $\text{CO}_2$  adsorption by the adsorbent takes place when the ambient air passes through the bed materials under the ambient temperature and pressure conditions. Due to the limit of measurement range of the  $\text{CO}_2$  analyser (ABB AO2020) used, the concentration of  $\text{CO}_2$  in



**Table 2**

Working conditions for air capture tests and adsorbent regeneration.

<b>Adsorption</b>	
CO <sub>2</sub> concentration in ambient air (ppm)	393.5
Air flow rate (l/min, 20 °C, 1 atm)	8
Adsorption temperature (°C)	Room temperature (ca. 20 °C)
Moisture content in ambient air (vol%)	ca. 0.9–1.4
Bed pressure	At ambient condition (1 atm)
<b>Desorption</b>	
Stripping N <sub>2</sub> flow rate (l/min, 20 °C, 1 atm)	8
Desorption temperature (°C)	130
Moisture content of the stripping gas (vol%, wet basis)	Saturated at 40 °C (ca. 8.8 vol%)

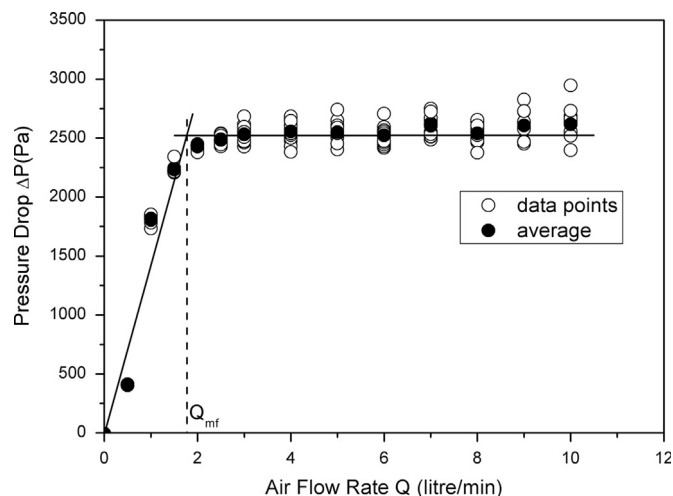
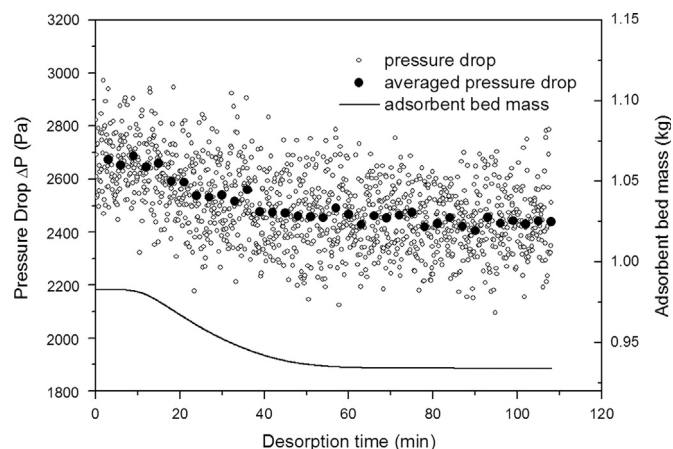
ppm range cannot be directly measured. Accordingly, the CO<sub>2</sub> uptake capacities were determined by integrating the CO<sub>2</sub> released during desorption tests conducted in the same reactor immediately after the adsorption tests had completed. The desorption tests were conducted by heating the BFB up to the temperature of 130 °C in pure nitrogen which acted as the stripping gas and the fluidization medium with a flow rate of 8 l/min. It should be noted that in practical applications, however, pure CO<sub>2</sub> or steam or a mixture of the two should be used as the stripping gas in order to achieve high purity CO<sub>2</sub> gas. The regeneration strategies for the PEI-silica adsorbent including the compositions of the stripping gas will be the focus of research activities in the near future. Saturated moisture at 40 °C (ca. 8.8 vol%) was added to the stripping gas to minimize the thermal and/or oxidative degradation effect under the desorption conditions. The air capture tests were conducted for different periods of time, each lasting between 4 and 14 days, while the adsorbent regeneration was accomplished shortly after an air capture test and lasted for a few hours.

### 3. Results and discussion

#### 3.1. Fluidization of PEI-silica adsorbent

According to Geldart's fluidization classification diagram (Geldart, 1973), the PEI-silica adsorbent used in this study falls into the category of Group B powders. Fluidization tests with ambient air have verified this by the observation of the smooth bubbling phenomenon emerging once the minimum fluidization condition was achieved. Fig. 2 shows a typical pressure drop diagram that indicates a linear increase with air flow rate when the bed is static and a subsequent levelling tendency irrespective of further increase in air flow rate when the PEI-silica bed has already been fluidized. The transition point corresponds to the minimum fluidization condition with the flow rate being around 2 l/min. During adsorption and desorption tests, a flow rate of 8 l/min was chosen in order to achieve fairly vibrant bubbling fluidization to facilitate sufficient gas–solid contact and mass and heat transfer.

As desorption was conducted at a higher temperature, the actual superficial velocity in bed was almost 6 times of the minimum fluidization velocity, leading to a more turbulent fluidization with vibrant pressure drop fluctuations, as shown in Fig. 3. The averaged values of the pressure drops indicated by scattered dots can be regarded as a representation of the total bed mass. It can be seen that the averaged pressure drop decreased in the first hour of the desorption process and stabilized afterwards, implying that the loss of adsorbent bed mass due to CO<sub>2</sub> desorption takes place within around 1 h. The variation of the calculated bed mass is also illustrated in Fig. 3 which shows a similar tendency with that of the averaged pressure drop.

**Fig. 2.** Bubbling fluidization behaviour of PEI-silica adsorbent.**Fig. 3.** Pressure drop fluctuations and bed mass variation during desorption.

#### 3.2. Performance of PEI-silica adsorbent in air capture

The CO<sub>2</sub> uptake capacity, as the most important performance indicator, is defined as the ratio between the captured CO<sub>2</sub> mass and the loaded adsorbent mass. Under the desorption conditions where temperature is swung to 130 °C and pure N<sub>2</sub> saturated with moisture at 40 °C is used as the stripping gas, the total mass of the released CO<sub>2</sub> in desorption stage equals to the CO<sub>2</sub> mass adsorbed during the adsorption stage. As shown in Fig. 4, the amount of the desorbed CO<sub>2</sub> mass can be calculated by integrating the detected CO<sub>2</sub> concentration with time at the corresponding flow rates. Fig. 4 shows that nearly all of the CO<sub>2</sub> has been desorbed during 2 h when the bed temperature was elevated to around 130 °C.

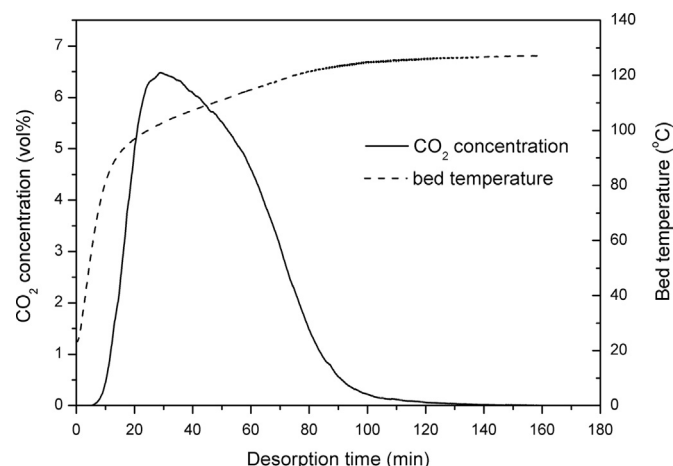


Fig. 4. Profiles of CO<sub>2</sub> concentration (on a dry basis) and bed temperature during desorption.

To determine the capture efficiency, the adsorbent capacity and regenerability characteristics, the testing time for air capture has been varied from 4 to 10 days for PEI-A and 6 to 14 days for PEI-B. For each test, ambient air was fed into the PEI-silica bed continuously to fluidize and make contact with the bed material. Two factors are defined here for the ease of interpretation:

$$\alpha = \frac{V_{de}}{V_{ad}} \quad (1)$$

$$q_{ad} = \frac{M_{CO_2}}{M_{bed}} \quad (2)$$

where  $V_{de}$  and  $V_{ad}$  are the total CO<sub>2</sub> volume released during desorption and that passed through the bed material during adsorption stage, respectively.  $M_{CO_2}$  is the accumulated mass of CO<sub>2</sub> that is released during desorption stage, while  $M_{bed}$  denotes the initial loaded mass of the adsorbent bed materials.  $\alpha$  represents the CO<sub>2</sub> capture rate whereas  $q_{ad}$  represents how much CO<sub>2</sub> has been adsorbed for a given amount of adsorbent. For the runs where the PEI-silica adsorbent has reached saturation condition,  $q_{ad}$  has the same meaning of the equilibrium CO<sub>2</sub> adsorption capacity.

The results of the air capture tests for the two batches of PEI-silica adsorbent are summarized in Table S1 (Supplementary information) and illustrated in Figs. 5 and 6. For the first three runs of partially degraded PEI-A batch which lasted for 4, 5 and 6 days, almost all the CO<sub>2</sub> that had been passing through the bed materials was captured, indicating a nearly 100% of capture efficiency. This implies that within a short gas-solid contact time of only 7.5 s, the adsorbent was capable of adsorbing almost all CO<sub>2</sub> contained in the ambient air. When the test time was longer than 6 days, however, the capture rate ( $\alpha$ ) decreased due to the fact that the loaded mass of PEI-silica adsorbent had achieved CO<sub>2</sub> saturation after around 6 days of adsorption. No more CO<sub>2</sub> could be captured beyond this point and the CO<sub>2</sub> contained in the air would escape from the top of the BFB. For the fresh PEI-B batch, CO<sub>2</sub> began to break through the adsorbent bed from around 7–8 days and the CO<sub>2</sub> saturation of the adsorbent was estimated to take place at around 10 days.

The saturation time is obviously dependant on the loaded bed mass and the adsorption capacity. After the adsorbent becomes saturated,  $q_{ad}$  represents the equilibrium adsorption capacity. As shown in Fig. 6(a) for PEI-A batch, this equilibrium adsorption capacity is found to be around 5.2 wt% over three runs (A-3 to A-5), comparing to 7.2 wt% for flue gas containing 15% CO<sub>2</sub> capture tests performed previously using the same adsorbent and in the

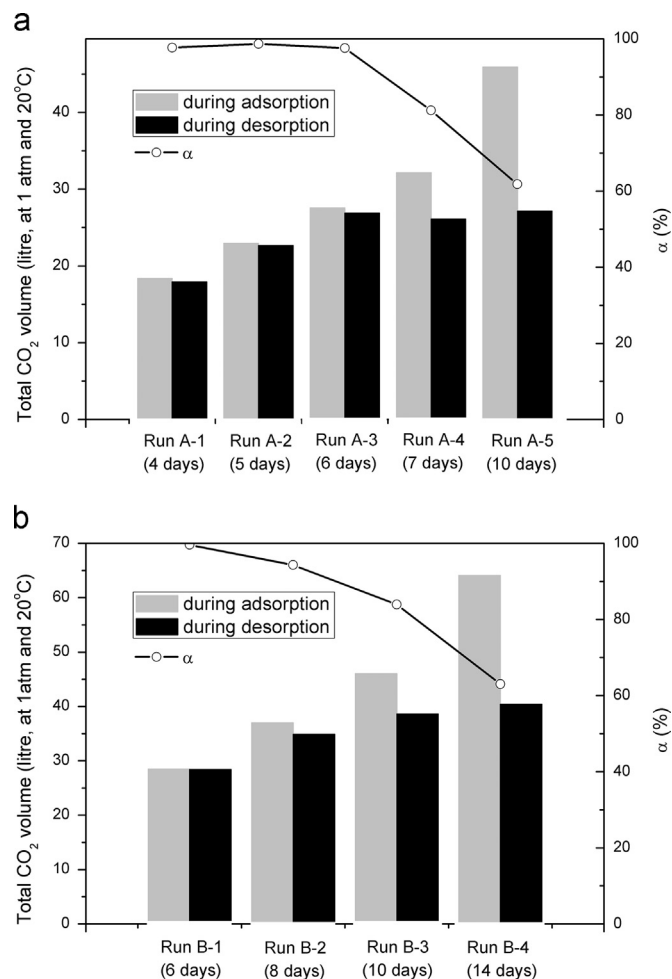


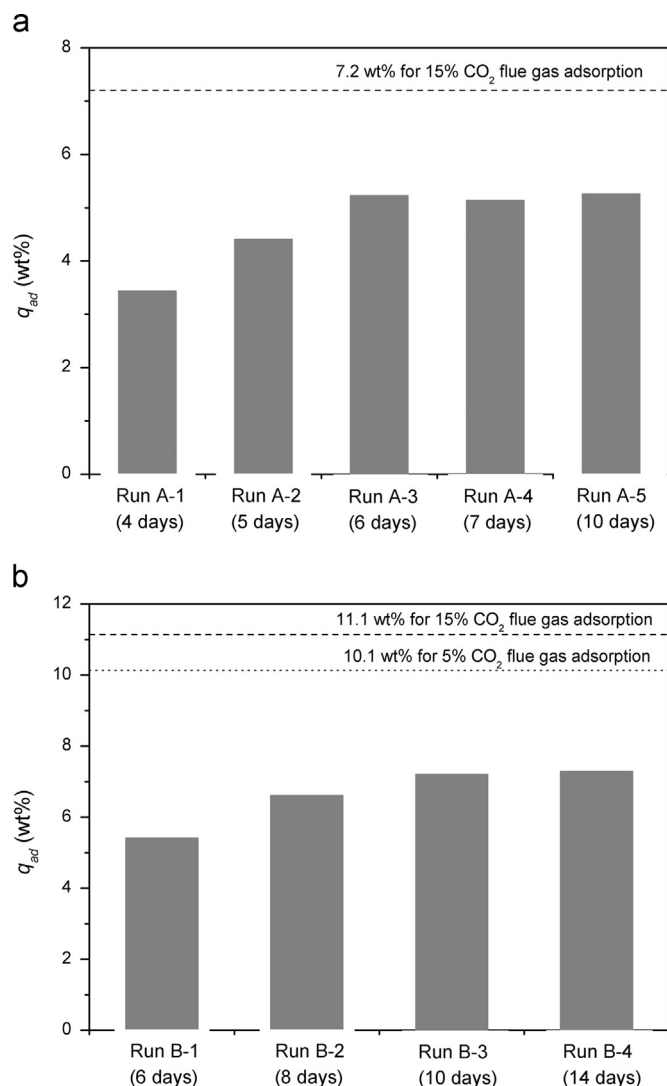
Fig. 5. Total CO<sub>2</sub> volume passing through the bed during adsorption, the amount released during desorption and the CO<sub>2</sub> capture rate ( $\alpha$ ) (a) for runs of A-1 to A-5, (b) for runs of B-1 to B-4 (CO<sub>2</sub> volume is at the condition of 1 atm and 20 °C).

same BFB reactor. For PEI-B batch in Fig. 6(b), the equilibrium adsorption capacity has decreased from 11.1 wt% for the flue gas (15% CO<sub>2</sub>) capture case to around 7.3 wt% for air capture case. The capacity of 10.1 wt% of PEI-B for capturing a lower concentration of CO<sub>2</sub> (5%) from the simulated flue gas is also included in Fig. 6 (b) for comparison.

No obvious reduction in CO<sub>2</sub> air capture capacity has been found with 5 cycles of PEI-A and 4 cycles of PEI-B (Fig. 6), indicating good cyclic regenerability of the PEI-silica adsorbent. However, more cycles of identical running time are needed to verify the long-term regenerability and stability of the PEI-silica adsorbent.

The adsorption capacities for air capture using PEI-silica adsorbent in this study are compared with those published in recent years (see Table 3). The relative factor  $\beta$  is defined as the ratio of adsorption capacity for air capture to that for the flue gas capture (containing 5–15% CO<sub>2</sub>) and it is used as an indicator to represent the relative loss in uptake capacities when the CO<sub>2</sub> concentration falls significantly from 5% to 15% down to ppm range. Choi et al. (2011b) reported a very high CO<sub>2</sub> adsorption capacity of around 9.0 wt% with simulated ambient air (400 ppm CO<sub>2</sub> in inert gas) by adding two types of stabilizing additives, namely 3-aminopropyltriethoxysilane (A-PEI/silica) and tetrapropyl orthotitanate (T-PEI/silica) to the normal prototypical PEI-silica adsorbent. They also obtained a maximum capacity of 7.6 wt% for the hyperbranched aminosilica (HAS) with the highest organic content of 42.5% using a packed bed reactor where 60–80 mg of

adsorbent was tested (Choi et al., 2011a). By impregnating PEI into fumed silica, Goepfert et al. (2011) also explored the potential of the prepared adsorbent in ambient air capture using 3 g of sample in a U-shape packed bed. The adsorption capacities were affected



**Fig. 6.** The ratio of adsorbed  $\text{CO}_2$  mass to the mass of bed materials (a) for runs of A-1 to A-5, (b) for runs of B-1 to B-4.

by the moisture present in the air and varied within the range of 5.2–7.8 wt%. Comparing with all the reference data, the adsorption capacities of around 7.3 wt% for air capture using fresh PEI–silica adsorbent in this study are amongst the most outstanding ones. Furthermore, the highest relative factor  $\beta$  implies that the adsorbent is one of the ideal universal candidates applicable for both flue gas and air capture purposes. For the first time, to the best knowledge of the authors, the mass of solid adsorbent tested for air capture purpose has been increased to 1 kg scale through this study in a laboratory-scale fluidized bed reactor. Thanks to the well-developed fluidized bed technologies over decades, it may be now possible to scale up the air capture facility to a practical application, as will be discussed in the next section.

### 3.3. Feasibility study of a proposed large-scale air capture concept

Currently, there are many promising mitigation options to deal with the climate change, such as increasing the end-user efficiency, carbon capture from centralized energy sources such as power plants, substitution of low-carbon electricity for gasoline and diesel fuel in vehicles, deployment of renewable energy sources, forest protection and afforestation and so on. No evidence, neither from experiment or demonstration nor from theoretical analysis, can support direct air capture technology to be an advantageous option than the above mentioned measures. However, from a longer-term perspective, as one of the very few truly carbon-negative technologies, direct air capture could play an important role in reducing the atmospheric  $\text{CO}_2$  concentration when the global warming issue becomes more serious in the future. Although a lot of efforts have been made on the adsorbent characterization and development for air capture purpose, very few investigations have addressed the performance of a practical air capture system in the context of process assessment. APS report (2011) made a detailed technological and economic assessment on a benchmark Direct Air Capture (DAC) system using a countercurrent air–liquid contactor by taking into account of both operating and capital costs. More recently, Mazzotti et al. (2013) further investigated the DAC system by optimizing its packing structure in the air contactor so that the avoided costs could be reduced from 7% to 16% for the three proposed packing designs comparing to the original benchmark DAC system in APS report (2011). Kulkarni and Sholl (2012) evaluated the performance of adsorption-based TSA processes for air capture using an amino-modified silica adsorbent in a structured monolithic contactor unit. In this section, the technological and economic feasibility of a large-scale air capture concept based on fluidized bed technology

**Table 3**

Comparison of adsorption capacities for air capture with simulated flue gas capture in the present study and in reported studies.

	Adsorption capacity for simulated flue gas $q_{fg}$ (wt%)	Adsorption capacity for ambient air $q_{air}$ (wt%)	Relative factor $\beta = q_{air}/q_{fg}$	Materials, scale and methodology
PEI-A (present work)	7.2 (15% $\text{CO}_2$ in humid flue gas)	5.2 (ambient air)	0.72	PEI–silica, 1.0 kg, in BFB
PEI-B (present work)	11.1 (15% $\text{CO}_2$ in humid flue gas)	7.3 (ambient air)	0.66	PEI–silica, 1.0 kg, in BFB
Belmabkhout et al. (2010)	9.0 (5% $\text{CO}_2$ in humid flue gas)	4.0 (300 ppm $\text{CO}_2$ in dry simulated air)	0.44	Triamine–silica, 1 g, in 120 mm long $\times$ 4.2 mm ID stainless steel tube
Chaikittisilp et al. (2011)	5.9–6.9 (10% $\text{CO}_2$ in dry flue gas)	2.8–3.8 (400 ppm $\text{CO}_2$ in dry simulated air)	0.47–0.62	Polyallylamine–silica, $\sim 20$ mg, by TGA
Choi et al. (2011a)	5.9–16.6 (10% $\text{CO}_2$ in humid flue gas)	0.7–7.6 (400 ppm $\text{CO}_2$ in humid simulated air)	0.12–0.46	Hyperbranched aminosilica, 60–80 mg, in a packed bed flow reactor
Choi et al. (2011b)	–	9.0 (400 ppm $\text{CO}_2$ in dry simulated air)	–	A-PEI/silica and T-PEI/silica, $\sim 20$ mg, by TGA
Goepfert et al. (2011)	–	5.2–7.8 (ambient air, humid or dried)	–	PEI-fumed silica, 3 g, packed in a U-shaped glass tube
McDonald et al. (2012)	9.9 (15% $\text{CO}_2$ in dry flue gas)	4.4 (390 ppm $\text{CO}_2$ in dry simulated air)	0.44	Alkylamine-appended MOF, $\sim 20$ mg, by TGA

and PEI-silica adsorbent, referred as “PEI-CFB air capture system”, is evaluated at the process level and compared with the benchmark DAC system in [APS report \(2011\)](#) and Kulkarni and Sholl's system (2012).

### 3.3.1. Limitation and scale of an air capture plant

Due to the basic fact that the CO<sub>2</sub> concentration in the air is around 300 times less than that in the flue gas from a coal-fired power plant, direct air capture cannot be a cost-effective and efficient measure to compete with post-combustion capture (PCC) where 90% of the CO<sub>2</sub> in the flue gas can be captured. The total CO<sub>2</sub> emissions for a typical 550 MWe subcritical coal power plant with 38% LHV efficiency are around 4 Mt-CO<sub>2</sub> per annum. If two post-combustion capture (PCC) units are equipped with such a power plant and operated at a capture efficiency of 90%, the CO<sub>2</sub> removal capacity for each unit is around 1.8 Mt/yr. However, the CO<sub>2</sub> capture capacity for an air capture unit with similar dimensions is much smaller due to the low CO<sub>2</sub> concentration in ambient air. To accomplish the task of capturing same quantities of CO<sub>2</sub>, the air capture system will need enormous capital expenditure. Capturing CO<sub>2</sub> directly from the flue gas will no doubt be more efficient and cost-effective than emitting the CO<sub>2</sub> into atmosphere in the first place and then using air capture technology to capture it afterwards. Therefore, the large scale deployment of air capture can only be feasible and serve as a complementary measure for CO<sub>2</sub> capture after the decarbonization of the large point energy sources such as power plants by CCS has largely been implemented.

As large point sources only account for about one-third of the total anthropogenic CO<sub>2</sub> emissions ([Jones, 2011](#)), air capture is thought to be possibly helpful with capturing the remaining two thirds of CO<sub>2</sub> emissions associated with distributed energy sources such as vehicles. However, air capture needs to demonstrate its advantages over other alternative paths to decarbonize these decentralized sources such as electrification of vehicles and substitution with low-carbon fuels. The necessity of deployment of air capture may be defended by arguing that there are some un-avoided CO<sub>2</sub> emissions that have to be captured under a more strict mitigation policy where negative carbon capture technologies such as air capture need to be largely deployed as a remedial measure for compensation, most likely in medium to long term. One example is that a 550 MWe power plant equipped with PCC with 90% capture efficiency, as adopted as an objective by most PCC technologies, still emits 0.4 Mt-CO<sub>2</sub>/yr which will accumulate in the atmosphere and may have to be dealt with by air capture technologies in a later stage. Another example is that the associated CO<sub>2</sub> emissions from CO<sub>2</sub> transportation by ocean ships which have not been fully decarbonized need to be captured by air capture technologies in the meantime.

From an economic perspective, the scale of an air capture plant cannot be too small as the captured CO<sub>2</sub> will have to be compressed and transported for sequestration. A reference scale of 1 Mt-CO<sub>2</sub>/yr may be sensible to match the commercial-scale CO<sub>2</sub> pipelines and injection wells, as suggested by [APS report \(2011\)](#) and will also be adopted in this study. Such an air capture plant can offset 2.5 times of the CO<sub>2</sub> emissions emitted previously from a 550 MWe power plant which has already been equipped with CCS with 90% capture efficiency.

### 3.3.2. Technological feasibility of applying fluidized bed technology to air capture

Fluidized beds have been well developed since the 1920s and served as efficient gas/solid contactors for many industrial applications such as fluidized bed catalytic cracking, coal/biomass combustion and gasification due to the inherent high gas–solid contact efficiency and high mass and heat transfer rates. Recently,

an [ADA report \(2010\)](#) made a comprehensive survey which encompassed a broad range of gas–solid contactors and thermal regeneration technologies including fluidized beds, entrained flow, gravitational cross flow, moving bed, radial flow, fixed bed, etc. A series of weighted scoring criteria were used to analyse the various technologies and finally fluidized beds were screened as the most reliable, cost-effective and promising candidates for PCC of flue gas from power plants. The viability of the solid sorbents as a PCC retrofit technology was further assessed on a 1 MWe pilot testing rig with Circulating Fluidized Bed (CFB) serving as the CO<sub>2</sub> adsorber by ADA-ES Inc. ([Starns et al., 2012](#)). Another attempt was made for continuous CO<sub>2</sub> capture from simulated flue gas in a laboratory-scale CFB reactor using supported amine sorbents (PMMA, polymethylmethacrylate) and a very high CO<sub>2</sub> adsorption capacity of 15 wt% has been reported ([Veneman et al., 2012](#)). Technically speaking, there is no big difference between the applications of CFB to air capture and to flue gas capture as both cases are operated at similar working conditions such as pressure, temperature and fluidization velocity. Therefore, a CFB riser is proposed here to serve as the air–solid contactor and CO<sub>2</sub> adsorber for the air capture application in large scale.

The proposal of a CFB riser, rather than a BFB reactor as used in the laboratory tests, as the contactor and adsorber is based on several considerations. (1) Solid adsorbents in the adsorber need to be constantly replenished with the regenerated adsorbents to maintain a high capture efficiency in the adsorber and continuous running. This can be realized in a CFB system where the CFB riser is used as the adsorber and the return leg is used as the desorber; (2) To increase the CO<sub>2</sub> throughput for each unit as much as possible, high air intake velocity is preferred so that more CO<sub>2</sub> can pass through the adsorber for adsorption. The typical fluidizing velocity of a CFB riser can be more than 10 times bigger than that of a BFB reactor and therefore, a CFB riser is more effective to be used as the adsorber. For the proposed CFB air capture system, a fluidizing velocity of 5 m/s for the CFB riser is adopted in the design, which is higher than the terminal velocity of the as-prepared PEI-silica adsorbent. The drag force at such velocity provided by the air flow can then drive the bed material for circulation in the loop; (3) The CFB riser provides a more turbulent gas flow and highly efficient gas–solid contact in the whole riser filled with dispersed solid adsorbents; (4) For the same gas–solid contact time, a CFB riser needs much less inventory bed mass due to the significantly diluted solid phase, leading to much lower bed pressure drop compared to a BFB reactor.

It should be noted that the main purpose of using the BFB reactor in the present study is to examine the performance of the PEI-silica adsorbent for ambient air capture at a much bigger scale (kg-adsorbent materials) than typical small-scale fixed bed investigations (mg- or g-scale adsorbent materials) such as by TGA. The data generated from the BFB tests are valuable for the feasibility study and design of a large-scale air capture system using the PEI-silica adsorbent. The high adsorption equilibrium capacities and the fast reaction kinetics (capture efficiency of nearly 100% achieved within a short gas–solid contact time of 7.5 s) of air capture by the PEI-silica adsorbent verified by the BFB tests indicate that it may be feasible and economical to capture CO<sub>2</sub> from ambient air at large-scales.

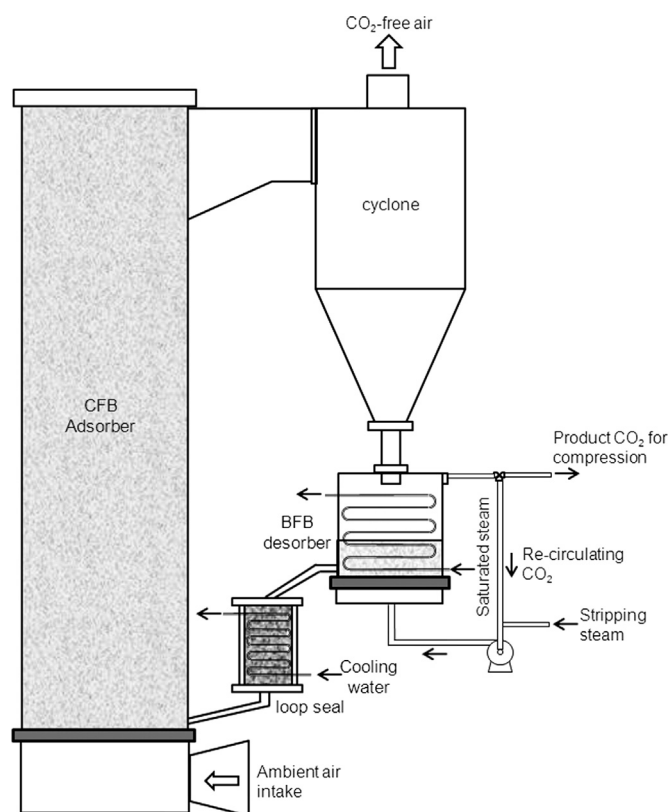
Based on the above rationales, the “PEI-CFB air capture system” is conceptually designed and compared with the benchmark Direct Air Capture (DAC) system proposed by the [APS report \(2011\)](#) (and further evaluated by [Mazzotti et al. \(2013\)](#)) in [Table 4](#). The concept of the design is illustrated in [Fig. 7](#) and key specifications are summarized in [Table S2](#) (Supporting information). The proposed air capture system consists of a CFB adsorber to capture the CO<sub>2</sub> from the ambient air with integrated booster compressors, a cyclone to separate and collect entrained solids



**Table 4**

Comparison of PEI-CFB conceptual design with the benchmark DAC system (APS, 2011).\*

	DAC (APS, 2011)				Proposed PEI-CFB air capture system		
Specifications							
CO <sub>2</sub> capture plant capacity (Mt/yr)	1				1		
CO <sub>2</sub> capture rate (%)	50				90		
Air velocity (m/s)	2				5		
Pressure drop through absorber/adsorber (Pa)	280				1592		
Adsorber unit dimension (m)	12 in diameter, 2.8 in height				12 × 12 × 40		
CO <sub>2</sub> captured per unit (t-CO <sub>2</sub> /day)	8.3				40		
Total number of units	330				68		
Energy and costs							
Electricity (GJ <sub>e</sub> /t-CO <sub>2</sub> )	1.8				3.4		
Thermal Energy (GJ <sub>t</sub> /t-CO <sub>2</sub> )	6.1				3.2		
Total energy requirement (GJ/t-CO <sub>2</sub> )	7.9				6.6		
Operating cost associated with electricity and thermal energy (\$/t-CO <sub>2</sub> captured)	81 <sup>S1</sup>	81 <sup>S1a</sup>	91 <sup>S2</sup>	306 <sup>S3</sup>	91 <sup>S1a</sup>	108 <sup>S2</sup>	227 <sup>S3</sup>
Avoided CO <sub>2</sub> as a fraction of CO <sub>2</sub> captured	0.70 <sup>S1</sup>	0.29 <sup>S1a</sup>	0.55 <sup>S2</sup>	1.0 <sup>S3</sup>	0.21 <sup>S1a</sup>	0.71 <sup>S2</sup>	1.0 <sup>S3</sup>
Operating cost associated with electricity and thermal energy (\$/t-CO <sub>2</sub> avoided)	116 <sup>S1</sup>	281 <sup>S1a</sup>	164 <sup>S2</sup>	306 <sup>S3</sup>	425 <sup>S1a</sup>	152 <sup>S2</sup>	227 <sup>S3</sup>

<sup>S1</sup> : Electricity supplied by average power grid, thermal energy by combustion of natural gas with CO<sub>2</sub> capture.<sup>S1a</sup> : Electricity supplied by average power grid, thermal energy by combustion of natural gas without CO<sub>2</sub> capture.<sup>S2</sup> : Electricity supplied by Advanced NGCC with CCS, thermal energy by combustion of natural gas without CO<sub>2</sub> capture.<sup>S3</sup> : Electricity supplied by wind power plants, thermal energy by advanced nuclear.\* S1–S3 are different scenarios defined in Section 3.3.4. Data from APS report (2011) have been adapted for comparison under these scenarios with additional data of energy costs and CO<sub>2</sub> emission rates adopted from Kulkarni and Sholl (2012).**Fig. 7.** Conceptual design of a PEI-silica solid adsorbent based CFB system for large scale air capture.

from the CO<sub>2</sub>-depleted air, a BFB desorber to regenerate the CO<sub>2</sub>-rich adsorbent, and a loop seal to return the CO<sub>2</sub>-lean adsorbent back to CFB adsorber.

The CFB adsorber has a square cross sectional area of 144 m<sup>2</sup> and a height of 40 m, both of which are typical dimensions of the available industrial-scale CFB facilities. The height is chosen to ensure 8 s of gas–solid contact time with the air intake velocity being 5 m/s, which is higher than 2 m/s adopted by the benchmark

DAC system (APS, 2011). The lower air velocity in the DAC system is based on the consideration that excessive evaporative loss of solvent liquid and/or entrainment of the absorbent solution may become serious at higher velocities. Although the capture efficiency is not a critical factor for air capture process (50% assumed for the benchmark DAC), the BFB tests have shown that as high as 90% can be achieved due to the high performance of the PEI-silica adsorbent. The working capacity of the PEI-silica adsorbent used in the conceptual design is 5%, a conservative assumption which is about 70% of the equilibrium capacity (7.3%) obtained from the BFB tests. The CO<sub>2</sub> capture capacity of such a designed unit is 40 t-CO<sub>2</sub>/day and a total number of 68 units is required to accomplish the capturing task of 1 Mt-CO<sub>2</sub>/yr for an air capture plant, compared to 8.3 t-CO<sub>2</sub>/day and 330 units for the benchmark DAC system (APS, 2011).

A gas–solid separator, such as a cyclone, is located at the exit of the CFB adsorber and plays an essential role in separating the solid adsorbent entrained by the CO<sub>2</sub>-depleted air and circulating it in the CFB–BFB loop. The illustrated vertical-axis cyclone with a tangential inlet and axial discharge in Figure S1 (Supporting information) is the most common design used in CFB applications.

A cylindrical BFB desorber with a smaller dimension of 4 m in diameter and 4.8 m in height is designed to act as the regenerator (desorber) for the PEI-silica adsorbent at an elevated temperature of 130 °C. As the stripping gas has a much smaller flow rate, the BFB desorber is operated at the bubbling fluidization regime. To get high purity CO<sub>2</sub> product in practical scale, pure CO<sub>2</sub> can be used as the stripping gas during the regeneration; however this may cause thermal degradation and lower working capacity (Drage et al., 2008; Veneman et al., 2012). Using some steam in the stripping gas can prevent the PEI-silica adsorbent from thermal degradation at the high desorption temperature, as has been demonstrated by many researchers (such as Choi et al., 2009; Sayari and Belmabkhout, 2010; Li et al., 2010). Pure steam was suggested by some researchers (Drage et al., 2008; Gray et al., 2009; Li et al., 2010) to improve this problem at the cost of more thermal energy penalty and additional water management. Before we conclude our study on the regeneration strategies of the PEI-silica sorbent including the composition of the stripping gas, we propose a mixture gas containing 75 vol% CO<sub>2</sub> and 25 vol% steam to be used as the stripping gas and fluidization medium, being fed



from the bottom of the BFB desorber by recirculating a portion of the product CO<sub>2</sub> gas flow. A heat exchanger needs to be installed in the loop seal for cooling down the hot adsorbent before entering the CFB adsorber and also for recovering a portion of sensible heat contained in the hot adsorbent.

### 3.3.3. Energy required to operate the air capture system

Although application of the proposed “PEI-CFB air capture system” is not especially technically difficult, the economic performance associated with the energy requirement and operating cost has to be carefully evaluated. The cost of dealing with CO<sub>2</sub> beyond the boundary of the capture facility such as sequestration cost is not included in our evaluation, whereas the electricity required for CO<sub>2</sub> compression to pipeline pressure is accounted. The overall required energy mainly consists of the thermal heat associated with regeneration of the adsorbent and the electricity demand associated with moving the air and adsorbent in the system loop.

**3.3.3.1. Thermal energy requirement.** The thermal energy required for regeneration depends mostly on the characteristics of a specific adsorbent and it is less relevant to the process. It can be calculated using the following equation (3) with a reasonable degree of accuracy. Similar equations have also been proposed to evaluate the economic performance of solid adsorbents for post-combustion CO<sub>2</sub> capture (Sjostrom and Krutka, 2010).

$$Q_r = \frac{1-\theta}{q_w} C_{p,s} (T_{de} - T_{ad}) - \Delta H_r \quad (3)$$

where  $Q_r$  is the regeneration heat requirement (kJ/kg-CO<sub>2</sub> adsorbed),  $q_w$  is the working capacity of the selected adsorbent (wt%),  $C_{p,s}$  is specific heat capacity of the adsorbent (kJ/kg K),  $T_{ad}$  and  $T_{de}$  are the temperatures of adsorption and desorption processes respectively (°C),  $\Delta H_r$  is the heat of adsorption (kJ/kg-CO<sub>2</sub> adsorbed, negative value for exothermal adsorption),  $\theta$  is the percentage of the sensible heat that can be recovered by an appropriate process design such as by using heat exchangers. The first term on the right hand side of Eq. (3) represents the sensible heat required to elevate the adsorbent to the desorption temperature while the second term represents the latent heat needed to break the bond between the CO<sub>2</sub> and the adsorbent for regeneration.

With respect to the as-prepared PEI-silica adsorbent used in the present study, the specific heat capacity  $C_{p,s}$  was found to be 1.7 kJ/kg K by a DSC III device and the heat of reaction to be 2045 kJ/kg-CO<sub>2</sub> by a SENSYS Evo TG-DSC provided by SETARAM®. For the air capture process assessed here, desorption is performed at 130 °C and the adsorption temperature equals to ambient temperature (ca. 20 °C), giving a temperature difference of 110 °C. A recovery ratio  $\theta$  of 75%, as suggested by Veneman et al. (2013), is also assumed here for a two-stage solid-liquid heat exchanger (90% efficiency for each stage, and 10% of heat loss during liquid circulation). For comparison, the recovery ratio of 90% is often used for the lean/rich solvent heat exchanger in a typical liquid MEA scrubbing process. By substituting these parameters into Eq. (3), the regeneration heat can be estimated to be 3.0 GJ/t-CO<sub>2</sub> (subscript “t” indicates “thermal”). An additional heat of 0.2 GJ/t-CO<sub>2</sub> is required to generate the steam in the stripping gas, giving a total thermal heat requirement of 3.2 GJ/t-CO<sub>2</sub>. This value is only slightly higher than 2.6 GJ/t-CO<sub>2</sub> for the PCC case if the same adsorbent is used with however a higher working capacity of 8 wt% and a smaller temperature difference of 60 °C. It is significantly lower than 6.1 GJ/t-CO<sub>2</sub> in the benchmark DAC system and 6.0 GJ/t-CO<sub>2</sub> in the system proposed by Kulkarni and Sholl (2012). In the benchmark DAC system, the most energy

intensive regeneration step was realized by calcinations at 900 °C which has induced a massive heat requirement (Bacocchi et al., 2006). Whereas in the system of Kulkarni and Sholl (2012), 38% of the thermal heat was wasted in the monolith contactor.

For reference, the thermal energy required for a traditional (not advanced) PCC MEA scrubbing process is around 3.9–4.5 GJ/t-CO<sub>2</sub> (Tarka et al., 2006; Rao et al., 2006; Abu-Zahra et al., 2007). This comparison, however, does not support the argument that the cost of the proposed air capture system is comparable to the MEA process by taking into account of the huge differences in the capturing capacity and the corresponding capital expenditure as discussed earlier in Section 3.3.1.

**3.3.3.2. Electricity requirement.** Electricity is required for the operation of booster compressors, fans, pumps, etc. to overcome the pressure drop in the whole process. Large air/adsorbent specific contact area and long air-solid contact time can facilitate the reaction kinetics for air capture, which however will increase the pressure drop needed to drive the air through the adsorbent surface. Optimization of an air/adsorbent contacting system with the lowest possible pressure drop is therefore critically important to maintain an affordable electricity demand. An open passive air collector (Keith et al., 2006; Lackner, 2009) acting as a large filter system with narrow passages, which is driven by natural wind flow, can be regarded as an ideal solution. The air-side stagnation pressure is however only 15–50 Pa, which is not viable to operate a solid-based system without the aid of external driving forces.

The pressure drop in the CFB riser with the designed specifications is determined to be 572 Pa which is not significantly higher than 280 Pa in the benchmark DAC system. However, more pressure drop needs to be overcome in the cyclone which is a necessary component in the CFB system. According to the methodology presented by Muschelknautz and Greif (1997), the calculated pressure drop in the designed cyclone is around 1020 Pa, giving a total pressure drop of 1592 Pa. Assuming an isentropic efficiency of 80% for the booster compressor, the total compression work needed for overcoming the pressure drop in the CFB riser and cyclone is 3.0 GJ<sub>e</sub>/t-CO<sub>2</sub> (subscript “e” indicates “electricity”). Although the BFB desorber is operated under a higher pressure drop of around 6554 Pa, the compression work (0.02 GJ<sub>e</sub>/t-CO<sub>2</sub>) can be neglected due to the fact that the flow rate of stripping gas to be compressed is much lower than that of the air flow. The total electricity demand for the proposed air capture system is 3.4 GJ<sub>e</sub>/t-CO<sub>2</sub> by adding 0.4 GJ<sub>e</sub>/t-CO<sub>2</sub> of electricity for CO<sub>2</sub> compression to 100 bar (as adopted by the APS report (2011)). This electricity demand is noticeably higher than 1.8 GJ<sub>e</sub>/t-CO<sub>2</sub> of the benchmark DAC system and 0.8 GJ<sub>e</sub>/t-CO<sub>2</sub> of the system of Kulkarni and Sholl (2012). However, the total energy requirement, inclusive of thermal energy and compression work, for these three systems are comparable (6.6 GJ/t-CO<sub>2</sub> for the proposed PEI-CFB air capture system, 7.9 GJ/t-CO<sub>2</sub> for the benchmark DAC system, and 6.6 GJ/t-CO<sub>2</sub> for the system of Kulkarni and Sholl (2012)). The higher electricity demand induced by the higher pressure drop in the proposed PEI-CFB system is not surprising as the pressure drop does not only drive the air through the adsorber but also contributes to lifting and circulating the solid sorbents. Whereas in the other two reference systems (the benchmark DAC system and the system of Kulkarni and Sholl (2012)) additional supporting structure has to be installed inside the adsorber to support the flowing solvent or the solid adsorbent, which in turn will certainly increase the operating cost and capital investment associated with the complexity of the adsorber. There are always trade-offs between the operating cost and the capital cost. The economic performance of a specific air capture system can only be justified based on a comprehensive survey of capital cost, which however falls beyond the scope of this study at the present time for

the proposed “PEI-CFB air capture system” but should be carried out in the future.

### 3.3.4. Operating cost and net carbon issues

The estimation of operating cost for an air capture system largely depends on the availability and strategy of various energy sources including electricity, coal, natural gas, solar thermal power, wind power, or nuclear heat, etc. An air capture system can claim to be carbon-negative only if the amount of CO<sub>2</sub> captured is larger than the CO<sub>2</sub> released during operation of such a system. Kulkarni and Sholl (2012) suggested the operating cost to be of the order \$80–150/t-CO<sub>2</sub> captured by assessing a wide range of electricity sources. The data of energy costs and CO<sub>2</sub> emission rates in their paper have been used in the present study (Table S9 in Supporting information, Kulkarni and Sholl, 2012).

Three scenarios are defined according to the increasing urgency of air capture in different periods where decarbonization technologies are becoming more mature.

**Scenario 1:** This is the scenario adopted by APS report (2011) for the benchmark DAC system where electricity is supplied by the average US power grid and the thermal energy for the kiln that regenerates CaO and releases CO<sub>2</sub> is provided by combustion of natural gas. The APS report (2011) assumed that the CO<sub>2</sub> emissions produced from burning natural gas in the calciner do not contribute to CO<sub>2</sub> emissions because they are ready to be captured from the kiln exhaust. The avoided CO<sub>2</sub> fraction under this assumption for the benchmark DAC system had a high level of 0.7. The operating costs under this scenario for every tonne of CO<sub>2</sub> captured and avoided with the benchmark DAC system are listed in Table 4 for comparison. This scenario corresponds to an idealized near-term strategy.

**Scenario 1a:** This is a modified version from Scenario 1 as the CO<sub>2</sub> capture technology from the natural gas combustion assumed by the APS report (2011) is considered not to be applicable to the proposed air capture system in this paper. To study the effect of the CO<sub>2</sub> emissions associated with the combustion of natural gas on the operating cost and avoided CO<sub>2</sub> as a fraction of the CO<sub>2</sub> captured, Scenario 1a is proposed to include the CO<sub>2</sub> emissions from combustion of natural gas and compared with Scenario 1. The avoided CO<sub>2</sub> fraction has significantly dropped to 0.29 for the benchmark DAC system under this scenario. For the proposed PEI-CFB air capture system, the avoided CO<sub>2</sub> fraction is only 0.21 which results in a higher operating cost for every tonne of CO<sub>2</sub> avoided than that of the benchmark DAC system. Although PEI-CFB air capture system has a similar operating cost (\$91) for every tonne of CO<sub>2</sub> captured compared to the benchmark DAC system (\$81), the penalty arising from the smaller avoided CO<sub>2</sub> fraction is more crucial for the PEI-CFB air capture system, which requires more electricity with a higher CO<sub>2</sub> emission rate (0.17 t-CO<sub>2</sub>/GJ for electricity and 0.05 t-CO<sub>2</sub>/GJ for combustion of natural gas).

**Scenario 2:** This scenario is defined based on the assumption that decarbonization of power plant has extensively realized by integrating CCS technology into IGCC or Advanced NGCC plants in medium-term. Although electricity costs increase from \$66/MWh (conventional NGCC) to \$136/MWh (Advanced NGCC with CCS), the CO<sub>2</sub> emissions will drop significantly from 0.40 t-CO<sub>2</sub>/MWh (conventional NGCC) to 0.08 t-CO<sub>2</sub>/MWh (Advanced NGCC with CCS). With a much improved avoided CO<sub>2</sub> fraction of 0.71, the operating cost of the proposed PEI-CFB air capture system for every tonne of CO<sub>2</sub> avoided has dropped dramatically from \$425 under scenario S1a to \$152, which is now comparable to \$164 for the benchmark DAC system under the same scenario 2 (Table 4). The comparison of Scenario 1a and Scenario 2 for the PEI-CFB system has the implication that the air capture concept can only be economically promising when the decarbonization of power

plants by CCS technology has been largely implemented in medium-term.

**Scenario 3:** This is an even more idealized scenario in long-term where the urgency of mitigating CO<sub>2</sub> emissions has dominated over the considerations of costs, in which case CO<sub>2</sub>-free energy sources will have to be supplied for all the energy requirements. Table 4 shows an example where electricity is supplied by wind power plants and thermal energy is provided by advanced nuclear energy. Although the operating cost appears to be higher than Scenario 2 (\$227 vs \$152 per t-CO<sub>2</sub> avoided, in Table 4) at the current energy prices for renewable energies, the air capture has turned into a complete carbon-negative process, with the final convergence of the costs associated with every tonne of CO<sub>2</sub> captured and avoided.

The capital cost and associated maintenance cost, together with labour and consumables costs can contribute over 80% to the total cost for an air capture system as estimated by the APS report (2011). Further research on the 40 t-CO<sub>2</sub>/day “PEI-CFB air capture system” proposed in this study is still needed, which should include the evaluation of capital costs and the experimental investigation with a laboratory-scale CFB air capture system mimicking the proposed “PEI-CFB air capture system” shown in Fig. 7.

## 4. Conclusions

PEI-silica adsorbent developed for post-combustion CO<sub>2</sub> capture has been tested in a bubbling fluidized bed reactor for ambient air CO<sub>2</sub> capture where nearly 100% CO<sub>2</sub> capture rate can be achieved with an air/adsorbent contact time of 7.5 s owing to the fast reaction kinetics of the adsorbent. The equilibrium adsorption capacities of around 7.3 wt% obtained by the BFB tests in this study are amongst the highest values reported so far for air capture.

Inspired by the high performance of the PEI-silica adsorbent demonstrated in BFB tests, a conceptual design for air capture mainly consisting of a CFB adsorber and a BFB desorber has been completed for large scale applications (capturing up to 40 t-CO<sub>2</sub> per day). The proposed “PEI-CFB air capture system” has higher electricity demand due to the higher pressure drop required in the process; however it may have the potential in saving capital cost and associated operating costs owing to its simplicity in structure comparing to other reference air capture systems. The total energy requirement for the proposed air capture system is 6.6 GJ/t-CO<sub>2</sub>, which is comparable to the reference air capture systems. The economic feasibility of the proposed “PEI-CFB air capture system” can be claimed only when the decarbonization of large point energy sources such as power plants has been largely implemented by integration of CCS technologies. The operating cost of the proposed “PEI-CFB air capture system” under this scenario is estimated to be \$108/t-CO<sub>2</sub> captured and \$152/t-CO<sub>2</sub> avoided with an avoided fraction of 0.71.

Further research on the proposed “PEI-CFB air capture system” should include the evaluation of capital costs and the experimental investigations of air capture in a laboratory-scale CFB system using the PEI-silica adsorbent.

## Acknowledgement

The authors wish to acknowledge the financial support of UK EPSRC (EP/J020745/1, EP/G063176/1).

## Appendix A. Supporting information

Supporting information associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.ces.2014.05.018>.

## References

- ADA Report, Topical Report 1, 2 and 3: Technology Survey, Screening and Final Selection. DOE Award No. DE-NT0005649, Project Director: Sjöström, S., Issued on July 2010.
- APS (American Physical Society) report, Direct Air Capture of CO<sub>2</sub> with Chemicals, A Technology Assessment for the APS Panel on Public Affairs. June 1, 2011. (<http://www.aps.org/policy/reports/assessments/upload/dac2011.pdf>) (accessed on 1 February 2014).
- Abu-Zahra, M.R.M., Schneiders, L.H.J., Niederer, J.P.M., Feron, P.H.M., Versteeg, G.F., 2007. CO<sub>2</sub> capture from power plants, Part I. A parametric study of the technical performance based on monoethanolamine. *Int. J. Greenh. Gas Control* 1, 37–46.
- Bacocchi, R., Sorti, G., Marzotti, M., 2006. Process design and energy requirements for the capture of carbon dioxide from air. *Chem. Eng. Process.* 45, 1047–1058.
- Belmabkhout, Y., Serna-Guerrero, R., Sayari, A., 2010. Amine-bearing mesoporous silica for CO<sub>2</sub> removal from dry and humid air. *Chem. Eng. Sci.* 65, 3695–3698.
- Carey, R., Gomezplata, A., Sarich, A., 1983. An overview into submarine CO<sub>2</sub> scrubber development. *Ocean Eng.* 10, 227–233.
- Chaikittisilp, W., Khunsupat, R., Chen, T.T., Jones, C.W., 2011. Poly(allylamine)-mesoporous silica composite materials for CO<sub>2</sub> capture from simulated flue gas or ambient air. *Ind. Eng. Chem. Res.* 50, 14203–14210.
- Choi, S., Drese, J.H., Jones, C.W., 2009. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem* 2, 796–854.
- Choi, S., Drese, J.H., Eisenberger, P.M., Jones, C.W., 2011a. Application of amine-tethered solid sorbents for direct CO<sub>2</sub> capture from the ambient air. *Environ. Sci. Technol.* 45, 2420–2427.
- Choi, S., Gray, M.L., Jones, C.W., 2011b. Amine-tethered solid adsorbents coupling high adsorption capacity and regenerability for CO<sub>2</sub> capture from ambient air. *ChemSusChem* 4, 628–635.
- DallBauman, L., Finn, J., 1999. Adsorption processes in spacecraft environmental control and life support systems. In: Dabrowski, A. (Ed.), *Adsorption and Its Applications in Industry and Environmental Protection: Applications in Environmental Protection*, vol. II. Elsevier, New York, pp. 455–471.
- Drage, T.C., Arenillas, A., Smith, K.M., Pevida, C., Piippo, S., Snape, C.E., 2007. Preparation of carbon dioxide adsorbents from the chemical activation of urea-formaldehyde and melamine-formaldehyde resins. *Fuel* 86, 22–31.
- Drage, T.C., Arenillas, A., Smith, K.M., Snape, C.E., 2008. Thermal stability of polyethyleneimine based carbon dioxide adsorbents and its influence on selection of regeneration strategies. *Microporous Mesoporous Mater.* 116, 506–512.
- Geldart, D., 1973. Types of gas fluidization. *Powder Technol.* 7 (5), 285–292.
- Goeppert, A., Czaun, M., May, R.B., Prakash, G.K.S., Olah, G.A., Narayanan, S.R., 2011. Carbon dioxide capture from the air using a polyamine based regenerable solid adsorbent. *J. Am. Chem. Soc.* 133, 20164–20167.
- Gray, M.L., Hoffman, J.S., Hreha, D.C., Fauth, D.J., Hedges, S.W., Champagne, K.J., Pennline, H.W., 2009. Parametric study of solid amine sorbents for the capture of carbon dioxide. *Energy Fuels* 23, 4840–4844.
- Herzog, H., Assessing the feasibility of capturing CO<sub>2</sub> from the air. Publication No. MIT LFEE. 2003-002 WP, (<http://lfec.mit.edu/publications/>), accessed on 18 November 2013.
- Hicks, J.C., Drese, J.H., Fauth, D.J., Gray, M.L., Qi, G., Jones, C.W., 2008. Designing adsorbents for CO<sub>2</sub> capture from flue gas – hyperbranched aminosilicas capable of capturing CO<sub>2</sub> reversibility. *J. Am. Chem. Soc.* 130, 2902–2903.
- House, K.Z., Baclig, A.C., Ranjan, M., Nierop, E.A., Wilcox, J., Herzog, H.J., 2011. Economic and energetic analysis of capturing CO<sub>2</sub> from ambient air. *PNAS* 108 (51), 20428–20433.
- IEA (International Energy Agency), WEO (World Energy Outlook), released on 12 November, 2013, (<http://www.worldenergyoutlook.org/publications/weo-2013/>).
- Jones, C.W., 2011. CO<sub>2</sub> capture from dilute gases as component of modern global carbon management. *Annu. Rev. Chem. Biomol. Eng.* 2 (1), 31–52.
- Keith, D.W., Ha-duong, M., Stolaroff, J.K., 2006. Climate strategy with CO<sub>2</sub> capture from the air. *Clim. Change* 74, 17–45.
- Keith, D.W., 2009. Why capture CO<sub>2</sub> from the atmosphere? *Science* 325, 1654–1655.
- Kulkarni, A.R., Sholl, D.S., 2012. Analysis of equilibrium-based TSA processes for direct capture of CO<sub>2</sub> from air. *Ind. Eng. Chem. Res.* 51, 8631–8645.
- Lackner, K.S., Ziock, H., Grimes, P., 1999. Carbon dioxide extraction from air: Is it an option? In: *Proceedings of the 24th International Conference on Coal Utilization & Fuel Systems*, Clearwater, FL.
- Lackner, K.S., 2009. Capture of carbon dioxide from ambient air. *Eur. Phys. J. (Spec. Top.)* 176, 93–106.
- Lackner, K.S., Brennan, S., Matter, J.M., Park, A.-H., Wright, A., van der Zwaan, B., 2012. The urgency of the development of CO<sub>2</sub> capture from ambient air. *Proc. Nat. Acad. Sci.* 109 (33), 13156–13162.
- Li, W., Choi, S., Drese, J.H., Hornbostel, M., Krishnan, G., Eisenberger, P.M., Jones, C.W., 2010. Steam-stripping for regeneration of supported amine-based CO<sub>2</sub> adsorbents. *ChemSusChem* 3, 899–903.
- Lu, C., Bai, H., Wu, B., Su, F., Hwang, J.F., 2008. Comparative study of CO<sub>2</sub> capture by carbon nanotubes, activated carbons, and zeolites. *Energy Fuels* 22, 3050–3056.
- Mazzotti, M., Bacocchi, R., Desmond, M.J., Soclow, R.H., 2013. Direct air capture of CO<sub>2</sub> with chemicals: optimization of a two-loop hydroxide carbonate system using a countercurrent air-liquid contactor. *Clim. Change* 118, 119–135.
- McDonald, T.M., Lee, W.R., Mason, J.A., Wiers, B.M., Hong, C.S., Long, J.R., 2012. Capture of carbon dioxide from air and flue gas in the alkylamine-appended metal-organic framework mmen-Mg<sub>2</sub> (dobpdc). *J. Am. Chem. Soc.* 134, 7056–7065.
- Muschelknauf, E., Greif, V., 1997. Cyclone and other gas-solids separators. In: Grace, J.R., Avidan, A.A., Knowlton, T. (Eds.), *Circulating Fluidized Beds*. Blackie Academic, London, pp. 181–213.
- Nikulshina, V., Ayesa, N., Galvez, M.E., Steinfeld, A., 2008. Feasibility of Na-based thermochemical cycles for the capture of CO<sub>2</sub> from air – thermodynamic and thermogravimetric analyses. *Chem. Eng. J.* 140 (1–3), 62–70.
- Nikulshina, V., Gebald, C., Steinfeld, A., 2009. CO<sub>2</sub> capture from atmospheric air via consecutive CaO-carbonation and CaCO<sub>3</sub>-calcination cycles in a fluidized-bed solar reactor. *Chem. Eng. J.* 146 (2), 244–248.
- NOAA: National Oceanic and Atmospheric Administration (NOAA). Trends in Atmospheric Carbon Dioxide. (<http://www.esrl.noaa.gov/gmd/ccgg/trends/>) (accessed on 18 November 2013).
- Rao, A.B., Rubin, E.S., Keith, D.W., Morgan, M.G., 2006. Evaluation of potential cost reductions from improved amine-based CO<sub>2</sub> capture systems. *Energy Policy* 34, 3765–3772.
- Sayari, A., Belmabkhout, Y., 2010. Stabilization of amine-containing CO<sub>2</sub> adsorbents: dramatic effect of water vapor. *J. Am. Chem. Soc.* 132, 6312–6314.
- Siriwardane, R.V., Shen, M.S., Fisher, E.P., Poston, J.A., 2001. Adsorption of CO<sub>2</sub> on molecular sieves and activated carbon. *Energy Fuels* 15, 279–284.
- Sjöström, S., Krutka, H., 2010. Evaluation of solid sorbents as a retrofit technology for CO<sub>2</sub> capture. *Fuel* 89, 1298–1306.
- Solomon, S., Qin, D., Manning, M., et al., 2007. IPCC Fourth Assessment Report (AR4): Climate Change. Cambridge University Press.
- Spector, N.A., Dodge, B.F., 1946. Removal of carbon dioxide from atmospheric air. *Trans. Am. Inst. Chem. Eng.* 42, 827–848.
- Starns, T., Sjöström, S., Krutka, H., Wilson, C., Ivie, M., 2012. Solid sorbents as a retrofit CO<sub>2</sub> capture technology: update on 1 MWe pilot progress, paper # 2012-A-53-MEGA-AWMA. ADA Environmental Solutions ([http://www.adaes.com/wp-content/uploads/2012-A-53-MEGA-AWMA-Solid-Sorbents-as-a-Retrofit-CO2-Capture-Technology-Update-on-1-MW-Pilot-Progress\\_Rev3.pdf](http://www.adaes.com/wp-content/uploads/2012-A-53-MEGA-AWMA-Solid-Sorbents-as-a-Retrofit-CO2-Capture-Technology-Update-on-1-MW-Pilot-Progress_Rev3.pdf)) (accessed on 1 February 2014).
- Tarka, T.J., Ciferno, J.P., Gray, M.L., Fauth, D., 2006. CO<sub>2</sub> capture systems using amine enhanced solid sorbents. In: *Proceedings of the 5th annual conference on carbon capture and sequestration*, Pittsburgh, PA.
- Veneman, R., Li, Z.S., Hogendoorn, J.A., Kersten, S.R.A., Brilman, D.W.F., 2012. Continuous CO<sub>2</sub> capture in a circulating fluidized bed using supported amine sorbents. *Chem. Eng. J.* 208, 18–26.
- Veneman, R., Kamphuis, H., Brilman, D.W.F., 2013. Post-combustion CO<sub>2</sub> capture using supported amine sorbents: a process integration study. *Energy Procedia* 37, 2100–2108.
- Wagner, A., Steen, B., Johansson, G., Zanghellini, E., Jacobsson, P., Johansson, P., 2013. Carbon dioxide capture from ambient air using amine-grafted mesoporous adsorbents. *Int. J. Spectrosc.* (Article ID 690186), <http://dx.doi.org/10.1155/2013/690186>.
- Zhang, W., Liu, H., Sun, C., et al., 2014. Performance of polyethyleneimine-silica adsorbent for post-combustion CO<sub>2</sub> capture in a bubbling fluidized bed. *Chem. Eng. J.* 251, 293–303.