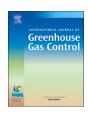
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Cyclic performance evaluation of a polyethylenimine/silica adsorbent with steam regeneration using simulated NGCC flue gas and actual flue gas of a gas-fired boiler in a bubbling fluidized bed reactor



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ARTICLE INFO

Keywords: polyethylenimine/silica adsorbent Cyclic working performance Post-combustion CO₂ capture Steam regeneration Actual flue gas

ABSTRACT

To accelerate the deployment of Carbon Capture and Storage (CCS) based on the solid amine adsorbents towards a practical scale application relevant to Natural Gas Combined Cycle (NGCC) power plants, this study has evaluated the cyclic performance of a polyethylenimine/silica adsorbent of kg scale in a laboratory scale bubbling fluidized bed reactor. A high volumetric concentration 80-90 vol% of steam mixed with N_2 and CO_2 has been used as the stripping gas during a typical temperature swing adsorption (TSA) cycle. Both the simulated NGCC flue gas and the actual flue gas from a domestic gas boiler have been used as the feed gas of the CO_2 capture tests with the solid adsorbent. Various characterization has been carried out to elucidate the possible reasons for the initial capacity decline under the steam regeneration conditions. The effect of presence of CO_2 in the stripping gas has also been studied by comparing the working capacities using different regeneration strategies. It has been demonstrated that the breakthrough and equilibrium CO_2 adsorption capacities can be stabilized at approximately 5.9 wt% and 8.6 wt%, respectively, using steam regeneration for both the simulated and actual natural gas boiler flue gases. However, using a concentration of 15 vol% CO_2 in the stripping gas has resulted in a significantly low working capacity at a level of 1.5 wt%, most likely due to the incomplete CO_2 desorption and degradation in a CO_2 containing environment.

1. Introduction

 ${\rm CO}_2$ concentration in the atmosphere has increased significantly over the past century from the preindustrial level of about 280 ppmv to a recently recorded level of 409.95 ppmv in August 2019 (NOAA, 2019). NASA's research laboratory estimated that if fossil-fuel burning continues at a business-as-usual rate over the next few centuries, ${\rm CO}_2$ will continue to rise to levels of order of 1500 ppmv (NASA, 2017). Up to now there are only a few industrial-scale post-combustion capture (PCC) systems which have been commercialized using aqueous amine based absorption technologies. Extensive research and deployment of CCS in large scales are urgently required to achieve the objectives set by the Paris Agreement (COP Paris Agreement, 2020). The more recent IPCC special report (IPCC, 2018) has highlighted a number of climate change impacts that could be avoided by limiting global warming to 1.5 °C compared to 2 °C. Global net human-caused emissions of carbon dioxide (CO₂) would need to fall by about 45 % from 2010 levels by

2030, reaching 'net zero' around 2050.

The application of CCS technologies to date have mainly focused on coal-fired power plants. However, according to the report published by IEA (International Energy Agency) (2017), the role of natural gas-fired power generation in the 2 °C Scenario (2DS) has been identified as a lower-carbon alternative to coal-fired generation. Coal-to-gas switching will be of particular importance in the short term until 2025-30 in the 2DS. It was projected that natural gas will overtake coal in 2030 to become the second-largest fuel in the global energy mix (IEA (International Energy Agency), 2018).

The key features of typical supercritical coal-fired and natural gas-fired power plants are summarized in Table 1. The composition of the flue gas of a Natural Gas Combined Cycle (NGCC) power plant differs much from that of a coal-fired power plant in terms of much lower CO_2 concentration and much higher O_2 concentration. Carbon capture from the NGCC power plant flue gas requires solvents or adsorbents with much higher efficiency and higher resistance to oxidative degradation.

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Table 1
Key features of typical supercritical coal-fired and natural gas-fired power plants (NETL, 2010).

	Coal	NGCC
Net Power (MW)	550	555
Efficiency (%, HHV)	39.3	50.2
Flue gas composition		
CO ₂ (vol%)	13.53	4.04
H ₂ O (vol%)	15.17	8.67
O ₂ (vol%)	2.40	12.09
N ₂ (vol%)	68.08	74.32
Flue gas flow rate (tonne/hr)	2138	3231

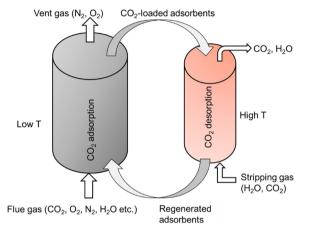


Fig. 1. Conceptual design of a solid adsorbent based ${\rm CO}_2$ capture system using Temperature Swing Adsorption (TSA).

Aqueous amine scrubbing has been the most mature PCC technology, although it suffers from a series of technical and economic issues. Solid adsorbent based CO_2 capture systems have been regarded as a promising alternative to replace the conventional aqueous amine scrubbing (Choi et al., 2009; Nelson et al., 2017; Yaumi et al., 2017; Salaudeen et al., 2018 and Azarabadi and Lackner, 2019). In order to achieve continuous CO_2 capture with a high capture rate and high purity of the product gas, a conceptual solid adsorbent based carbon capture system (Fig. 1) mainly consisting of a circulating fluidized bed (CFB) adsorber and a bubbling fluidized bed (BFB) desorber has been proposed (Zhang et al., 2017).

Up to now, most research interests have been focusing on the material design and development of high capacity adsorbents (Choi et al., 2009; Wang et al., 2014; Lee and Park, 2015; Yaumi et al., 2017; Nie et al., 2018; Sun et al., 2018). There have been very limited research addressing the effects of the regeneration conditions on the processrelated performance indicators such as working capacity, thermal stability and desorption kinetics. Temperature Swing Adsorption (TSA) has been determined to be an effective means to provide sufficient driving force to achieve a fast and thorough regeneration for amine based solid adsorbents. Using stripping gas during the regeneration provides another driving force originated from the gradient of CO₂ partial pressure. Using CO2 and steam as the stripping gas for regeneration has been recognized as two potential practical approaches to improve the product purity. Some research has been reported on the sorbent regeneration in a pure CO2 stream (Kim et al., 2005; Drage et al., 2008; Radosz et al., 2008 and Ntiamoah et al., 2016). A few studies in relation to steam regeneration have also been carried out. For example, the stability of adsorbents upon long time exposure to steam was evaluated for amine based adsorbents using different supports (Li et al., 2010a; Chaikittisilp et al., 2011; Wilfong et al., 2015). The impact of steam regeneration on amine supported adsorbents was investigated in fixed bed reactors (Li et al., 2010b; Hammache et al., 2013; Sandhu

et al., 2016). The effect of CO_2 or steam partial pressure on the CO_2 capture efficiency was studied in a two-interconnected bubbling fluidized bed system (Kim et al., 2011). Recently, the feasibility of a TSA process based on steam stripping in combination with structured carbon adsorbents was evaluated (Plaza et al., 2017). Various regeneration conditions in batch experiments including vacuum swing adsorption were experimentally studied for the amine-grafted mesoporous silica (Serna-Guerrero et al., 2010).

Research on solid amine adsorbents at a process level is still at its early stage comparing to the aqueous amines. Despite of the large number of publications on solid sorbents, there still exist apparent deficiencies in most of the current research:

- Most research focuses on the development and testing of a certain sorbent using milligram quantities of sorbent in a TGA or small fixed bed reactor;
- (2) Pure N₂ is used as the stripping gas for a thorough regeneration. However, this is practically not feasible as this will produce a mixture of N₂ and CO₂ in the product gas;
- (3) A mixture of CO_2 and N_2 has been used to simulate the flue gas. However the effect of other gas components in the actual flue gas on the solid sorbents has not been addressed.

This study has made several extensive attempts to develop the research methodologies and to investigate the effects of practically feasible regeneration strategies on the cyclic performance of the solid adsorbent. In a laboratory scale bubbling fluidized bed (BFB) reactor, with kg scale adsorbents preloaded, continuous TSA cycles have been carried out using various configurations of stripping gas such as pure N_2 , a mixture of N_2 and steam, and a mixture of CO_2 and steam. A simulated NGCC flue gas as well as the actual flue gas from a domestic natural gas boiler have been used to verify if the impurities in the actual flue gas have any detrimental effects on the performance of the solid sorbent. To the best of our knowledge, this study presents the first original attempt to investigate the performance of amine-based adsorbents using actual flue gas with practically feasible regeneration strategies in a laboratory scale fluidized bed reactor.

2. Experimental

2.1. Flue gas CO2 capture facilities

A laboratory scale Bubbling Fluidized Bed (BFB) reactor system has been designed and purpose-built to investigate the CO_2 capture performance of various solid adsorbents. The configurations of the BFB and evaluation of an amine-based adsorbent in capturing CO_2 from simulated flue gases and ambient air can be found in previous publications (Zhang et al., 2014a; and 2014b). In this study, several modifications and developments have been made so that the BFB system can be used for multi-purpose research on carbon capture. First of all, the free board section of the fluidized bed has been extended, resulting in an increase of the total bed height from 1.7 m to 2.1 m. This is to alleviate the entrainment of fine particles at the specific superficial velocities used in the experiments. A heat exchanger tube is inserted in the bed from the top flange to shorten the time needed for cooling down the BFB back to the room temperature.

As illustrated in Fig. 2, at the bottom inlet of the BFB, N_2 and CO_2 from gas cylinders, together with compressed air, are regulated by the individual mass flow controllers to simulate the flue gas from a NGCC power plant with typical gas composition. The simulated flue gas is humidified to carry a certain level of moisture by passing through a moisture saturator operated under a corresponding temperature. A dedicated steam generator is installed to provide steam for stripping use during regeneration. The flow rate of the steam has been calibrated by the needle valve.

A real flue gas supply system has been designed and established in

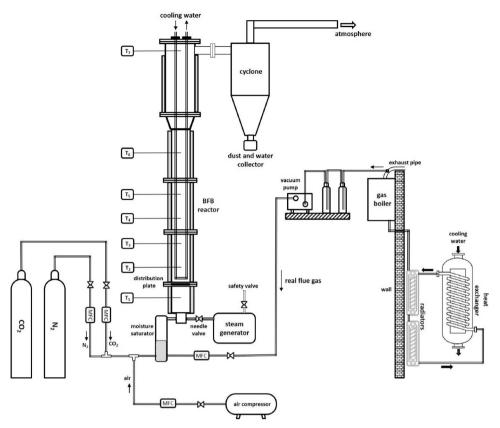


Fig. 2. Bubbling fluidized bed reactor with steam generator and actual flue gas feed system.

order to investigate the performance of the selected adsorbent under the actual flue gas condition. A small stream of the actual flue gas was extracted from the exhaust pipe of a domestic natural gas boiler by a vacuum pump. The moisture contained in the flue gas was removed using ice bath before the flue gas was fed into the BFB. Two large radiators and a heat exchanger tank with continuously running through cooling water were used to dump the heat so that the gas boiler could run continuously during each CO_2 capture test.

2.2. Materials

The adsorbent used in this study was synthesised by impregnating a mass ratio of 40% PEI (Polyethylenimine, supplied by Sigma-Aldrich, UK) into an inorganic mesoporous silica support with BET surface area of approximately 250 m²/g, pore volume of 1.7 cc/g and mean pore diameter of approximately 20 nm. The PEI has a molecular mass (MM) of 1800 in hyperbranched forms. The physical properties including diameter, density, shape, surface morphology, BET surface area, pore information, as well as fluidization behaviour of the PEI-silica adsorbent can be found in previous publications (Zhang et al., 2014b, 2016, 2017). Zhang et al. (2016) and Zhang et al. (2017) highlighted the advantages of the PEI-silica adsorbent over traditional MEA technology in terms of regeneration heat. The regeneration heat for the proposed CFB (adsorber) - BFB (desorber) CO₂ capture system using the PEI/silica adsorbent was found to be around 3 GJ/tCO₂, in comparison with 3.9 GJ/tCO₂ for a typical aqueous 30 % MEA CO₂ capture system and 3.3 GJ/tCO2 for an advanced MEA system (Zhang et al., 2017).

2.3. Experimental procedures and conditions

As the single BFB system described in Section 2.1 was used for both adsorption and desorption, a typical adsorption/desorption cycle based on Temperature Swing Adsorption (TSA) was carried out in five steps:

(1) bed preheating from room temperature to the adsorption temperature; (2) CO_2 adsorption using the simulated or actual flue gas; (3) bed preheating to the desorption temperature; (4) CO_2 desorption using selected stripping gas; and (5) cooling of the bed.

The experimental conditions are summarised in Table 2. Fresh batches of 2 kg PEI/silica adsorbent were used for continuous TSA cycles with steam regeneration under the simulated and the actual flue gas conditions. Another degraded batch of 1.2 kg PEI/silica adsorbent was used for TSA cycles using a mixture of steam and CO_2 as the stripping gas. The simulated and actual flue gas both have a volumetric composition of 5 vol% CO_2 , 12 vol% O_2 (dry basis) balanced by N_2 and a moisture content of around 9 vol% (wet basis), representing the typical composition of the flue gas from NGCC power plants (Table 1). The flow rates of the flue gas and stripping gas were chosen to ensure a sufficient fluidization of bed materials, while at the same time the

Table 2 Experimental conditions for carbon capture with steam/N $_2$ and CO_2 regeneration.

Adsorption	
Mass of PEI-silica adsorbent in bed (kg)	Fresh batch: 2.0
	Degraded batch: 1.2
CO ₂ concentration (vol%, dry basis)	5
O2 concentration (vol%, dry basis)	12
Moisture concentration (vol%, wet basis)	9 (saturated at 40 °C)
Simulated or actual flue gas flow rate (L/min, 20 °C, 1 atm)	8
Adsorption (bed) temperature (°C)	60
Desorption	
Stripping gas flow rate (L/min)	Steam: 10 (100 °C, 1 atm)
	N ₂ : 2 (20 °C, 1 atm)
	or CO ₂ : 1.4 (20 °C, 1 atm)
Desorption (bed) temperature (°C)	Fresh batch: 120
	Degraded batch: 130

superficial velocity was not too high to cause significant entrainment of fine particles. A small stream of N2 (2 L/min at room temperature), was mixed with the saturated steam (10 L/min at 100 °C) to constitute the stripping gas during steam regeneration. Unlike TGA tests where the CO₂ adsorption capacities can be determined directly by the weight difference before and after adsorption, the total volume of CO2 adsorbed or desorbed during the TSA cycle can only be calculated by integrating the volume flow rate of CO_2 over the adsorption or desorption time period. If pure steam was used as stripping gas, the mixture product gas after desorption would contain only steam and CO2. With steam being condensed before entering the gas analyser, CO2 concentrations detected by the gas analyser would always be 100 % during the desorption process. This would make it impossible to monitor the progress of the desorption process and determine when desorption was completed or near its completion. Therefore, the addition of a small flow of N2 in the stripping gas was used to provide the possibility to observe the CO2 concentration variations during desorption. A small stream of CO2 (1.4 L/min at room temperature) was mixed with the steam to study the effect of presence of CO2 in the stripping gas on the degradation behaviour. The volumetric concentration of steam in the stripping gas was 80 vol% for steam/N2 mixture and 85 vol% for steam/ CO₂ mixture. The desorption temperature of 120 °C used for fresh batch tests was slightly lower than 130 °C chosen for previous tests (Zhang et al., 2014a,b). Thermocouples were attached directly on the reactor walls of different sections and the measured temperature values were used as the feedback to the PIV controllers of the external heaters. The external heaters automatically turned off immediately once the detected wall temperatures reached the set values. This was to prevent over-heating so that the thermal degradation and amine vaporization during the preheating and CO2 desorption stages could be minimized. Seven more thermocouples were inserted into the centre of the reactor column to measure the bed/sorbent temperature or the reactor temperature.

The CO_2 adsorption capacities for the fresh and spent samples were also characterized by using Thermogravimetric Analysis (TGA) (TA Q500) and the results were used to compare with those obtained from the BFB reactor. In a typical TGA test, around 20 mg of a fresh or spent sample was loaded into TGA and was heated up to 105 °C to remove any pre-adsorbed CO_2 and moisture by a purge gas of N_2 at a flow rate of 100 ml/min. The sample was then cooled down and maintained at the desired adsorption temperature of 60 °C for 2 h when the simulated flue gas (5 % CO_2 balanced with N_2) at a flow rate of 100 ml/min was fed into the TGA furnace. Subsequently, the TGA furnace was heated up to the desorption temperature of 120 °C at a heating rate of 10 °C/min and the sample was maintained at this temperature for 3 h with 100 ml/min of N_2 as the purge gas.

3. Results and discussion

The performance indicators of cyclic behaviour of the PEI/silica adsorbent investigated in this study include the $\rm CO_2$ adsorption breakthrough capacity, equilibrium capacity, thermal stability and degradation. Special efforts have been made on revealing the behaviour of the adsorbent under the conditions of steam stripping and $\rm CO_2$ capture from the actual flue gas.

3.1. TSA cycles with steam/ N_2 regeneration using simulated flue gas

Steam stripping is potentially a more promising strategy for adsorbent regeneration as it provides both thermal swing driving force and partial pressure driving force. Product gas with high CO_2 purity can easily be yielded by condensing the steam in the gas mixture. Therefore, TSA cycles using the simulated flue gas during adsorption and steam/ N_2 stripping during desorption have been first carried out to examine the effect of high concentration of steam on the cyclic performance of the PEI/silica adsorbent. Variations of bed pressure drop, CO_2

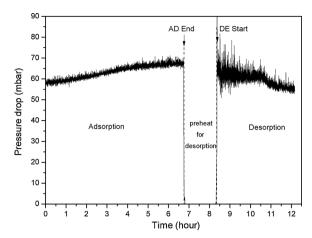


Fig. 3. Variation of pressure drop during a TSA cycle with steam/ N_2 regeneration.

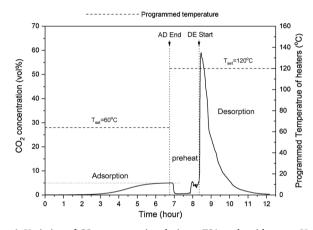


Fig. 4. Variation of ${\rm CO_2}$ concentration during a TSA cycle with steam/N $_2$ regeneration.

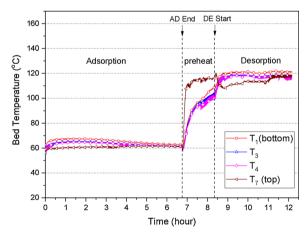


Fig. 5. Bed temperature profiles during a TSA cycle with steam/ N_2 regeneration.

concentration at the exit of the BFB and bed temperature profiles for a typical TSA cycle with steam/ N_2 regeneration are illustrated in Figs. 3–5. In a TSA cycle test, the BFB was firstly preheated to the target adsorption temperature of 60 °C in the pure N_2 environment, then the simulated flue gas was switched on and introduced to the bottom of the BFB to initiate the CO_2 adsorption. Depending on the mass of the PEI/ silica adsorbent batch loaded in the bed (2 kg in this series of tests), the adsorption process usually took nearly 7 h to finish when the CO_2

concentration at the exit of BFB approached the inlet feed level of 5 vol % (Fig. 4). It was considered that by the end of the adsorption process the bed materials had achieved a saturated condition in CO₂ adsorption. The equilibrium CO2 adsorption capacity was thus calculated by integrating the amount of adsorbed CO_2 over the adsorption time, divided by the mass of the loaded PEI/silica adsorbent. The breakthrough point in this study is defined according to a capture rate of 90 % when the detected CO2 concentration at the exit of BFB reaches 10 % of the inlet level. The CO2 uptake up to the breakthrough point is denoted as the "breakthrough capacity". Due to the accumulation of CO2 molecules adsorbed on the adsorbent surface, the bed pressure drop has shown a clear increasing tendency in Fig. 3, which is in accordance with the increase of bed mass. Fig. 5 illustrates the temperature profiles at different heights of the BFB, with T₁ showing the temperature of the bottom and T₇ showing the top of the bed. Except for the top zone in the freeboard section where the particle concentration was low, bed temperatures in all other zones have shown a slight increase of around 6-7 °C in the first several hours during adsorption. This temperature increase was attributed to the heat of adsorption released during the exothermal CO2 adsorption reaction with PEI/silica adsorbent.

The bed materials were preheated to the desorption temperature after the adsorption process had finished. Steam could not be introduced into the bed during preheating as this would lead to steam being condensed and mixed with the sorbent particles when the bed temperature was lower than 100 °C. Any other sweeping gas such as N2 could not be used either as this would initiate the desorption process by providing a pressure gradient driving force. Therefore, the bed had to be kept static during the preheating without any gas passing through the bed. To prevent any possible steam condensation in the bed in the subsequent desorption process with steam, the temperatures in all the zones of the bed had to be elevated to higher than 100 °C. The preheating took around two hours to finish as the bed was not fluidized during this stage and the required temperature increase mainly depended on the slow conductive heat transfer from external heaters to the bed materials via the stainless reactor wall. It should be noted that preheating was a necessary step based on current batch configurations as the BFB was used for both adsorption and desorption. While in a practical system, a separate regenerator is operated under desorption temperature with solid adsorbents circulating between the adsorber and the regenerator for continuous CO2 capture and adsorbent regeneration. There was little amount of CO₂ desorbed during the preheating (as shown in Fig. 4) as the concentration of CO₂ was based on a small flow rate (around 0.5 L/min) which was extracted by the pumps of the gas analyser. Desorption process in a fixed bed was largely prohibited without the aid of stripping gas due to the local environment with high CO₂ concentration, even though the bed temperature has been elevated.

The stripping gas consisting of 80 vol% steam and 20 vol% $\rm N_2$ was switched on to start the desorption process, which lasted for around 4 h until the detected $\rm CO_2$ concentration approached zero. The bed pressure drop curves during desorption in Fig. 3 have shown a clear decreasing tendency with strong fluctuations due to the higher superficial gas velocity at the higher bed temperature. Most zones of the BFB were maintained at the desorption temperature of 120 °C, as shown in Fig. 5. At the end of each cycle with steam regeneration, the water condensed in the cyclone and collected at the bottom of the cyclone was weighed and compared with the consumption of steam during this cycle. The comparison showed a good consistency which implied that negligible steam condensation had occurred in the BFB.

Fig. 6 illustrates the cyclic breakthrough and equilibrium capacities for continuous 9 cycles with steam/ N_2 regeneration using the simulated flue gas. The first 4 cycles have shown a noticeable decline in the equilibrium capacities, from 9.8 wt% for the first cycle to 8.7 wt% for the 4th cycle, indicating a relative 11.5 % loss in the equilibrium capacities. This relative loss was slightly higher than the relative 5 % loss which was observed in the previous tests (Zhang et al., 2016) using moist N_2 (containing around 9 vol% moisture) as the stripping gas.

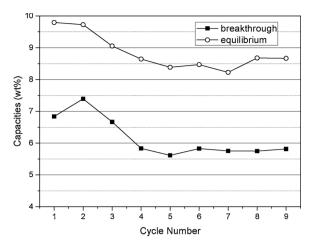


Fig. 6. Cyclic capacities with steam/ N_2 regeneration using simulated flue gas.

Similarly, Hammache et al. (2013) also found a relative CO₂ uptake loss of around 15.6 % during the first 4 cycles using a mixture of 90 vol% steam balanced by He as the stripping gas at the desorption temperature of 105 °C. Entrainment of fine adsorbent particles and evaporation of light and unstable amine groups might be two reasons for this initial loss. More characterization needs to be carried out to find out other possible reasons, which will be discussed in the next section. As shown in Fig. 6, the decline tendency has however stopped with capacities getting stable after the 4th cycle. The stabilized equilibrium capacity of 8.6 wt% and breakthrough capacity of 5.9 wt% were comparable to the previous results with moist N2 regeneration where equilibrium capacity was 9.5 wt% and breakthrough capacity was 7 wt% (Zhang et al., 2014b). The above comparison demonstrated that using a large concentration of steam up to 80 vol% in the stripping gas has not exposed a significantly adverse effect on the cyclic adsorption performance for the PEI/silica adsorbent.

The effect of flow rate of the stripping gas on desorption kinetics has also been investigated in this study. As shown in Fig. 7, the steam flow rate was increased from 10 L/min (for cycle 1–6) to 19 L/min (for cycle 10 and 11). Accordingly, the mole fraction of steam in the stripping gas increased from 80 vol% to 90 vol% while keeping the flow rate of $\rm N_2$ unchanged. The desorption time taken to accomplish 80 % of the complete $\rm CO_2$ desorption was around 45 min for the lower flow rate, compared to 30 min for the higher flow rate. To accomplish 90 % of the complete $\rm CO_2$ desorption, the desorption time taken was 75 min and 45 min for the lower and higher flow rates, respectively. These results indicate that increasing the flow rate of the stripping gas can

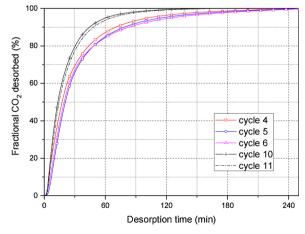


Fig. 7. Effect of flow rate of the stripping gas on desorption kinetics (12 L/min for cycle 4–6, 21 L/min for cycle 10 and 11).

Table 3Characterization of fresh and used PEI/silica adsorbent samples following TSA cycles with steam regeneration.

	0C	3C	6C	9C
BET surface area (m ² /g) Pore Volume (cm ³ /g) Pore size (nm)	53.9 0.27 12.2	36.1 0.22 14.8	35.5 0.24 16.4	39.9 0.28 16.6
CO ₂ adsorption capacity ^a (wt%)	9.87	8.91	8.77	8.41

^a CO₂ adsorption capacity in this table was measured using TGA.

significantly improve the desorption kinetics, mainly due to the fact that a higher flow rate can purge CO_2 molecules off from the adsorbent surface more effectively, thus providing a higher CO_2 partial pressure gradient and a stronger driving force for desorption. With a higher flow rate, the solid residence time required to achieve a thorough desorption in the regenerator can be shortened and therefore the bed inventory, regenerator size can also be reduced.

3.2. Sample characterization after steam/ N_2 regeneration

In order to evaluate the impact of steam regeneration on the adsorbent performance, various techniques have been used to characterize the adsorbent samples subjected to different number of cycles. The results are compared with the original fresh samples. In this section, the fresh sample and those which have undergone 3, 6 and 9 TSA cycles with steam regeneration are denoted as OC, 3C, 6C and 9C respectively. N2 physisorption isotherms at 77 K were used to characterize the BET surface area, pore volume and pore size of the fresh and used samples. The results presented in Table 3 indicate that the impregnation of PEI onto the silica support has resulted in a significant loss in the surface area from 250 m²/g to 53.9 m²/g, a massive decrease in the pore volume from 1.7 cm³/g to 0.27 cm³/g and a decrease in the pore size from 20 nm to 12.2 nm. Both BET surface areas and pore sizes showed noticeable changes for the spent samples compared with the fresh sample. The BET surface area decreased from 53.9 m²/g to 36.1 m²/g after the first 3 cycles followed by no significant further changes up to 9 cycles. The pore sizes gradually increased from 12.2 nm to 16.6 nm after 9 cycles. The pore volume however didn't show any obvious changes up to 9 cycles in this study. For comparison, Hammache et al. (2013) found that the BET surface area decreased from original 53 m²/g to 35 m²/g after 6 steam cycles while the pore volume decreased from original 0.43 cm³/g to 0.28 cm³/g after 6 steam cycles. On the contrary, Sandhu et al. (2016) found almost no changes in surface area and pore volume for their PEI/silica samples after 5 h of steam treatment. The inconsistency between this study and other studies (Hammache et al., 2013; Sandhu et al., 2016) may be attributed to the different experimental procedures and configurations, and different regeneration conditions such as desorption temperature and stripping gas compositions.

The increase in pore size found in this study may imply an amine loss from the internal pores due to evaporation and/or leaching of the amines from the support in the steam abundant environment. From the observation and regular checks inside the BFB furnace between the cycles, small amount of dark coloured and sticky condensed residues were found on the inner reactor wall. TGA characterization of these residues gave the results of 60.3 wt% for organic contents which was much higher than that in the adsorbent samples (around 42.8 wt%). This indicates that the evaporation of amine and condensation of amine vapour did happen in the reactor.

The apparent decrease in BET surface area after 3 cycles was possibly attributed to the blockage of the pores which was caused by condensation of amine contents on the adsorbent surface during steam regeneration. The loss of active $\rm CO_2$ adsorption sites has led to the loss in the adsorption capacity, as verified by common TGA tests on the fresh and spent samples under simulated NGCC flue gas conditions. The TGA results of equilibrium capacities in Table 3 for all samples showed

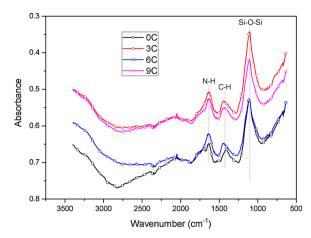


Fig. 8. FTIR spectra of the PEI/silica adsorbents subjected to a certain number of TSA cycles with steam/N₂ regeneration.

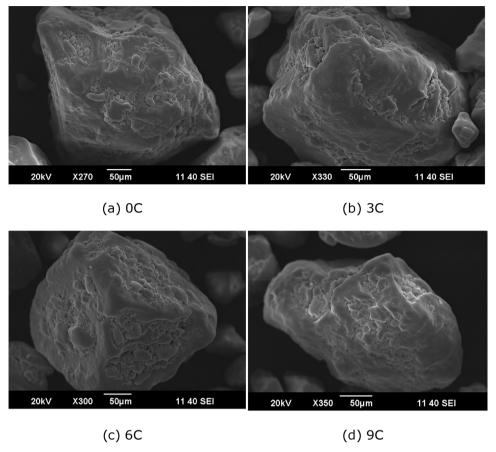
a very good consistency with those obtained in the BFB tests (Fig. 6).

To verify if the changes in the nature of the amines could be one possible reason for the loss of adsorption capacity, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) analysis has been carried out for the fresh and spent samples. Drage et al. (2008) reported the formation of urea linkages when PEI/silica adsorbents were exposed to pure CO₂ at temperatures higher than 135 °C under dry conditions. Similarly, Sayari and Belmabkhout (2010) found the formation of urea linkages when the amine adsorbents were exposed to pure CO2 under dry conditions. Bacsik et al. (2010) also identified the carbonyl stretch at 1701 cm⁻¹ in FTIR spectra as an evidence of formation of carbamic acid groups associated with the reaction between amines and CO₂. Differing from the observations of the above-mentioned studies using dry regeneration conditions, the FTIR results shown in Fig. 8 didn't however give any evidence of urea formation, carbonyl stretches or other changes in the chemistry of PEI for the spent samples after 9 TSA cycles with steam regeneration.

The SEM images of the fresh and spent samples are shown in Fig. 9 where no significant changes have been observed on the surface morphology after a number of TSA cycles with steam/ N_2 regeneration. Furthermore, a comparison of these images shows there were no noticeable attrition signs after many hours of fluidization in the BFB under the working conditions used in this study.

3.3. TSA cycles with steam/CO₂ regeneration using simulated flue gas

The presence of CO2 in the stripping gas increases the CO2 partial pressure, and as a result, the desorption of CO2 molecules from the adsorbent surface may be significantly hindered. To provide sufficient driving force for a thorough desorption, higher desorption temperature may have to be used at a higher risk of more serious thermal and CO2 induced degradation. To investigate the effect of CO₂ in the stripping gas on the adsorbent performance, TSA cycles with a mixture of steam and CO₂ as the stripping gas have been carried out. The volumetric flow rates of steam and CO₂ were fixed at 10 L/min (at 100 °C and 1 atm) and 1.4 L/min (at 20 °C, 1 atm), respectively, resulting in a volumetric 85 vol% of steam concentration. A batch of 1.2 kg PEI/silica adsorbents which had undergone more than 60 cycles from previous tests (Zhang et al., 2014b) was used for this study. Although the batch had been partially degraded due to amine loss in the first several cycles, the cyclic adsorption capacities were stabilized when moist N2 was used during desorption (Zhang et al., 2014b). Therefore, any further significant degradation observed in this study can be attributed to the introduction of steam and/or CO₂ in the stripping gas. To facilitate the desorption process, the desorption temperature was set to 130 °C, which was 10 °C higher than that used in the steam/N₂ regeneration tests in Section 3.1.



 $\textbf{Fig. 9.} \ \ \text{SEM images of the PEI/silica adsorbents subjected to a certain number of TSA cycles with steam/N_2 regeneration.}$

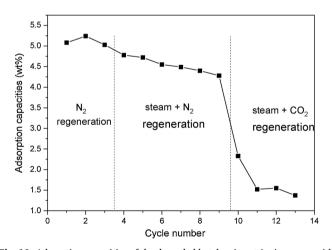


Fig. 10. Adsorption capacities of the degraded batch using stripping gases with different compositions.

Pure N_2 (with 9 vol% moisture) was used as the stripping gas for the first 3 cycles to establish a baseline for comparison, followed by 6 cycles of steam/ N_2 regeneration and 4 cycles of steam/ CO_2 regeneration. The results are illustrated in Fig. 10.

The equilibrium adsorption capacities of the first 3 cycles with moist N_2 regeneration was around 5.0 wt%, which was used as a reference value. The following 6 cycles with steam/ N_2 regeneration, however, haven't shown a similar levelling off tendency as has been observed in the tests shown in Fig. 6. The most possible reason was that the desorption temperature of 130 °C used for this degraded batch may cause more significant thermal degradation especially during the process of preheating (for desorption). The subsequent cycles 10–13 with steam

and CO_2 as the stripping gas have resulted in a dramatic decline in the adsorption capacities. With 15 vol% of CO_2 in the stripping gas for only 4 TSA cycles, the adsorption capacities have dropped significantly to only about 1.5 wt% (Fig. 10). The results have demonstrated an undoubted detrimental effect of CO_2 in the stripping gas on the cyclic performance of the PEI/silica adsorbent.

Fig. 11 shows the CO_2 concentration detected during the preheating stage from room temperature to the adsorption temperature using pure N_2 as the purge gas. At room temperature before preheating started, a sharp peak of CO_2 release was observed once the purge gas was switched on. During the preheating, more CO_2 has been released with the temperature increase. This implies that the steam/ CO_2 regeneration in

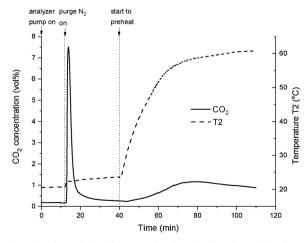


Fig. 11. CO₂ release during the stage of preheating (for adsorption) after a TSA cycle with steam/CO₂ regeneration.

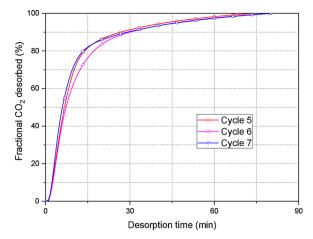


Fig. 12. Desorption kinetics for cycles with Steam/ N_2 regeneration using degraded batch under 130 °C desorption temperature. (flow rate of the stripping gas was 12 L/min).

the previous cycle has led to an incomplete desorption. The ultimate low adsorption capacities in cycle 10–13 cannot simply be attributed to the severe and irreversible thermal or CO_2 induced degradation. They can also be accounted by the loss in availability of CO_2 adsorption sites due to incomplete desorption in the previous cycle. Therefore, "Working capacity" is a better term to describe the adsorption capacity under specific regeneration conditions as the cyclic performance of an adsorbent depends on both adsorption and desorption working conditions. A further increase in desorption temperature might lead to a more thorough desorption and a higher working capacity, however it may also cause much more serious thermal and CO_2 induced degradation. The difficulty in choosing proper regeneration conditions such as the desorption temperature makes steam/ CO_2 regeneration much less favourable than steam/ N_2 regeneration.

Desorption kinetics for three typical cycles 5–7 with steam/N $_2$ regeneration using the degraded batch under 130 °C desorption temperature is illustrated in Fig. 12. The average desorption time taken to accomplish a fractional CO $_2$ desorption of 80 % and 90 % was 15 min and 30 min respectively, in comparison with 45 min and 75 min required for the steam/N $_2$ regeneration cycles under 120 °C desorption temperature (shown in Fig. 7). It was evident that increasing desorption temperature by only 10 °C can significantly improve the desorption kinetics. Therefore, selection of an appropriate desorption temperature for the PEI/silica adsorbent used in this study is of extreme importance. It has to be determined by considering various process related parameters including thermal stability, working capacity, degradation rate, and desorption kinetics.

3.4. TSA cycles with steam/ N_2 regeneration using actual flue gas

In comparison with aqueous amine based carbon capture technologies which have been commercialized, deployment of industrial scale carbon capture process using solid adsorbents is still far away from reality. Generally, simulated flue gases containing 5-15 vol% of $\rm CO_2$ balanced with an inert gas have been used in carbon capture tests by most researchers. In comparison, the performance of the solid adsorbents capturing $\rm CO_2$ from actual flue gases has only been investigated by a few studies. For example, the demonstration of a pilot scale of up to 10 MW $\rm CO_2$ capture system using regenerable potassium carbonate sorbents has been attempted for capturing a slip stream of the actual flue gas from a coal-fired circulating fluidized bed combustor (Park et al., 2011). ADA Environmental Solutions screened over 100 materials using a laboratory fixed bed system with a simulated flue gas and also with an actual flue gas on a 1 kW pilot scale testing rig (Sjostrom et al., 2011). Rezaei and Jones (2013) addressed the effects of

impurities (such as NO, NO₂, SO₂ etc.) present in the actual flue gas on the CO_2 adsorption performance. The effect of the actual flue gas on the performance of amine based solid adsorbents, especially when a practical regeneration strategy is implemented, has not been reported so far. Therefore, an actual flue gas generation and feeding system was established and integrated with the BFB CO_2 capture rig in this study.

A standard domestic central heating system comprising a natural gas boiler, a recirculating pump and two large radiator panels was installed in the same laboratory of the BFB carbon capture rig. In order to produce the flue gas with stabile gas composition for several continuous hours during the adsorption tests, the radiator panels were installed on the outside walls so that the generated heat could be completely dumped. Additionally, a heat exchanger tank with cooling water running through continuously was used to cool down the recirculating water before returning to the gas boiler. These measures ensured the gas boiler to be working at a full design load. A stream of exhaust flue gas was extracted from the exhaust pipe and cooled down immediately using ice bath to remove moisture and prevent the moisture condensation along the flue gas line which may lead to possible blockage. The dried flue gas was then introduced into the moisture saturator to carry a controlled level of moisture, resulting in a moist flue gas to be fed into the BFB adsorber. The compositions of the actual flue gas was further regulated by diluting with compressed air at a specific mixing ratio. The gas compositions were continuously monitored by the gas analysers for at least 3 h and the results showed that the CO_2 and O_2 concentrations were stabilized at 5 vol% and 12.5 vol%, respectively, which were at the same levels as in the simulated flue gas used in previous tests.

To compare the cyclic performance of PEI/silica adsorbent using actual flue gas with that using the simulated flue gas, another fresh batch of 2 kg PEI/silica adsorbent was loaded into the BFB and continuous 10 cycles of CO₂ capture tests with steam/N₂ regeneration have been carried out using the same adsorption and desorption conditions listed in Table 2. As the multiple gas analyser used for CO₂ monitoring also has a measurement module for NOx, the evolution of NOx concentration during a typical TSA cycle with steam/N2 regeneration has also been recorded by the analyser, as shown in Fig. 13. The NOx level in the feed flue gas was also plotted in the figure as a reference. The detected NOx concentrations levelled at around 5 ppm during the flue gas adsorption process, indicating an approximate capture rate of 58 % for NOx adsorption comparing with the initial NOx level in the feed flue gas which is around 12 ppm. In comparison with CO₂ variations during adsorption process illustrated in Fig. 4, the breakthrough of NOx occurred much faster and the equilibrium adsorption of NOx could not be achieved within 7 h of adsorption due to the much lower concentration of NOx in the feed gas. When the bed temperature was elevated to 120 °C for CO2 desorption, NOx desorption was also identified by a sharp

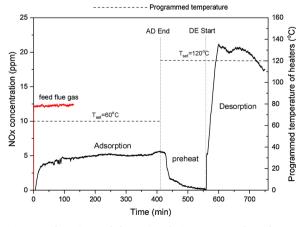


Fig. 13. NOx adsorption and desorption during a TSA cycle with steam/ N_2 regeneration.

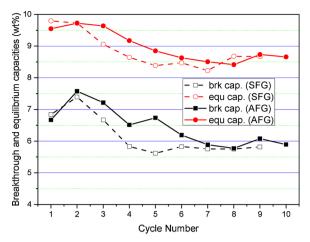


Fig. 14. Cyclic adsorption capacities under actual flue gas (AFG) compared with those under simulated flue gas (SFG).

increase in its concentration. It was evident that the co-adsorption and co-desorption of NOx took place at the same time with CO_2 adsorption and desorption in the temperature swing process. The co-adsorption of acid gases such as CO_2 and NOx on some physical adsorbents has been investigated (such as by Saha et al., 2010), however, the behaviour of co-adsorption on amine-based adsorbents has not been reported so far. Although this is not the main research objective in this study, the results presented in Fig. 13 have revealed the potential of the PEI/silica adsorbent as an effective multi-pollutant adsorption material.

As illustrated in Fig. 14, the cyclic adsorption capacities under actual flue gas also showed an initial decline in the first several cycles and the subsequent levelling tendency in the following cycles. The stabilized equilibrium and breakthrough capacities after 10 cycles with the actual flue gas were very similar with those using the simulated flue gas. This comparison has demonstrated that the actual flue gas extracted from the exhaust pipe of the domestic gas boiler didn't expose any obvious detrimental effect on the cyclic performance of the PEI/silica adsorbent. The impact of impurities in the actual flue gas and the co-adsorption of other acid gases such as NOx and SO₂ (almost undetectable as the flue gas from natural gas combustion contains very low level of SO₂) on the CO₂ adsorption behaviour is negligible according to the working conditions used in this study.

3.5. Further discussion on solid sorbents based CCS system

Implementing efficient solid sorbents to the CCS system of an actual NGCC plant requires a careful assessment of many processes within the whole CCS chain including the design of CO2 adsorption-desorption reactors and configuration, sorbent regeneration, ${\rm CO}_2$ purification, compression and utilization or storage. Future development of solid sorbents should aim at not only high CO2 capture capacity, but also excellent regeneration properties, such as high regeneration efficiency and low regeneration heat requirement. High purity CO2 product gas is especially favourable for the subsequent utilization and storage as the energy penalty associated with impurity removal and CO₂ compression can be minimized. Recently, regeneration of solid sorbents in the pure CO2 flowing environment to yield high purity CO2 product gas has attracted significant research interest for both physisorption based adsorbents (Radosz et al., 2008; Ntiamoah et al., 2016) and chemisorption based adsorbents. A novel potassium-based sorbents was developed to exhibit high CO2 capture capacity and excellent regeneration ratios of 90 % or more in the presence of 100 vol% CO₂ at 200 °C (Cho et al., 2018). Amine-based solid sorbents such as the PEI/silica adsorbent evaluated by this study are promising candidates for post-combustion CO2 capture owing to their proved high adsorption capacities and low regeneration energy requirement. However, their long-term thermal stability in a TSA operation under higher regeneration temperatures needs to be further improved, for example, by chemical modification of the amino functional groups, if CO2 regeneration is to be used. A simulation research (Pirklbauer et al., 2018) revealed that with an adsorber temperature of 75 °C, the minimum regeneration temperature in order to still reach the separation task used so far would be 166 °C. A novel Alkyl-functionalized-APTES zeolite showed higher sorption capacity and stability than APTES zeolite and PEI silica in TSA operation at CO₂ mixture sorption and CO₂ flow regeneration (Liu et al., 2020). Solid sorbents having strong physical or chemical affinity with CO₂, while having weak affinity with moisture are promising candidates as less moisture is adsorbed during adsorption and carried over to the regenerator. Energy requirement for vaporization and separation of the moisture adsorbed can be much reduced by developing and applying such sorbents in the CCS process. The mechanical properties of any newly synthesized sorbents, such as attrition resistance, also need to be evaluated so that their suitability to industrial-scale reactors, which are likely of the type of fluidized beds or moving beds, can be ascertained.

4. Conclusions

In order to evaluate the cyclic performance of PEI/silica adsorbent at kg scale with steam as the main component of the stripping gas, a series of batch-type adsorption/desorption cycle tests have been carried out in a laboratory scale BFB using the simulated NGCC flue gas and the actual flue gas of a domestic gas boiler. After the decline in the first few cycles, the cyclic adsorption capacities have been stabilized at a similar level in comparison with that using pure N2 as the stripping gas. It has also been found that the desorption temperature and flow rate of the stripping gas both have prominent influences on the desorption kinetics. Characterizations by use of BET surface area, pore volume and pore size, TGA, FTIR and SEM have suggested that the amine vaporization from the pores and surface may be a possible reason to account for the initial capacity loss. No significant evidence has been found for the detrimental effect or degradation caused by steam regeneration. The use of a small mole fraction of 15 vol% of CO₂ in the stripping gas has however induced a significant loss in the working capacity, mainly due to the incomplete desorption and the possible thermal and CO2 induced degradation. The cyclic performance of the PEI/Silica adsorbent with the actual flue gas generated from a domestic natural gas boiler was found to be similar to that with the simulated NGCC flue gas, indicating that the impurities contained in the actual flue gas had no significant negative impact on the cyclic performance under the experimental conditions.

Although further research with a fully coupled adsorber-desorber system is still needed, the results of this study and our previous process simulation study (Zhang et al., 2017) indicate that using a small amount of low-grade steam as the stripping gas can be a practically and economically feasible measure for a commercial scale carbon capture system using the PEI/silica adsorbent.

Regeneration of solid sorbents in a pure CO_2 environment can effectively yield high-purity CO_2 product gas, avoiding the use of additional stripping steam, and the subsequent condensing and separation process. In order for this regeneration strategy to be applicable to amine-based sorbents, the thermal stability under higher regeneration temperatures needs to be further improved, for example, by chemical modification of the amino functional groups.

CRediT author statement

Wenbin Zhang: Conducting the majority of the experiments, data analysis and drafting the manuscript.

Chenggong Sun and Colin E. Snape: Co-supervising the research, providing assists to the data analysis, reviewing the manuscript.

 ${\bf Xuezhong\ Sun:}$ Conducting all of the FTIR analyses and assisting the manuscript preparation

Hao Liu: leading the research, supervising the FB experiments and the results analysis, reviewing and finalising the manuscript

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Engineering and Physical Sciences Research Council, UK [grant numberEP/J020745/1]. The authors would like to thank Dr Lee Stevens for his contribution in the $\rm N_2$ physisorption characterization of samples.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.ijggc.2020.102975.

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