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A new honeycomb carbon monolith for CO₂ capture by rapid temperature swing adsorption using steam regeneration

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HIGHLIGHTS

- Carbon monolith allow adsorption CO₂ at high interstitial flow rates (> 3m/s).
- Heating of the monolith above 100 °C in a few seconds using direct steam contact.
- Carbon monolith retains its capacity in consecutive cycles with steam regeneration.
- Cycle time was reduced by optimisation of the drying and cooling step.

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ABSTRACT

A rapid process for CO₂ capture is of key importance for the economic feasibility of the process in industry, consequently short adsorption/desorption cycles are crucial. With this aim in mind, a carbon based honeycomb monolith was evaluated for CO₂ capture in a thermal swing adsorption process at short contact times. The effect of (1) regeneration time, (2) presence of water vapor during adsorption and desorption and (3) regeneration method (steam versus hot air) on CO₂ adsorption was studied. The monolith was characterized in terms of porosity and CO₂, N₂, and H₂O isotherms. Cyclic adsorption/desorption experiments were performed using different synthetic gas mixtures with concentrations of CO₂ ranging between 6 and 15 vol%. The effect of water vapor in the synthetic gas mixture on adsorption capacity was limited but increases with relative humidity. Steam of 120 °C was used to heat the monolith and desorb CO₂. Advantages of steam usage are the facile separation of steam and concentrated CO₂ and the low (waste) heating energy cost of steam. It was demonstrated that the steam allows very fast heating and cooling of the monolith. However, the presence of residual condensation water after the cooling step reduces the cyclic adsorption capacity, requiring an additional drying step with hot or cold air.

1. Introduction

The use of fossil fuels is coupled to the emission of a huge amount of the greenhouse gas CO₂. Despite the enormous efforts in the development of sustainable energy sources, fossil fuels will remain the primary energy source in the near future. In order to stabilize the CO₂ content in the atmosphere, it is therefore of capital interest to reduce CO₂ emissions. An essential step in this process is the development of environmentally friendly and economically viable separation, capture, and storage processes of CO₂ from flue gas. Many studies have proven adsorptive separation of CO₂ on porous materials as the most efficient and affordable alternative [1,2]. Adsorption processes using solid

sorbents, able to reversibly capture CO₂ from flue gas streams, have many potential advantages compared to other separation techniques for CO₂ capture, such as reduced energy requirement for regeneration, greater capacity, selectivity, ease of handling, etc.

Together with the capture method, the regeneration of the adsorbent is a key step in the adsorption/separation process as it determines to a great extent energy costs and process efficiency [3]. An efficient reutilization of the adsorbent material will increase the viability of the complete procedure and therefore its industrial implementation. In this regard, various adsorbent regeneration methods have been evaluated. Among the major cyclic adsorption processes for the separation of gases, Pressure Swing Adsorption (PSA) and

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Temperature Swing Adsorption (TSA) are commercially available technologies and are used in commercial H₂ productions, bulk separation of O₂, and in the removal of CO₂ from natural gas [4]. Although PSA is often considered as a promising option for the separation of CO₂ from flue gas due to its ease of applicability and its low capital investment cost, it is based on the preferential adsorption of CO₂ at high pressure and recovery at low pressure. However, due to the low partial pressure of CO₂ in flue gases, very low pressure should be obtained for the desorption step, making the process very costly. A process combining Pressure and Temperature Swing Adsorption (PTSA) has been tested at a bench and pilot scale by Tokyo Electric Power Company (TEPCO) & Mitsubishi Heavy industries, respectively. Compared to PSA, using PTSA reduces the power consumption required for the separation by 11% [5].

From the industrial point of view, a major challenge to deal with in CO₂ capture processes is, next to the low partial pressure of CO₂, the huge volumes, given that an average 600 MWe coal-fired plant emits 500 m³/s of flue gas [6]. This leads to the need of (very) fast adsorption/desorption cycles, in order to reduce adsorbent inventory and unit size. CO₂ capture systems using solid adsorbents reports cycle times ranging between 15 and 30 min, but also longer cycles are often reported [7]. This would lead to an excessive size and cost of the system, and therefore faster cycles are needed. This is translated into rapid heating processes and adsorbents with fast mass and heat transfer kinetics.

The high gas flow rates encountered in CO₂ capture also require the use of structured adsorbents such as monoliths, which allow to reduce pressure drop by an order of magnitude as compared to traditional packed beds. Recent studies have revealed that structured adsorbents, with interconnected and branched macroporous channels, such as monoliths or hollow fibers, have a better performance than conventional beads or granules [8–11]. It was shown that CO₂ adsorption kinetics in zeolite monoliths are improved by a factor 6 compared to beads, while heating and cooling times are drastically reduced from hours to minutes [11,12].

All of this leads to a growing interest in Rapid Thermal Swing Adsorption (RTSA) based technologies for CO₂ capture. Through the RTSA process, the energetic cost of capturing CO₂ could be dramatically reduced with appropriate heat integration strategies [13]. Within an RTSA scheme proposed in literature, four beds are operated in different stages: adsorption, heating, sweeping and cooling [14]. CO₂ is adsorbed by contacting cooled flue gas with the adsorbent (step 1). Once the column is saturated, the temperature is rapidly increased (step 2), desorbing the adsorbed CO₂. The desorbed and concentrated CO₂ is recuperated (step 3) and finally, the column is cooled down to its initial temperature (step 4). A recycle, a purge or a second heating step could be used to further optimize the process [15]. Various methods of supplying heat to the adsorbent for regeneration have been proposed, including microwave energy (U.S. Pat. No. 4312641), installation of electrical heaters inside the packed adsorbent bed of the adsorber (U.S. Pat. No. 4269611), or direct application of electric current to the adsorber for electrodesorption (U.S. Pat. No. 4094652). On top of that, steam is known to be an effective regenerating method for activated

carbons and is nowadays used for solvent recovery in temperature swing cycles [16–18]. As a consequence of the high heat of condensation of steam, the temperature of the adsorbent quickly raises to desorb the adsorbate [19]. Furthermore, adsorbed water competes with the adsorbate for pore volume of the adsorbent to enhance desorption. Direct steam injection therefore allows both temperature and pressure swing adsorption at the same time. After steaming and drying, the carbon is ready for service again [20]. Moreover, steam is easily available in the industry or can be generated at relatively low cost by skid mounted boiler units [19].

The use of steam is not (yet) very developed for CO₂ capture applications. However, it could be appealing using specific porous solids. In the recent years, a large number of porous solids have been developed and/or tested for CO₂ capture, including porous carbons, zeolites (e.g. 13X, 5A), amine-modified silicas, and new classes of hybrid crystalline solids (e.g. MOFs, ZIFs, COFs, MCPs, PCPs). Amongst all different types of adsorbents, the most promising ones are zeolites and activated carbons given their robustness, large adsorption capacity, and commercial availability. From the group of zeolites, the best candidate is zeolite 13X with a demonstrated CO₂ adsorption capacity of about 200 g/kg at 1 bar and 22 °C and a very large affinity at low CO₂ pressure, typical for flue gas mixtures (130 g/kg at 0.15 bar and 22 °C) [21–22]. Porous carbons exhibit similar or larger adsorption capacities for CO₂ at high pressure (88–210 g/kg at 1 bar and 0–30 °C) but have a lower capacity at low relative pressure (40 g/kg at 0.15 bar and 25 °C) [23–25]. On the other hand, the weaker interaction between CO₂ and active carbon materials as compared to zeolites allows for an easier regeneration.

A crucial aspect for the use of steam regeneration on porous materials is their stability under conditions of high humidity and high temperature. Generally, porous carbon materials (activated carbon, carbon molecular sieves) are well known for their hydrophobic properties and excellent stability in water, while this is less evident for many other porous solids [26–28]. It is for this reason and due to their industrial applications that the use of steam for the regeneration of activated carbons has been widely studied for example for solvent recovery [12,17,18,28,29]. Some studies were performed on carbon capture using steam regeneration (see Table 1).

Plaza et al. studied an adsorption-based post-combustion capture process using a carbon honeycomb monolith, regenerated by steam stripping. They performed a dynamic simulation of the process, where, next to steam stripping, the thermal swing was aided by indirect heating and cooling. The specific heat duty obtained was 3.59 MJ/kg. In case the adsorption kinetics are slightly improved, the value drops to 2.89 MJ/kg, which is lower than the benchmark technology [30].

Berger et al. analysed a sorbent-polymer composite (SPC) comprising a powdered solid sorbent into a hydrophobic polymer substrate for CO₂ capture with direct steam regeneration. To cool down the composite, direct contact with cold water was performed to minimize the cycle time. An amine silica adsorbent was used for dynamic experiments. From the mass and heat transfer capacity of the material, they estimated that an SPC could be cycled in less than 60 s. However, a significant effort should be done in equipment design, optimisation and

Table 1
Overview of the state-of-art of steam regeneration for CO₂ capture.

Reference	Material	Results
Radosz et al. [32]	Activated carbon filter	Direct-steam at 100 °C to regenerate adsorbent in less than 2 min
Dutcher et al. [33]	Activated carbon bed (coal)	CO ₂ capture with steam-aided vacuum swing adsorption, where steam is used to increase vacuum efficiency
Pröll et al. [34]	Amine-based sorbent	Direct-steam stripping to obtain highly concentrated CO ₂
Fujiki et al. [35]	Novel amine-based solid sorbent	Steam-aided vacuum swing adsorption was effective for recovering CO ₂ at high purity (> 98%) and recovery rate (> 93%)
Plaza et al. [30]	Carbon honeycomb monolith	Specific heat duty of 3.59 MJ/kg (could be lowered to 2.89 MJ/kg with slightly faster adsorption kinetics)
Berger et al. [31]	Sorbent-polymer composite	Based on the mass and heat transfer capacity of the material, theoretically, an adsorption cycle could be performed under 60 s

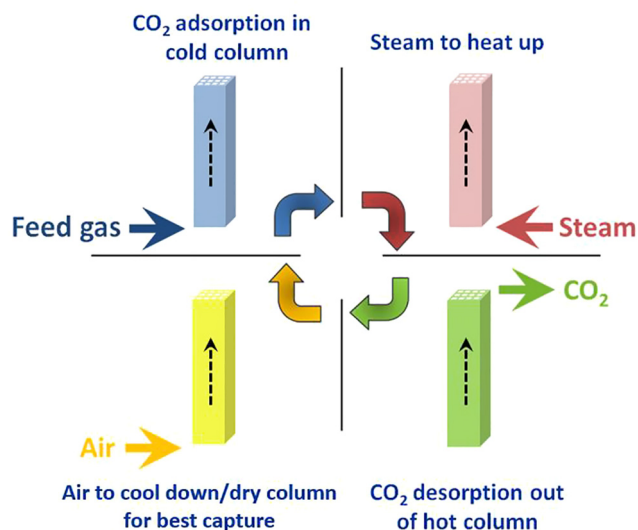


Fig. 1. Overview of the steam assisted TSA CO₂ capture process. 1) Synthetic flue gas mixture is sent into the cold monolith; 2) Steam for fast heating of the monolith in counter-current; 3) CO₂ desorbs; 4) Hot/cold air to cool down/dry the monolith. Both the inlet and the outlet of the monolith are open during each step.

testing [31].

Based on the benefits of RTSA and the use of steam for regeneration, the current work studies a steam-heating based TSA cycle using a carbon monolith for the adsorption and separation of CO₂ from flue gas (Fig. 1). The adsorption properties of the carbon honeycomb monolith are studied, its performance in dynamic and cyclic CO₂ separation is evaluated and attempts are made to minimize cycle time.

2. Experimental details

2.1. Characterization

All porous carbon materials were supplied by Solvay and produced using their proprietary technology [36–38].

The honeycomb carbon monolith has a length of 11.6 cm, with a mass of 5.16 g, and wall thickness of 0.70 mm. The width of the channels equals 0.86 mm. The cubic section of the monolith contains 6 × 5 squared channels with a surface section of 0.747 mm² per channel and a total channel surface of 22.4 mm². The monolith is packed into a heat shrink tubing to avoid gas leakage through the porous walls.

Textural properties of the monolith were determined by CO₂, Ar and Hg porosimetry using an Autosorb-1 (Quantachrome Instruments, Odelzhausen, Germany) device and a Thermo-Finnigan Hg intrusion porosimeter (Waltham, Massachusetts, USA). Ar and CO₂ isotherms were treated using the Quenched Solid Density Functional Theory (QSDFT) for Ar and the Nonlocal Density Functional Theory (NLDFT) for CO₂ to calculate the pore volumes and pore size distribution (Figs. S1 and S2 from the Electronic Supporting Information, ESI). Water adsorption isotherms (Fig. S3) were determined at room temperature by means of a gravimetric technique (VTI, TA Instruments, New Castle, Pennsylvania, USA).

2.2. Dynamic separation experiments

Adsorption/desorption cycles have been studied by performing cyclic breakthrough experiments using the 4-step-process mentioned before (Fig. 1): (1) the carbon monolith is exposed to a dry or humidified CO₂-containing mixture, then (2,3) cocurrent desorption of the adsorbates from the column is obtained using high flow of cold air (20

Nl/min) or by increasing the temperature using either hot air or steam, during which desorption of CO₂ in the open monolith. Then (eventually) (4) the column is cooled down by a continuous flow of cold air and ready for the next cycle. The synthetic flue gas is made with pure CO₂ (purity 99,995 vol%) from a 50 l gas cylinder, diluted in pressurized air from the network of the university and, eventually, evaporated water is added to this gas stream. The pressurized air has a typical air composition, except that water was removed (~78% N₂, 21% O₂ and 1% Ar). The dew point of this air stream is -66 °C.

A new experimental setup was built in-house to allow high gas velocities and perform thermal regeneration using hot air or steam (Fig. S4). To simulate industrial conditions, gas velocities between 0.15 m/s and 3.4 m/s can be obtained, which corresponds to contact times of 0.8 s to 0.04 s in the monolith. Analysis of the gas mixture composition at the monolith outlet was performed on-line using a Mass Spectrometer (MS) (Hiden Analytical, Warrington, England). Four thermocouples (150 μm) are located at different positions inside the monolith channels to obtain temperature profiles of the process (at 1 cm, 4.5 cm, 8 cm, and 11 cm).

For the regeneration methods, various approaches were used: (a) a compressed air stream at 28 °C and 20 Nl/min was used for cold air regeneration; (b) regeneration with hot air was studied by heating an air flow using an in-line heater to 180 °C. This allowed to reach a temperature of 100 °C at the end of the monolith (only after at least 10 min due to heat losses over the setup and the monolith). A cooling step is needed afterwards; this was normally done with cold air (20 Nl/min); (c) regeneration with steam. A steam evaporator produces steam at a temperature between 100 °C and 200 °C, which can be sent through the column at various flow rates (0–2000 g/h). Ideally, the whole regeneration step should occur counter-currently. However, due to technical limitations this was not yet possible in our experimental setup. Since the presence of a large amount of water could have an impact on the adsorption capacity of the material, drying of the column is also performed using compressed air at different temperatures, which is also needed to cool down the monolith.

3. Results and discussion

3.1. Monolith properties

The carbon monolith was characterized for its textural and adsorption properties (Table 2). First, the porosity was assessed for the monolith (Fig. S1). The micropore volume determined using Ar at 87 K is substantial and equals 0.321 cm³/g. Measurement of the smallest micropores in carbon with Ar is difficult since the molecules do not, or only very slowly, penetrate the smallest pores at 87 K. Measurement using CO₂ at 0 °C is therefore more suitable, since it does not only occur faster, but it will also allow to see some ultra-micropores which are only accessible to CO₂, which is relevant in this case of CO₂ capture. From Table 2, it can be seen that the volume of pores smaller than 1.5 nm measured with Ar and CO₂ respectively differ only by 0.012 cm³/g. This volume of 0.012 cm³/g thus corresponds to the smallest pores in the

Table 2
Adsorbent properties.

# channels	30
Length	11.6 cm
Mass	5.16 g
Wall thickness	0.700 mm
Cross section 1 channel	0.747 mm ²
Pores < 1.5 nm (CO ₂ at 0 °C)	0.321 cm ³ /g
Pores < 1.5 nm (Ar at 87 K)	0.309 cm ³ /g
Pores 1.5–2.0 nm (Ar at 87 K)	0.010 cm ³ /g
Mesopores (2–50 nm) (Ar at 87 K)	0.021 cm ³ /g
Pores > 7.5 nm (Hg at high P)	0.492 cm ³ /g
ΔH for CO ₂	-25.6 kJ/mol

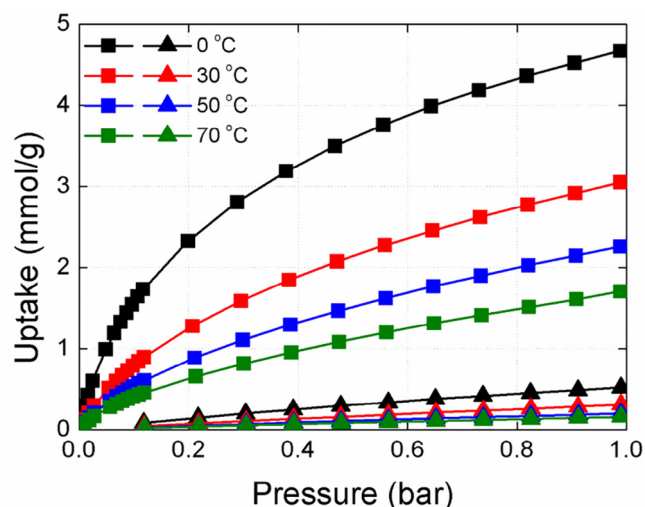


Fig. 2. Adsorption isotherms of CO₂ (squares) and N₂ (triangles) at different temperatures.

material that can only be measured with CO₂ at 0 °C. Next, the measurement with Ar shows that mesopores have a very low volume of 0.021 cm³/g. From the measurement with Hg at high pressure, pores larger than 7.5 nm can be measured (Fig. S2). Therefore, combining the results of Ar and Hg porosimetry, the amount of macropores (> 50 nm) equals 0.483 cm³/g. Hence, this material has mainly micropores in the range 0.3–2 nm, directly accessible through large macropores (1–10 μm).

Fig. 2 shows the pure component adsorption isotherms of CO₂ and N₂ at different temperatures, obtained on a fragment of the monolith. Generally, the amount of CO₂ adsorbed is 8–20 times larger than that of N₂ at any temperature and pressure. Especially at a low pressure of CO₂, the selectivity for CO₂ over N₂ is high. At a pressure of 0.15 bar, 1.03 mmol/g of CO₂ is adsorbed, as compared to 0.054 mmol/g for N₂. Based on these results, the monolith is expected to show a very selective behavior towards CO₂.

Water adsorption isotherms are depicted in Fig. S3 from the ESI. The material shows a hydrophobic behavior since very low water adsorption (< 1 mmol/g) is observed for a relative humidity (RH) below 20% (about 8.4 mbar partial pressure at 30 °C). However, a steep increase in water adsorption occurs when exceeding a relative humidity of 40%, leading to a water content of 12 mmol/g at 80% RH. Adsorption and desorption profiles are almost identical. Note that the water content of most common flue gases varies between 6 vol% and 15 vol% [39,40].

3.2. Dynamic separation using dry air regeneration

3.2.1. Effect of flow rate

Firstly, the effect of flow rate (gas velocity) on the adsorption capacity of the monolith was studied in breakthrough experiments, to identify mass transport limitations (Fig. 3). Five different flow rates spanning from 0.2 to 5 NL/min (corresponding to interstitial gas velocities between 0.15 and 3.23 m/s) were analysed using a mixture containing 85 v% air – 15 v% CO₂ at room temperature (Fig. 3a and b). To ensure the reproducibility of the results, each measurement was repeated. After each breakthrough measurement, the material was fully regenerated with a 20 NL/min flow of cold air (28 °C) during 300 s (Fig. 3c and d). As expected, the breakthrough time decreases with gas flow rate, from about 170 s average breakthrough time at 0.2 NL/min to 8.71 s at 5 NL/min.

The shape of the breakthrough curves is not symmetric, rather showing an extended tail. This is, at least partially, related to heat transfer limitations (vide infra). For the higher flow rates, the

breakthrough curve is less sharp due to mass transfer limitations. This results in rapid breakthrough of CO₂-molecules before the monolith is equilibrated, since they do not have the time to diffuse into the (micro) pores before being blown out. On the other hand, there seems to be no macropore limitation, even at higher velocity.

Surprisingly, the adsorption capacity increases at higher flow rates. It varies from 0.76 mmol/g at a gas velocity of 0.15 m/s (~0.8 s contact time) to 0.85 mmol/g at 3.23 m/s (~0.04 s contact time). This can be explained by the relatively high temperature increase during adsorption, related to the exothermic character of adsorption (Fig. 2). As a result, the adsorption column is not completely cooled down at the end of the adsorption step (when capacity is calculated) if low flow rates are used (+4 °C). At higher flow rates, the material is cooled down more efficiently such that the initial temperature will be reached. This means that even at very low contact time, no major impact could be seen on the adsorption capacity, demonstrating the fast uptake kinetics of CO₂ on the monolithic material.

Note that the equilibrium capacity for pure CO₂ at 0.15 bar as obtained in volumetric experiments equals 1.02 mmol/g at 30 °C (Fig. 2). The lower capacity in the breakthrough experiments (0.76 – 0.85 mmol/g) as compared to the equilibrium capacity can be related to the non-isothermal conditions during breakthrough experiments, the presence of nitrogen and mass and heat transfer limitations.

3.2.2. Temperature profile

Together with the concentration profiles, temperature profiles inside the monolith channels were measured during the adsorption/desorption cycles (Fig. 4). Temperature profiles were obtained for different flow rates, but only the results obtained at a gas flow rate of 0.5 NL/min are discussed here. During the adsorption step (300 s), a rise of temperature is observed. Close to the inlet, the temperature rapidly rises (within 10 s) of about 14 °C, which is lower than the adiabatic temperature rise (order of 30 °C). The fairly effective radial heat transfer to the surrounding heat shrink tubing (with a weight which is twice the weight of the carbon monolith), which heats up as well, reduces the temperature rise in the gas and monolith. Further down the column, it takes a longer time before the temperature starts to increase, which is explained by the dynamic migration of the adsorption front to the column outlet. Remarkably, the temperature profiles are strongly tailed; temperature only decreases very slowly, and the starting temperature is only reached after more than 300 s. This is again a consequence of heat accumulation in the heat shrink tubing, which cools down slowly and thereby slows down the cooling of the monolith. Moreover, during the cooling-down stage, the equilibrium adsorption capacity of the material increases again, which result in the additional uptake of CO₂ and the corresponding adsorption heat. So, while 80% breakthrough at the column already occurred after circa 80 s (Fig. 3a), temperature is still changing significantly.

3.2.3. Effect of desorption time on the cyclic performance

It was investigated how efficiently CO₂ can be desorbed at ambient temperature by purging with air. Adsorption/desorption cycles were ran while decreasing the desorption time (Fig. 5). Cycles with regeneration times ranging from 25 s to 10 s were studied. Fig. 5a shows the breakthrough curve of CO₂ as obtained after full thermal regeneration at 140 °C (base case), together with CO₂ breakthrough curves obtained after three cycles when air stripping (at room temperature) regeneration was used. For regeneration times of 25 s and 20 s, the breakthrough curves are identical to the base case. When the regeneration time is reduced to 15 s, immediate elution of CO₂ in low concentration occurs, followed by a premature full breakthrough of CO₂. Since not all CO₂ is desorbed for regeneration times of 15 s or 10 s, the CO₂ present in the material near the column outlet elutes immediately. Better performance is to be expected when regeneration is performed in counter-current mode, such that CO₂ is pushed back to the monolith inlet. As shown in Fig. 5b, for 15 s regeneration time, 90% of

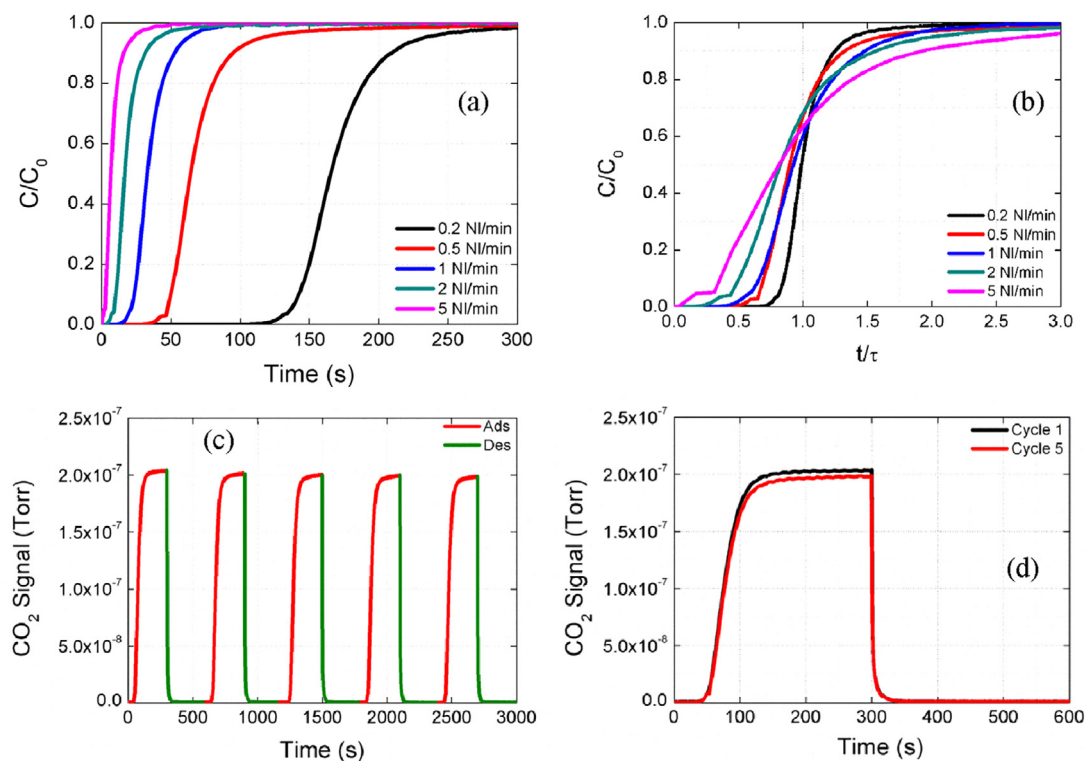


Fig. 3. Adsorption breakthrough curves at different flow rates as a function of a) time and b) normalized time (time over the breakthrough time obtained by integration (τ)). c) Adsorption/desorption CO_2 signal for 0.5 NI/min d) Overlay of breakthrough profiles after several adsorption/desorption cycles. Adsorption flow rate and regeneration using 20 NI/min of air during 300 s, both at 28 °C from a mixture containing 85 v% air – 15 v% CO_2 . (COLOR).

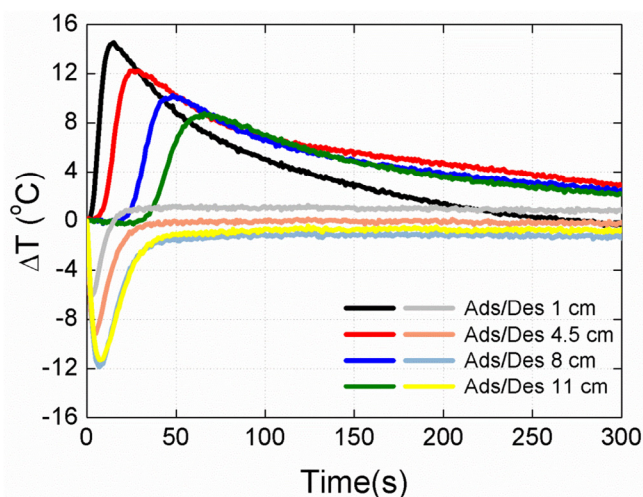


Fig. 4. Temperature profiles (temperature is normalized with respect to the temperature measured right before starting the adsorption experiment) obtained at different positions inside the monolith (distance from the inlet) for adsorption and desorption, using a mixture containing 85 v% air – 15 v% CO_2 . Adsorption takes place with 0.5 NI/min flow rate of the mixture, while desorption is achieved using 20 NI/min of compressed air.

the original capacity is reached, while this is reduced to less than 80% for a regeneration time of 10 s. Interestingly, this capacity remains constant between cycles.

3.2.4. Effect of water on cyclic adsorption capacity

To evaluate the effect of water on the CO_2 separation and adsorption capacity, cyclic adsorption/desorption experiments were performed using CO_2 -air mixtures with different humidity levels. To study the

influence on the adsorption part, each experiment consisted of six consecutive cycles under the same conditions, from which the CO_2 adsorption capacity was derived (Fig. S5). Adsorbent regeneration was performed by flowing 20 NI/min of cold air through the monolith at 28 °C during 500 s, which was shown to be sufficient to ensure the complete removal of the adsorbates.

Thereafter, real flue gas mixtures were simulated: (a) a pulverized coal combustion gas was mimicked by using a relatively low concentration of water (6 v%) and a CO_2 concentration of 11 v%, (b) fired natural gas was simulated by generating about 14.6 v% of water while CO_2 content was reduced to 7.5 v%, and (c) finally a higher water content of 25 v% was used, which is well above the maximum amount of water present in common flue gases (11.25 v% of CO_2) (Fig. 6). In these experiments, the adsorption step was executed for 200 s (0.5 NI/min), while it was attempted to minimize regeneration time for each gas mixture composition.

For the pulverized coal flue gas (6 v% H_2O), the amount of water that enters the monolith per cycle is small (about 0.16 g for 5.16 g of adsorbent). Note that this amount of water would be lower if the adsorption was stopped at breakthrough (around 70 s), therefore reducing the impact of water on the regeneration. The cyclic adsorption capacity does only decrease when the regeneration time is reduced below 50 s. More than 12% of the capacity is lost for a regeneration time lower than 20 s.

For the mixture with 14.6 v% of water, the cyclic capacity remains unaffected as long as the regeneration time is at least 150 s. The negative values in Fig. 6 are related to the decrease in temperature in the monolith after a couple of cycles, from 30 to 25 °C, due to the endothermic desorption of water from the monolith. Below 150 s, a slight (6%) decrease in CO_2 capacity effect is observed for a regeneration time of 100 s. Further reduction in regeneration time to 50 s increases the impact on the adsorption capacity, with a reduction of more than 13%, as the water molecules adsorbed in the pores of the material could not be completely removed. In these conditions, about 0.392 g of water is

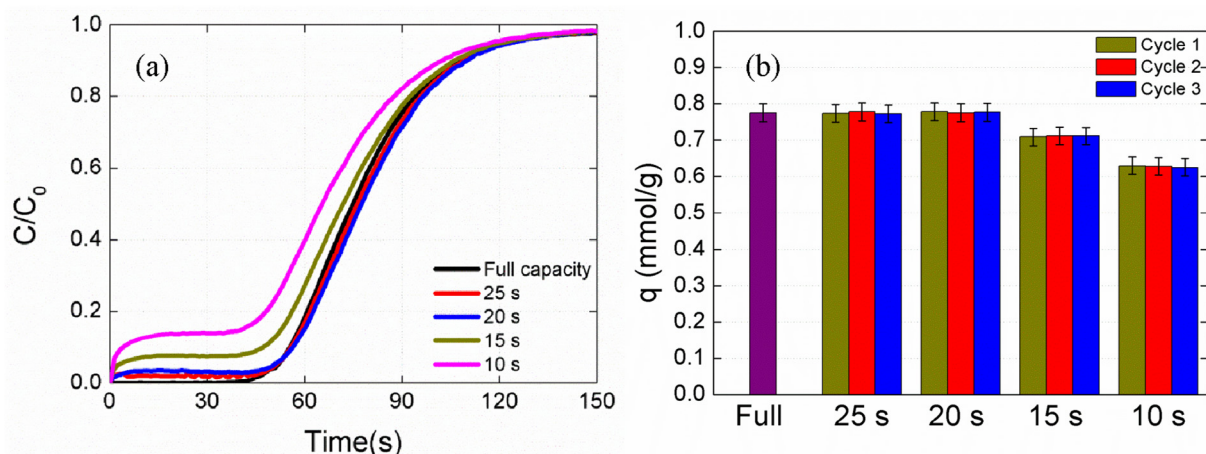


Fig. 5. a) Adsorption breakthrough curves in the second adsorption step of an adsorption/desorption cycle. Feed conditions: 0.5 NL/min of mixture containing 85 v% air – 15 v% CO_2 ; regeneration: 20 NL/min of cold air at different regeneration times. b) Adsorption capacity after different adsorption/desorption cycles for regeneration times of 25 s, 20 s, 15 s and 10 s as compared to the full capacity obtained after thermal regeneration at 140 °C.

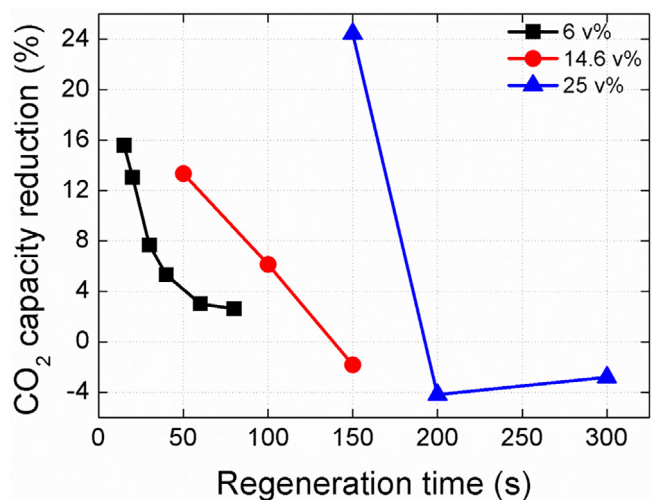


Fig. 6. Reduction of the CO_2 adsorption capacity in presence of water vapor for different regeneration times in adsorption/desorption cycles of air- CO_2 -water mixtures. Each point corresponds to the ratio of the capacity after 5 adsorption/desorption cycles at a specific regeneration time and the initial capacity. Regeneration is performed using 20 NL/min of cold air at 28 °C.

fed to the monolith per cycle, of which a certain fraction is adsorbed. Therefore, larger regeneration times than for the gas mixture containing 6 v% water are needed to fully recover the adsorption capacity of the monolith.

Finally, for mixtures containing 25 v% of water, again a shift to larger regeneration times is needed for a full recovery of cyclic adsorption capacity. In this case, about 0.670 g of water goes through the monolith during each adsorption step. A regeneration time above 200 s is needed in this case to restore capacity, since an important decrease of 24% in capacity is found for shorter regeneration time (150 s). Still, the carbon-based monolith allows separating CO_2 from its mixture in humid conditions and is less sensitive to water as compared to hydrophilic CO_2 adsorbents such as 13X zeolite.

3.3. Dynamic separation using steam regeneration

Since the adsorption is not affected by water as long as the drying time is long enough, adsorbent regeneration with steam was studied. Fig. 7 shows the temperature profiles at the column inlet and outlet during the steam regeneration and cooling, together with the

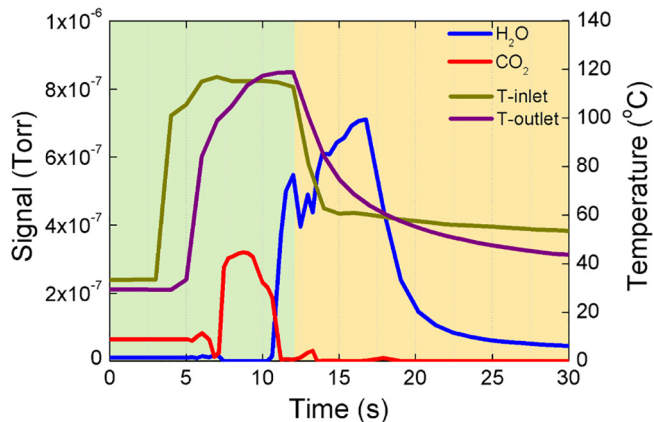


Fig. 7. Temperature and concentration profiles during the steaming and cooling process. This was performed after the adsorption of a mixture containing 85v % air – 15 v% CO_2 at 28 °C. Regeneration takes place by combining 20.7 NL/min of steam during 12 s followed by a flow of cold air at 20 NL/min (start after 12 s). (COLOR).

concentration profile of CO_2 and H_2O . In this experiment, steam with a temperature of 120 °C was sent into the saturated monolith at a flow rate of 20.7 NL/min during 12 s. Temperature at the column inlet increases very rapidly, in 3 s to about 100 °C, while the temperature at the outlet follows with a delay of a few seconds. After 7 s, CO_2 starts to elute from the column; its concentration at the column outlet increases steeply as CO_2 desorbs efficiently due to the temperature increase and displacement by water. Desorbed CO_2 concentration reaches a maximum after ~7.5 s, remains constant for 3 s, and then drops to zero. Only when the CO_2 concentration has almost returned to zero, water starts to elute from the monolith. Once CO_2 is completely desorbed, steam is not further needed. A shorter contact time will imply that part of the CO_2 will remain adsorbed in the monolith, while a longer time will result in the presence of an excessive amount of water in the pores of the monolith or in the monolith channels during the cooling down step, therefore requiring longer regeneration/drying time. The monolith is then dried/cooled down introducing cold air (28 °C) at a flow rate of 20 NL/min. The temperature drops remarkably faster after the use of a steam stripping step as compared to heating cycles using dry air. Cooling the monolith from 120 °C to 45 °C only takes 35 s, while this lasts for 285 s if the monolith was heated with hot air. This fast cooling-down phenomenon is probably due to the evaporation of water that condensed previously, which will effectively subtract heat from the

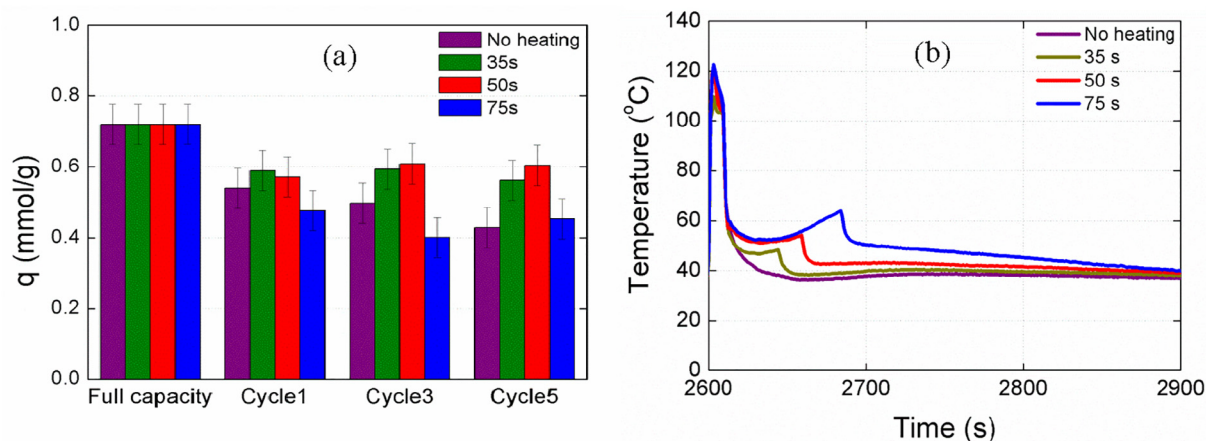


Fig. 8. CO₂ adsorption capacity (a) and temperature profile at the inlet of the monolith (b) for regeneration with different durations of hot and cold air after the adsorption of 0.5 NL/min from a mixture containing 85 v% air – 15 v% CO₂ during 250 s at 28 °C. Regeneration takes place by flowing 1000 g/h of steam during 12 s, 20 NL/min of hot air (preheated at 140 °C), and 15 NL/min of cold air (at 28 °C). Total duration of the hot and cold air flow is always 300 s.

surroundings.

Next, the effect of drying gas temperature on the cyclic capacity was analysed (Fig. S6). As expected, when a higher temperature is used during drying, the regeneration time can be reduced while achieving the same recovery of the adsorbent. However, at higher temperature at the start of the adsorption, the capacity decreases.

Therefore, various drying procedures were evaluated, using a combination of hot and cold air as drying agents after adsorption of dry and humid flue gas and regeneration with steam (Fig. 8). The purpose of the introduction of hot air after steaming is to remove as much water as possible from the monolith channels and the pores of the adsorbent, as was shown with previous experiment. Fig. 8a shows the evolution of the CO₂ adsorption capacity in consecutive cycles obtained after adsorption of a dry gas mixture (85 v% air – 15 v% CO₂) and steam regeneration, using a drying sequence in which hot air (at 180 °C) is first used to remove water from the adsorbent, followed by a flow of cold air (at 28 °C) to further cool and dry the material. Three different durations (35 s, 50 s, and 75 s) were applied for the flow of preheated air, together with a base case without use of hot air (0 s), while maintaining the total drying time at 300 s.

When only cold air is used (during 5 min) to cool and dry the monolith after steaming, the adsorption capacity drops significantly between the first cycle with a fully activated material (0.720 mol/g) and the second cycle (0.456 mol/g). After 5 cycles, the capacity has further dropped by 40%. When using an intermediate drying step with hot air (during 35 s or 50 s) a significant improvement is obtained. Especially when using a contact time of 50 s with hot air, followed by 250 s flow of cold air, the cyclic adsorption capacity drops only from 0.720 mol/g to 0.60 mol/g and remains constant from cycle to cycle. When further increasing the exposure time to hot air (75 s), the cyclic adsorption capacity drops. This is explained by the temperature profiles in the monolith during the drying process, as depicted in Fig. 8b. Looking at the evolution of the temperature, it can be observed that after about 60 s using only cold air, the temperature at the inlet of the monolith returned to about 40 °C. When hot air is used in the initial drying stage, the temperature drops at the same rate in the first seconds, but then levels off at an intermediate level without directly returning to the initial temperature of 40 °C. When hot air is introduced during 35 s, the temperature in the monolith decreases from 120 °C to 47 °C and then levels off until the hot air flow is stopped and cold air is introduced, which results in a rapid decrease in temperature to 40 °C. When the contact time with hot air is increased to 50 s, this plateau of constant monolith temperature is extended, resulting in a deeper drying of the adsorbent. Upon further increasing the contact time with hot air to 75 s, a pronounced increase in temperature is again observed. As

soon as most water has been removed from the monolith by the hot air flow, this hot flow will again heat up the monolith instead of causing water evaporation. When this point is reached, it takes a longer time to cool down the monolith again using cold air. Thus, the best performance is obtained when the use of hot air allows removing the maximal amount of water, while only causing a minor increase in temperature.

Therefore, when using optimal conditions, a cycle time of less than 330 s could be obtained if high flow rates for adsorption are used. However, further improvements could be made in the drying and cooling of the adsorbent to further reduce the cycle time.

4. Conclusions

A carbon based honeycomb monolith for CO₂ capture from flue gases was evaluated in a fast cycle adsorption process, using steam to regenerate the adsorbent. It was demonstrated that the material allows for CO₂ capture at very high gas flow rates and in presence of humidity. Breakthrough experiments have been performed for an Air-CO₂ mixture using a flow of cold air to regenerate the monolith between cycles. Using a dry feed gas, cycle time could be drastically reduced to 20 s without affecting the capacity. Besides mass transfer limitations at very high gas velocities, it was found that heat effects as a result of the exothermic nature of CO₂ adsorption also have an important influence when cycling at low temperature. An important effect of operating temperature on cyclic adsorption capacity was found. In the case of humidified feed gases, a longer regeneration time was needed to maintain cyclic adsorption capacity. The higher the amount of water, the longer the time needed to regenerate the monolith before the start of a new cycle. Nevertheless, the adsorption capacity is not dramatically affected by large amounts of water, as a result it can be regenerated using steam. It was demonstrated that the drying step after steam regeneration is crucial to optimize cyclic adsorption capacity. The introduction of an intermediate drying step using hot air improves the cyclic capacity and allows to reduce cycle time. First attempts were made to optimize the adsorption cycle, reducing cycle time to 330 s. This is a significant improvement as compared to the cycle times between 15 and 30 min reported for Thermal Swing CO₂ capture systems. Obviously, further improvements are certainly possible, for example by counter-current regeneration and using larger monoliths in which thermal effects due to the housing of the monolith are much less important.

Author contributions

The manuscript was written through contributions of all authors. All

authors have given approval to the final version of 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2019.123075>.

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