

# Mitigation Strategies for CO<sub>2</sub> Capture with Advanced Techniques in Fluidized Beds

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Carbon dioxide (CO<sub>2</sub>) is one of the main greenhouse gases responsible for global warming and climate changes on a global scale. This work studies CO<sub>2</sub> capture and sequestration technology (CCS), with a particular focus on adsorption. An in-depth analysis is presented on the thermodynamic properties and structural characteristics of the materials used in separation processes, with special attention to innovative materials such as amino-functionalized adsorbents. The study also addresses the main operational and environmental challenges related to the implementation of CCS/CCU technologies in industrial plants, proposing optimized configurations to reduce costs and increase CO<sub>2</sub> capture efficiency. Finally, the experimental results obtained through testing on selected materials are discussed. Both the capture and regeneration phases of the sorbent were analyzed, maintaining the same equipment configuration, with the aim of identifying the optimal temperature and time conditions for each process.

## Keywords:

CO<sub>2</sub> capture, Carbon sequestration, Adsorption, Amino-functionalized silica gel, fluidized beds, Environmental impact, CCS, CCU, Climate change, Sorbent materials, Sustainable technologies.

## 1. Introduction

The disastrous effects of climate change are primarily caused by anthropogenic activities, requiring high energetic level, deriving of fossil fuel, and thus causing high CO<sub>2</sub> emissions. This is the main problem of the last century and requires an urgent solution. Among the various alternatives to reduce greenhouse gas emissions, such as reducing the consumption of fossil sources, increasing energy efficiency, using renewable sources or nuclear energy, all these solutions involve a radical change in energy policies, which therefore require a long period of implementation. In the medium term, without renounce to fossil fuels for energy production, several techniques are explored to mitigate or reduce CO<sub>2</sub> emissions, under the terms Carbon Capture Storage or Utilisation (CCS/U) (Sofia et al., 2015). It refers to a range of applications through which CO<sub>2</sub> is captured and also used either directly (i.e. not chemically altered) or indirectly (i.e. transformed) into various products (Energy Technology Perspectives 2024).

Among the current techniques mainly explored for CO<sub>2</sub> capture, there is physical and chemical adsorption on solid adsorbent (Younas et al., 2016), offering the possibility of reducing the costs of the process of Carbon Capture. This challenge requires efforts to select/synthesize suitable adsorbents (Varghese and Karanikolos, 2020), but also to design efficient units for CO<sub>2</sub> capture (Parket al., 2017).

The aim of the present work is to verify the efficacy of an amino-functionalized mesoporous silica as adsorbent for CO<sub>2</sub> capture and of the special type of contactor adopted. Specifically, the adsorption and desorption phases were studied within the same packed-fluidized bed configuration, eliminating the need for solid unloading or transport from the column.

The design of an apparatus with external heating system, capable of carrying out adsorption/desorption cycles could ensure a continuous process without handling the adsorbent solid, and the consequent optimization of the characteristic time of the single cycle could be explored. This study builds upon previous findings that the addition of packing material in a confined fluidized bed enhances mass transport from the gas to the solid during

the adsorption cycle (Girimonte & Vivacqua, 2011). It further investigates and confirms its effectiveness in improving heat transfer from the column walls to the sorbent during the desorption cycle.

## 2. Materials and Methods

### 2.1 Materials

The adsorbent material consisted of commercial silica gel, that was subsequently subjected to a functionalization procedure aimed at obtaining a suitable sorbent for CO<sub>2</sub> capture envisages the use of 3-aminopropyltriethoxysilane (APTES, >98%). Silica gel and the chemical were provided by Sigma-Aldrich (St. Louis, MO, USA). During the functionalization procedure, Ethanol (96%, analysis grade), provided by J.T. Baker-Avantor (Radnor, PA, USA), was used as a solvent.

### 2.2 Adsorbent Preparation

A modified procedure reported by Quang et al. (Quang et al., 2016) was used to prepare the amino-functionalized silica sample, by grafting amino groups on solid surface. Before the functionalization procedure, 100 g of silica gel were dried in an oven at 120 °C for 2 h. Subsequently, the solid sample was soaked with 400 g of an APTES and ethanol/water (20/80 w/w) impregnating solution in a laboratory flask at room temperature for 72 h, and at a later stage at 40 °C for 48 h, under mechanical stirring. The final stage of the procedure involved drying in an oven at 60 °C for 48 h.

### 2.3 Characterization

By sieving silica, a 400-500 µm sample was obtained; after, by a laser diffractometer Helos (Sympatec GmbH, Clausthal-Zellerfeld, Germany), its particle size distribution was determined. Particle shape characterization was obtained by means of a QicPic image analyzer (Sympatec GmbH, Clausthal-Zellerfeld, Germany).

The apparent particle density of amino-functionalized adsorbent (indicated as APTES20) was determined according to the method proposed by (Abrahamsen and Geldart, 1980) and widely explained in previous works (Girimonte et al., 2020). This method consists of a comparison of the porous adsorbent with a non-porous solid of known density and characterized by the same particle distribution and similar shape.

Several fluidization experiments, carried out in a confined fluidized bed and using air as gas, allowed a fluid-dynamic characterization of the amino-functionalized adsorbent. The experiments led to the determination of the minimum fluidization velocity and the corresponding bed voidage in the confined bed (Girimonte and Vivacqua, 2013).

A Thermogravimetric Analysis (TGA) was performed using a DSC-TGA STA 409C analyzer (Netzsch-Gerätebau GmbH, Selb, Germany) from 20 to 800 °C at a heating rate of 10 °C/min in static air to identify the thermal level for desorption without decomposition of the organic moieties.

*Table 1: Size, shape and fluidization properties of adsorbent particles.*

Sieve size [µm]	d <sub>10%</sub> [µm]	d <sub>50%</sub> [µm]	d <sub>90%</sub> [µm]	Span [-]	d <sub>v</sub> [µm]	φ [-]	ρ <sub>f</sub> [kg/m <sup>3</sup> ]	U <sub>mf</sub> [10 <sup>-2</sup> m/s]	ε <sub>mf</sub> [-]
400-500	363	532	773	0.770	553	0.75	1380	5.80	0.225

### 2.4 Experimental Apparatus and Procedure for Adsorption and Desorption Tests

The experimental campaign of CO<sub>2</sub> adsorption and desorption tests was carried out in a pyrex laboratory-scale fluidization column, with an internal diameter of 50 mm and height of 520 mm. The packed bed inside the fluidization column was created using glass beads with a diameter of 11 mm and density of 2.48 g/cm<sup>3</sup>, that work as packing material. A packing mass of 1000 g is used to form a bed with a height of 360 mm. Subsequently, 50 g of amino-functionalized silica adsorbent is introduced into the column, filling the void spaces within the packing.

Gas distribution was allowed by means of a porous distributor, placed on the bottom of the column. Each adsorption test was carried out with a gas mixture containing air, supplied by a compressor, and CO<sub>2</sub>, added from a cylinder. The gas flow rate was regulated by a set of rotameters covering the range 10-1600 NI/h. Before passing through the adsorbent bed, the air stream was fed to a moisture removal column, filled with zeolite and activated carbon.

The CO<sub>2</sub> concentration of the outlet stream was measured by a gas analyzer (GA-21 plus - Madur Polska Sp. z o.o., Zgierz, Poland) and the acquired data were subsequently elaborated to obtain the breakthrough curve,

from which calculate many parameters of interests: breakthrough time, saturation time, contact time, adsorption capacity and the fraction of bed used at the breakpoint.

CO<sub>2</sub> desorption tests were carried out in the same column to avoid solid carrying to another column for adsorbent regeneration, which may cause its abrasion, and to optimize the time required for each capture and regeneration operating cycle. To achieve the sorbent regeneration by Temperature Swing Adsorption (TSA), the column was equipped with an external heating system consisting of two IR lamps placed on its sides. The lamps R7S 118 mm light bulb was used, featuring a power of 400 W, luminous flux of 4000 lm, and operating voltage of 230 V. Compatible with all T3 118 mm versions, the bulb provides a 360° lighting angle, CRI of 99, and warm light.

The bulb was tested in applications such as ceiling lights, floor lamps, landscape lighting, and security lights, demonstrating easier maintenance and better light penetration in foggy conditions compared to LED solutions. The manufacturer offers a 90-day return policy for damaged products.

The temperature of the adsorbent bed was detected by a thermocouple and controlled by a programmable logic controller (PLC), which, comparing the measured value with the set point, acted by switching the lamps on and off. PID logic was used for the thermal control system. The CO<sub>2</sub> concentration at the column outlet was measured to obtain the desorption curve. Desorption time was also estimated.

### 3. Results and Discussion

#### 3.1 Adsorption Tests for Amino-functionalized Silica

A confined-fluidized bed configuration was adopted to perform CO<sub>2</sub> adsorption tests since in this apparatus fluidization occurs without bypass effects due to the bubbling regime, ensuring a better solid-gas contact for the adsorption process (Girimonte & Vivacqua, 2011). Furthermore, the previous fluid-dynamic characterization of the sorbent enabled the choice of the fluid-dynamic operating conditions to be set to optimize the contact time between solid and gas phases. By operating always under homogeneous expansion, with surface velocities higher than the minimum fluidization velocity, energy and mass transfer are improved and the heat generated during adsorption is dissipated more efficiently, as discussed in previous works (Girimonte et al., 2022).

For each adsorption test, 50 g of APTES20 was used and a superficial velocity of 8.4 cm/s was set, higher than the minimum fluidization velocity (i.e. equal to 1.45 u<sub>mf</sub>). The total volumetric flow rate of the air/CO<sub>2</sub> mixture fed to the column ( $Q_{mix}$ ), Eq (1), and the partial flow rates of air ( $Q_{air}$ ), Eq (2), and CO<sub>2</sub> ( $Q_{CO_2}$ ), Eq (3), were determined as follows:

$$Q_{mix} = Q_{air} + Q_{CO_2} = u A \quad (1)$$

$$Q_{CO_2} = Q_{mix} x_{CO_2} \quad (2)$$

$$Q_{air} = Q_{mix}(1 - x_{CO_2}) \quad (3)$$

where  $u$  represents the superficial velocity of the gas mixture,  $A$  is the column section and  $x_{CO_2}$  is the CO<sub>2</sub> volumetric concentration in the inlet mixture.

The breakthrough curve, defined as the ratio between the outlet concentration and the initial concentration of the stream versus time, was obtained for an inlet gas mixture containing 15% CO<sub>2</sub>. Its trend is shown in Figure 1.

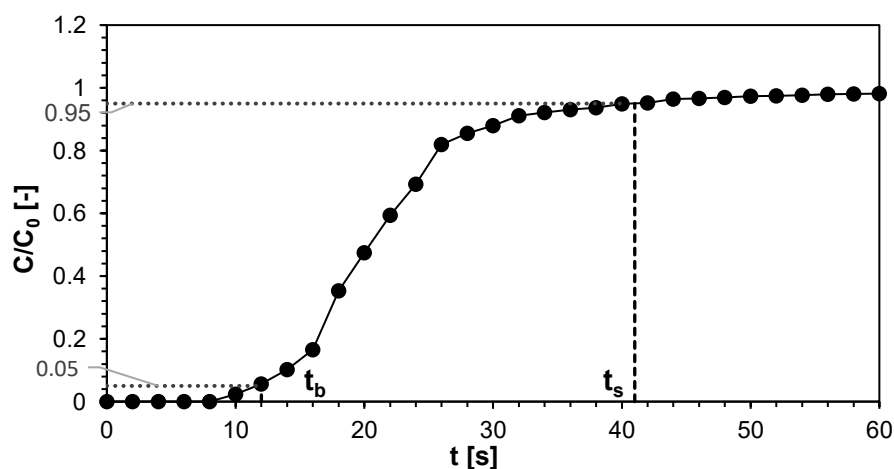


Figure 1. Breakthrough curve for APTES20 (mass of sorbent: 50 g) in confined expanded bed at  $u = 8.4$  cm/s.

The breakthrough time ( $t_b$ ) and the saturation time ( $t_s$ ) were directly estimated from the breakthrough curve. They respectively describe the time at which the CO<sub>2</sub> concentration of the outlet stream reaches 5 % and 95 % of the inlet value. The contact time ( $t_c$ ), Eq (4), was calculated as the ratio between the volume available for the gas flow in the confined-fluidized bed configuration and the inlet flow rate of the mixture (Girimonte et al., 2022):

$$t_c = \frac{V_{open}}{Q_{mix}} = \frac{AH_{fc}\varepsilon_p - \frac{m_f}{\rho_f}}{Q_{mix}} \quad (4)$$

The amount of CO<sub>2</sub> captured on the solid surface was determined by integration of the breakthrough curve between zero and  $t_s$ , Eq (5). As reported in the previous work (Girimonte et al., 2022), a differential mass balance in time was defined on the column to calculate the amount of adsorbed CO<sub>2</sub>, by assuming that pressure and temperature remained constant through the particle bed:

$$m = \frac{\pi MW}{RT} Q_{mix} x_{CO_2,in} \int_0^{t_s} \left(1 - \frac{x_{CO_2,out}}{x_{CO_2,in}}\right) dt \quad (5)$$

*Table 2: Characteristic parameters of adsorption tests on APTES20, for a superficial velocity of 8.4 cm/s and an inlet CO<sub>2</sub> concentration of 15 %vol.*

$t_b$ [s]	$t_s$ [s]	$t_c$ [s]	$m_{CO_2}$ [mg/g]	$W$ [%]
12.0	41.0	0.31	25.6	51.2

The adsorption capacity was defined as the amount of CO<sub>2</sub> adsorbed per unit mass of adsorbent ( $m_{CO_2}$ ), and it represents a suitable parameter for the comparison among different adsorbent materials. The results obtained in this study are consistent with those from previous research on similar sorbents, which report values in the range of 20 to 40 mg/g (Leal et al., 1995; Wei et al., 2013; Zheng et al., 2005; Quang et al., 2016). The bed utilization fraction at the breakpoint,  $W$  (Eq. 6), was calculated as the ratio between the amount of CO<sub>2</sub> adsorbed at the breakpoint and the total amount adsorbed at saturation. A detailed summary of all parameters can be found in Table 2.

$$W = \int_0^{t_b} \left(1 - \frac{x_{CO_2,out}}{x_{CO_2,in}}\right) dt / \int_0^{t_s} \left(1 - \frac{x_{CO_2,out}}{x_{CO_2,in}}\right) dt \quad (6)$$

### 3.2 Desorption Tests for Amino-functionalized Silica

After each adsorption stage, a desorption test of amino-functionalized silica adsorbent was carried out within the same experimental apparatus, avoiding the transport of the solid to a second column. Sorbent regeneration was operated by TSA, varying the temperature of the bed by means of the indirect heating system placed externally to the column. The regeneration temperature ( $T_{des}$ ) was set at 120°C, such as the thermogravimetric analysis carried out on the sorbent sample has indicated, due to the mass loss revealing the release of the adsorbed species on the solid surface in the range from room temperature and 150 °C. During this stage, thermal control was essential to avoid thermal overshoot and to ensure the stability of the adsorbent. Air was used as carrier gas to completely remove the CO<sub>2</sub> from the bed. The study of the release phenomenon involved the detecting of outlet CO<sub>2</sub> concentration versus time. Thus, the effectiveness of the external heating system was tested, which is important to enable the performance of both adsorption and desorption stages within the same column, minimizing the dead times between the two processes.

The surface velocity of the carrier was set to control the homogeneous expansion regime in the confined-fluidized bed configuration and the best value was determined to be higher than the minimum fluidization velocity. Compared to fixed bed configuration, the homogeneous expansion regime enhances the contact between the solid and gas phases, maximizing the mass and heat transfer. On the other hand, high velocities of the carrier, slows down the achievement of desorption temperatures in the core of the bed for the sorbent regeneration. Thus, working just up to the incipient fluidization balances the effects of heating and those related to an efficient removal of desorbed CO<sub>2</sub>. The confined-fluidized bed configuration is verified beneficial also for the desorption stage, since the presence of the packing material helps the heat transfer from the column walls to the core of the confined bed, and the heat transfer to the fine solid adsorbent is more efficient due to the homogenous fluidization without gas bubbles. The desorption curve, defined as the ratio between the outlet CO<sub>2</sub> concentration of the carrier and its maximum value versus time, was obtained and shown in the Figure 2.

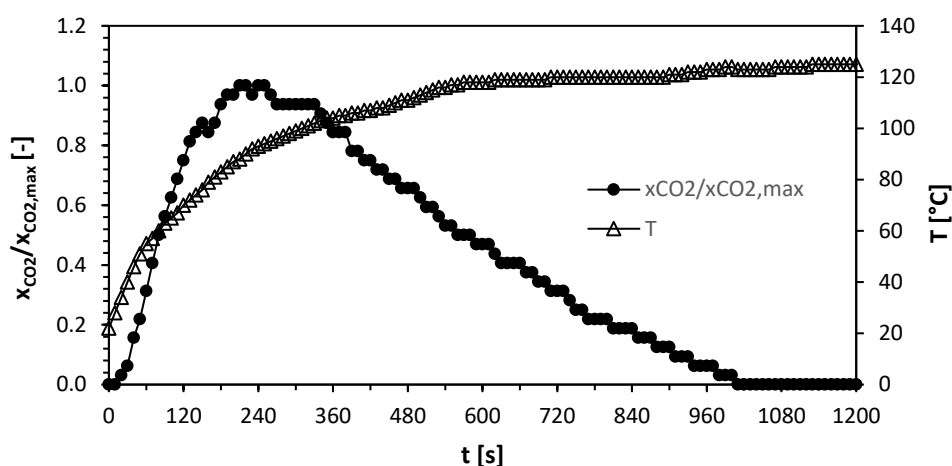


Figure 2. Desorption curve of APTES20 in homogeneous fluidization regime with air as carrier superficial and  $T=120\text{ }^{\circ}\text{C}$ .

During the desorption tests, the temperature was constantly measured in the particle bed, and the first  $\text{CO}_2$  release started when a bed temperature of  $43\text{ }^{\circ}\text{C}$  was reached. From this point on, the  $\text{CO}_2$  concentration increased with the rise in temperature until a maximum value was reached, as can be observed from the desorption curve. By keeping the system at the set regeneration temperature, the adsorbent released all the  $\text{CO}_2$  molecules retained on its surface and the outlet  $\text{CO}_2$  concentration of carrier started to decrease to zero. The use of a carrier gas allowed the tracking of the desorption phenomenon versus time, because a variation of  $\text{CO}_2$  concentration from the initial value, equal to zero, was detected by gas analyzer.

Thus, the effectiveness of the adopted indirect heating system was verified. Moreover, it made detecting the time required to obtain a complete release of  $\text{CO}_2$  and optimize the several operative parameters of desorption process. The PID control system was also efficient in keeping the temperature bed at the desired set point, avoiding the thermal degradation of the adsorbent, (see Table 3). In fact, Figure 3 shows how the adsorption capacity of the APTES20 after numerous adsorption/desorption cycles (i.e. 68 cycles) was preserved.

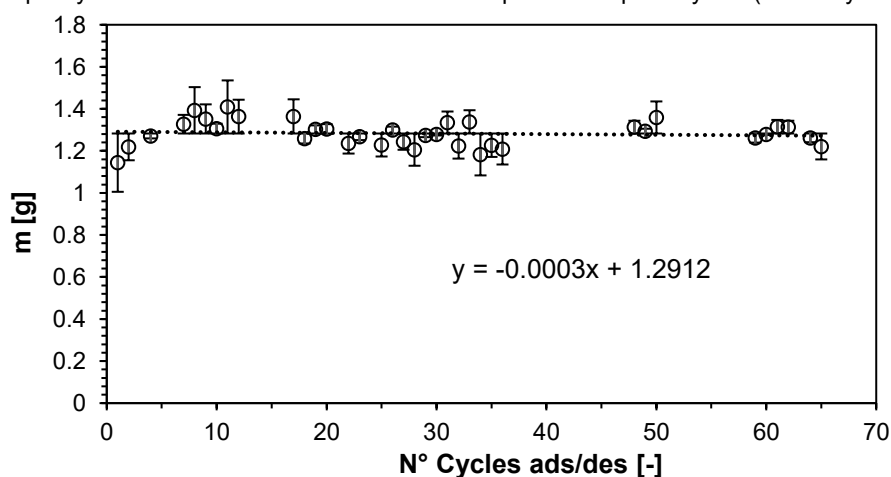


Figure 3. Stability curve of APTES20 versus adsorption/desorption cycles.

Table 3: Characteristic parameters for desorption tests on APTES20 with a carrier volumetric flow rate of  $450\text{ Nl/h}$  and regeneration temperature of  $120\text{ }^{\circ}\text{C}$ .

$x_{\text{CO}_2, \text{max}}$ [%vol]	$T_{\text{max}}$ [ $^{\circ}\text{C}$ ]	$t_{\text{des}}$ [min]
0.34	125	25

#### 4. Conclusions

The CCS strategies based on adsorption processes have two levels of investigation: the first concerning the choice of adsorbent material, and the second relating the type of contactor to maximize the performance. The first objective here was oriented towards the choice of an amino-functionalized porous adsorbent with particulate characteristics suitable for its use in a confined-fluidized bed. The second objective was investigated using a confined fluidized bed contactor designed to enhance heat and mass transfer. This setup proved effective for both the adsorption and regeneration phases, facilitated by the addition of external electrical resistances to the walls of the fluidization column.

#### Nomenclature

A – column section, cm <sup>2</sup>	$t_{des}$ – desorption time, min
C/C <sub>0</sub> – dimensionless CO <sub>2</sub> fraction in outlet gas, -	$t_s$ – saturation time, s
H <sub>fc</sub> – sorbent height in confined bed, cm	u – superficial gas velocity, cm/s
m <sub>CO<sub>2</sub></sub> – mass of CO <sub>2</sub> adsorbed per unit mass of sorbent, mg <sub>CO<sub>2</sub></sub> /g <sub>sorbent</sub>	u <sub>mf</sub> – minimum fluidization velocity, cm/s
m – mass of adsorbed CO <sub>2</sub> , g	V <sub>open</sub> – volume available for the gas, cm <sup>3</sup>
m <sub>r</sub> – mass of sorbent, g	W – fraction of bed used at the breakpoint, %
MW – CO <sub>2</sub> molecular weight, g/mol	x <sub>CO<sub>2</sub></sub> – CO <sub>2</sub> fraction in the inlet gas, %vol
Q <sub>air</sub> – volumetric flow rate of air, cm <sup>3</sup> /s	x <sub>CO<sub>2</sub>, max</sub> – maximum desorbed CO <sub>2</sub> fraction, %vol
Q <sub>CO<sub>2</sub></sub> – volumetric flow rate of CO <sub>2</sub> , cm <sup>3</sup> /s	T – adsorption temperature, °C
Q <sub>des</sub> – volumetric flow rate of the carrier, cm <sup>3</sup> /s	T <sub>des</sub> – desorption temperature, °C
Q <sub>mix</sub> – volumetric flow rate of the mixture, cm <sup>3</sup> /s	T <sub>max</sub> – maximum desorption temperature, °C
R – gas constant, atm/(mol K)	ε <sub>p</sub> – voidage of packing bed, -
t – time, s	π – adsorption pressure, atm
t <sub>b</sub> – breakthrough time, s	ρ <sub>f</sub> – particle density of sorbent, kg/m <sup>3</sup>
t <sub>c</sub> – contact time, s	φ – sphericity of solid particle, -

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